Etching Chemistry

- The etching process involves:
  - Transport of reactants to the surface
  - Surface reaction
  - Transport of products from the surface
- Key ingredients in any etchant:
  - Oxidizer
    - examples: $\text{H}_2\text{O}_2$, $\text{HNO}_3$
  - Acid or base to dissolve oxidized surface
    - examples: $\text{H}_2\text{SO}_4$, $\text{NH}_4\text{OH}$
  - Diluent media to transport reactants and products through
    - examples: $\text{H}_2\text{O}$, $\text{CH}_3\text{COOH}$

Redox Reactions

- Etching is inherently an electrochemical process:
  - It involves electron transfer processes as part of the surface reactions.
- The oxidation number is the net positive charge on a species.
- Oxidation is the process of electron loss, or increase in the oxidation number.
- Reduction is the process of electron gain, or decrease in the oxidation number.
- Redox reactions are those composed of oxidation of one or more species and simultaneous reduction of others.

HNA Etching of Silicon - 1

- Hydrofluoric acid + Nitric acid + Acetic acid
- Produces nearly isotropic etching of Si
- Overall reaction is:
  - $\text{Si} + \text{HNO}_3 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{HNO}_2 + \text{H}_2\text{O} + \text{H}_2$
  - Etching occurs via a redox reaction followed by dissolution of the oxide by an acid (HF) that acts as a complexing agent.
  - Points on the Si surface randomly become oxidation or reduction sites. These act like localized electrochemical cells, sustaining corrosion currents of $\approx 100 \text{ A/cm}^2$ (relatively large).
  - Each point on the surface becomes both an anode and cathode site over time. If the time spent on each is the same, the etching will be uniform; otherwise selective etching will occur.

Etch Anisotropy

- Isotropic etching
  - Same etch rate in all directions
  - Lateral etch rate is about the same as vertical etch rate
  - Etch rate does not depend upon the orientation of the mask edge
- Anisotropic etching
  - Etch rate depends upon orientation to crystalline planes
  - Lateral etch rate can be much larger or smaller than vertical etch rate, depending upon orientation of mask edge to crystalline axes
  - Orientation of mask edge and the details of the mask pattern determine the final etched shape
  - Can be very useful for making complex shapes
  - Can be very surprising if not carefully thought out
  - Only certain "standard" shapes are routinely used
Silicon is promoted to a higher oxidation state at an anodic site which supplies positive charge in the form of holes:

\[ \text{Si}^0 + 2h^+ \rightarrow \text{Si}^{2+} \]

NO\textsubscript{2} from the nitric acid is simultaneously reduced at a cathode site which produces free holes:

\[ 2\text{NO}_2 \rightarrow 2\text{NO}_2^- + 2h^+ \]

The Si\textsuperscript{2+} combines with OH\textsuperscript{-} to form SiO\textsubscript{2}:

\[ \text{Si}^{2+} + 2\text{OH}^- \rightarrow \text{Si(OH)}_2 \rightarrow \text{SiO}_2 + \text{H}_2\text{O} \]

The SiO\textsubscript{2} is then dissolved by HF to form a water soluble complex of H\textsubscript{2}SiF\textsubscript{6}:

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

Nitric acid has a complex behavior:

- Normal dissociation in water (deprotonation):
  \[ \text{HNO}_3 \leftrightarrow \text{NO}_3^- + \text{H}^+ \]
- Autocatalytic cycle for production of holes and HNO\textsubscript{2}:
  \[ \text{HNO}_2 + \text{HNO}_3 \rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O} \]
  \[ \text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2 \leftrightarrow 2\text{NO}_2^- + 2\text{H}^+ \]
  \[ 2\text{NO}_2^- + 2\text{H}^+ \leftrightarrow 2\text{HNO}_2 \]
- NO\textsubscript{2} is effectively the oxidizer of Si
  - Its reduction supplies holes for the oxidation of the Si.
- HNO\textsubscript{2} is regenerated by the reaction (autocatalytic)
- Oxidizing power of the etch is set by the amount of undissociated HNO\textsubscript{3}.

Role of acetic acid (CH\textsubscript{3}COOH):

- Acetic acid is frequently substituted for water as the diluent.
- Acetic acid has a lower dielectric constant than water
  - 6.15 for CH\textsubscript{3}COOH versus 81 for H\textsubscript{2}O
- This produces less dissociation of the HNO\textsubscript{3} and yields a higher oxidation power for the etch.
- Acetic acid is less polar than water and can help in achieving proper wetting of slightly hydrophobic Si wafers.
Anisotropic Etching of Silicon - 3

EXAMPLE:
HF:HNO₃:H₂O
3:2:5 ratio by volume

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Hydroxide Etching of Silicon

- Several hydroxides are useful:
  - KOH, NaOH, CeOH, RbOH, NH₄OH, TMAH: (CH₃)₄NOH
- Oxidation of silicon by hydroxyls to form a silicate:
  - Si + 2OH⁻ + 4H⁺ → Si(OH)₂⁺²⁺
- Reduction of water:
  - 4H₂O → 4OH⁻ + 2H₂ + 4H⁺
- Silicate further reacts with hydroxyls to form a watersoluble complex:
  - Si(OH)₂⁺²⁺ + 4OH⁻ → SiO₂(OH)₂⁻² + 2H₂O
- Overall redox reaction is:
  - Si + 2OH⁻ + 4H₂O → Si(OH)₂⁺²⁺ + 2H₂ + 4OH⁻

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KOH Etching of Silicon - 1

- Typical and most used of the hydroxide etches.
- A typical recipe is:
  - 250 g KOH
  - 200 g normal propanol
  - 800 g H₂O
  - Use at 80°C with agitation
- Etch rates:
  - ~1 μm/min for (100) Si planes; stops at p⁺⁺ layers
  - ~14 Angstroms/hr for Si₃N₄
  - ~20 Angstroms/min for SiO₂
- Anisotropy: (111):(110):(100) ~ 1:600:400

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Anisotropic Etching of Silicon - 2

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Anisotropic Etching of Silicon - 1

- Differing hybridized (sp) orbital orientation on different crystal planes causes drastic differences in etch rate.
- Typically, etch rates are: (100) > (110) > (111).
- The (111) family of crystallographic planes are normally the “stop” planes for anisotropic etching.
- There are 8 (111) planes along the ± x ± y ± z unit vectors.
- Intersections of these planes with planar bottoms produce the standard anisotropic etching structures for (100) Si wafers:
  - V-grooves
  - pyramidal pits
  - pyramidal cavities

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KOH Etching of Silicon - 1

- Simple hardware:
  - Hot plate & stirrer.
  - Keep covered or use reflux condenser to keep propanol from evaporating.
- Presence of alkali metal (potassium, K) makes this completely incompatible with MOS or CMOS processing!
- Comparatively safe and non-toxic.

KOH Etching of Silicon - 2

- Requirements:
  - Hot plate & stirrer.
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EDP Etching of Silicon - 1

- Ethylene diamine pyrocatechol
- Also known as Ethylene diamine - Pyrocatechol - Water (EPW)
- EDP etching is readily masked by SiO₂, Si₃N₄, Au, Cr, Ag, Cu, and Ta. But EDP can etch Al!
- Anisotropy: (111):(100) ~ 1:35
- EDP is very corrosive, very carcinogenic, and never allowed near mainstream electronic microfabrication.
- Typical etch rates for (100) silicon:
  - 70°C: 14 μm/hr
  - 80°C: 20 μm/hr
  - 90°C: 30 μm/hr = 0.5 μm/min
  - 97°C: 36 μm/hr

EDP Etching of Silicon - 2

- Typical formulation:
  - 1 L ethylene diamine, NH₂-CH₂-CH₂-NH₂
  - 160 g pyrocatechol, C₆H₄(OH)₂
  - 6 g pyrazine, C₄H₄N₂
  - 133 mL H₂O
- Ionization of ethylenediamine:
  - NH₂(CH₂)₂NH₂ + H₂O → NH₂(CH₂)₂NH₃⁺ + OH⁻
- Oxidation of Si and reduction of water:
  - Si + 2OH⁻ + 4H₂O → Si(OH)₄ + 2H₂
- Chelation of hydrosilica:
  - Si(OH)₄ → 3H₂(OH)₂ → Si(C₂H₄O₂)₃ + 6H₂O

EDP Etching of Silicon - 3

- Requires reflux condenser to keep volatile ingredients from evaporating.
- Completely incompatible with MOS or CMOS processing!
  - It must be used in a fume collecting bench by itself.
  - It will rust any metal in the nearby vicinity.
  - It leaves brown stains on surfaces that are difficult to remove.
- EDP has a faster etch rate on convex corners than other anisotropic etches:
  - It is generally preferred for undercutting cantilevers.
  - It tends to leave a smoother finish than other etches, since faster etching of convex corners produces a polishing action.

EDP Etching of Silicon - 4

- EDP etching can result in deposits of polymerized Si(OH)₄ on the etched surfaces and deposits of Al(OH)₃ on Al pads.
- Moser's post EDP protocol to eliminate this:
  - 20 sec. DI water rinse
  - 120 sec. dip in 5% ascorbic acid (vitamin C) and H₂O
  - 120 sec. rinse in DI water
  - 60 sec. dip in hexane, C₆H₁₄

Amine Gallate Etching of Silicon

- Much safer than EDP
- Typical recipe:
  - 100 g gallic acid
  - 305 mL ethanolamine
  - 140 mL H₂O
  - 1.3 g pyrazine
  - 0.26 mL FC-129 surfactant
- Anisotropy: (111):(100): 1:50 to 1:100
- Etch rate: ~1.7 μm/min at 118°C

EDP Etching of Silicon - 5

- Typical formulation:
  - 1 L ethylene diamine, NH₂-CH₂-CH₂-NH₂
  - 160 g pyrocatechol, C₆H₄(OH)₂
  - 6 g pyrazine, C₄H₄N₂
  - 133 mL H₂O
- Ionization of ethylenediamine:
  - NH₂(CH₂)₂NH₂ + H₂O → NH₂(CH₂)₂NH₃⁺ + OH⁻
- Oxidation of Si and reduction of water:
  - Si + 2OH⁻ + 4H₂O → Si(OH)₄ + 2H₂
- Chelation of hydrosilica:
  - Si(OH)₄ → 3H₂(OH)₂ → Si(C₂H₄O₂)₃ + 6H₂O
Anisotropic Etch Stop Layers - 1

- Controlling the absolute depth of an etch is often difficult, particularly if the etch is going most of the way through a wafer.
- Etch stop layers can be used to drastically slow the etch rate, providing a stopping point of high absolute accuracy.
- Boron doping is most commonly used for silicon etching.
- Requirements for specific etches:
  - HNA etch actually speeds up for heavier doping
  - KOH etch rate reduces by 20x for boron doping > 10^{20} \text{cm}^{-3}
  - NaOH etch rate reduces by 10x for boron doping > 3 \times 10^{19} \text{cm}^{-3}
  - EDP etch rate reduces by 50x for boron doping > 7 \times 10^{19} \text{cm}^{-3}
  - TMAH etch rate reduces by 10x for boron doping > 10^{19} \text{cm}^{-3}

TMAH Etching of Silicon - 1

- Tetra Methyl Ammonium Hydroxide
- MOS/CMOS compatible:
  - No alkali metals \{Li, Na, K, \ldots\}.  
  - Used in positive photoresist developers which do not use choline.  
  - Does not significantly etch SiO_{2} or Al! (Bond wire safe!)
- Anisotropy: (111):(100) ~ 1:10 to 1:35
- Typical recipe:
  - 250 mL TMAH (25% from Aldrich)
  - 375 mL H₂O
  - 22 g Si dust dissolved into solution
  - Use at 90°C
  - Gives about 1 \mu m/min etch rate

Anisotropic Etch Stop Layers - 2

- Heavily boron doped etch stop layer
- 2-5 \mu m thick membrane
- 400 - 500 \mu m thick wafer

Hydrazine and Water Etching of Silicon

- Produces anisotropic etching of silicon, also.
- Typical recipe:
  - 100 mL N₂H₄
  - 100 mL H₂O
  - ~2 \mu m/min at 100°C
- Hydrazine is very dangerous!
  - A very powerful reducing agent (used for rocket fuel)
  - Flammable liquid
  - TLV = 1 ppm by skin contact
  - Hypergolic: N₂H₄ + 2H₂O₂ → N₂ + 4H₂O (explosively)
  - Pyrophoric: N₂H₄ + O₂ → N₂ + 2H₂O (explosively)
  - Flash point = 52°C = 126°F in air.

Electrochemical Etch Effects - 1

- Produces anisotropic etching of silicon, also.
- Typical recipe:
  - 100 mL N₂H₄
  - 100 mL H₂O
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  - Hypergolic: N₂H₄ + 2H₂O₂ → N₂ + 4H₂O (explosively)
  - Pyrophoric: N₂H₄ + O₂ → N₂ + 2H₂O (explosively)
  - Flash point = 52°C = 126°F in air.
• HF normally etches SiO₂ and terminates on Si.
• By biasing the Si positively, holes can be injected by an external circuit which will oxidize the Si and form hydroxides which the HF can then dissolve.
• This produces an excellent polishing etch that can be very well masked by LPCVD films of Si₃N₄.
• If the etching is performed in very concentrated HF (48% HF, 98% EtOH), then the Si does not fully oxidize when etched, and porous silicon is formed, which appears brownish.

Electrochemical Etch Effects

(100) Si in 40% KOH at 60°C

- OCP: open-circuit potential
- PP: passivation potential
- n-type Si
- p-type Si

Increasing the wafer bias above the OCP will increase the etch rate by supplying holes which will oxidize the Si.
Increasing the wafer bias further will reach the passivation potential (PP) where SiO₂ forms.
  - This passivates the surface and terminates the etch.
  - The HF / H₂O solution does not exhibit a PP, since the SiO₂ is dissolved by the HF.