Key Technologies of Wet Etching

Profiles: Isotropic and Anisotropic

Applications: Silicon, Silicon Nitride, Silicon Dioxide, Metal

Controls: Doping, Electrochemical, Film Quality, Mask Materials

Wet Etching and Bulk Micromachining

Fundamentals of Micromachining
Dr. Bruce K. Gale

Wet Etching

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

Etching Chemistry

• The etching process involves:
  – Transport of reactants to the surface
  – Surface reaction
  – Transport of products from the surface

• Key ingredients in any wet etchant:
  – Oxidizer
    • examples: H₂O₂, HNO₃
  – Acid or base to dissolve oxidized surface
    • examples: H₂SO₄, NH₄OH
  – Diluent media to transport reactants and products through
    • examples: H₂O, CH₃COOH
Silicon Etching

(111) planes

- (111) planes etch the slowest, tend to be cleavage planes
- 54.74° (111) wrt (100)
- edge of “pit” lines up with (110)

Silicon Etching

Masking

- assume bulk crystalline (100) silicon substrate combined with anisotropic etch
- results in pyramidal shape
- bounding (111) planes can be reached using a variety of mask shapes
  - square mask opening, (100) wafer orientation, side of square is aligned to the (110) flat
  - what happens if you use a circular mask opening?
    - undercutting of the mask occurs until the (111) planes are reached
    - still forms a pyramidal pit!

Silicon Etching

Crystallographic etching

- recall crystal lattice is face centered cubic (FCC), with two atom basis [at (0,0,0) and (1/4, 1/4, 1/4)]
  - two “interpenetrating” FCC lattices

Silicon Etching

isotropic etching

anisotropic etching
KOH Etching

Etch Rate

(110) > (100) > (111)
(100) > (110) > (111) w/ IPA

Varies with Temperature and Concentration (see appendix C in Madou)

\[ R = k_0 \left[ H_2O \right]^4 \left[ KOH \right]^4 e^{\frac{E_a}{kT}} \]

Cross-section to Top View

Silicon Etching

Other mask openings

- in general mask is undercut until (111) planes are reached
- bars undercut until bounding planes are reached
- "cross"-shaped mask opening will also undercut to form pyramidal pit

Anisotropic Etching of Silicon - 2

Isotropic

(1) HF:HNO₃:CH₃COOH:H₂O (2) HF
(3) HF:NH₄F

Anisotropic

(1) KOH (2) EDP (Ethylenediamine Pyrocatechol)
(3) CsOH (4) NaOH (5) N₂H₄-H₂O (Hydrazine)

Masking Materials

(1) Photoresist (Acids Only) (2) Si₃N₄
(3) SiO₂
Mask Layer for KOH Etching

\( \text{Si}_3\text{N}_4 \)
- CVD films best
- Sputtered films poor

\( \text{SiO}_2 \)
- Thermal films best
- CVD films etch 30% faster
- Sputtered films poor

Anisotropic wet etch formulations

- alkali metal hydroxide etchants
  - examples: KOH, NaOH
  - typically 15 - 40w% concentration, diluant water or isopropanol, -70°C
- proposed reactions:
  - \( \text{Si} + 2\text{OH}^{-} \rightarrow \text{Si(OH)}_2^{2-} + 4e^- \)
  - \( 4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- + 2\text{H}_2 \) (gas)
  - \( \text{Si(OH)}_2^{2-} + 4\text{OH}^- \rightarrow \text{SiO}_2\text{(OH)}_2^{2-} + 2\text{H}_2\text{O} \)
  - overall: \( \text{Si} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2\text{(OH)}_2^{2-} + 2\text{H}_2 \) (gas)
- selectivities:
  - \((100):(111)\) about 40:1, \((111)\) rate - 1 \( \mu \text{m/min} \)
  - p type doping > -2x10^18, reduces etch rate
  - (oxide): \((111)\) about 1: 1000
- choice of concentration, etch temperature
  - affects etch rate, surface smoothness
  - generally, KOH tends to give very smooth (111) planes

Anisotropic Etching of Silicon

KOH Etching

- Masks
  - \( \text{Si}_3\text{N}_4 \) is best, very slow etch rate
  - Selectivity > 1000
  - \( \text{SiO}_2 \) works, selectivity \( \approx 100 \)

- Mask Design
  - KOH Etches exposed corners quickly
  - Use star pattern or create interior corners to create outer corners
**KOH Etching of Silicon - 2**

- 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 - 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

**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⁺⁺
- Reduction of water:
  - 4H₂O → 4OH⁻ + 2H₂ + 4H⁺
- Silicate further reacts with hydroxyls to form a water-soluble complex:
  - Si(OH)₂⁺⁺ + 4OH⁻ → SiO₂(OH)₂²⁻ + 2H₂O
- Overall redox reaction is:
  - Si + 2OH⁻ + 4H₂O → Si(OH)₂⁺⁺ + 2H₂ + 4OH⁻

**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**

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EDP Etching of Silicon - 2

- Typical formulation:
  - 1 L ethylene diamine, $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$
  - 160 g pyrocatechol, $\text{C}_6\text{H}_4(\text{OH})_2$
  - 6 g pyrazine, $\text{C}_4\text{H}_4\text{N}_2$
  - 133 mL $\text{H}_2\text{O}$

- Ionization of ethylene diamine:
  $$\text{NH}_2(\text{CH}_2)\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_2(\text{CH}_2)\text{NH}_3^+ + \text{OH}^-$$

- Oxidation of Si and reduction of water:
  $$\text{Si} + 2\text{OH}^- + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_6^{2-} + 2\text{H}_2$$

- Chelation of hydrous silica:
  $$\text{Si(OH)}_6^{2-} + 3\text{C}_6\text{H}_4(\text{OH})_2 \rightarrow \text{Si(C}_6\text{H}_4\text{O}_2)_3^{2-} + 6\text{H}_2\text{O}$$

EDP Etching of Silicon - 4

- EDP etching can result in deposits of polymerized $\text{Si(OH)}_4$ on the etched surfaces and deposits of $\text{Al(OH)}_3$ 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 $\text{H}_2\text{O}$
  - 120 sec. rinse in DI water
  - 60 sec. dip in hexane, $\text{C}_6\text{H}_{14}$

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.

Amine Gallate Etching of Silicon

- Much safer than EDP
- Typical recipe:
  - 100 g gallic acid
  - 305 mL ethanolamine
  - 140 mL $\text{H}_2\text{O}$
  - 1.3 g pyrazine
  - 0.26 mL FC-129 surfactant
- Anisotropy: (111):(100): 1:50 to 1:100
- Etch rate: $\sim 1.7 \mu\text{m/min}$ at 118°C
Hydrazine and Water Etching of Silicon

- Produces anisotropic etching of silicon, also.
- Typical recipe:
  - 100 mL N₂H₄
  - 100 mL H₂O
  - ~2 µm/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.

TMAH Etching of Silicon - 1

- Tetra Methyl Ammonium Hydroxide
- MOS/CMOS compatible:
  - No alkali metals {Li, Na, K, ... }.
  - Used in positive photoresist developers which do not use choline.
  - Does not significantly etch SiO₂ 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 µm/min etch rate

Hydrazine and Water Etching of Silicon

- Produces anisotropic etching of silicon, also.
- Typical recipe:
  - 100 mL N₂H₄
  - 100 mL H₂O
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  - Pyrophoric: N₂H₄ + O₂ → N₂ + 2H₂O (explosively)
  - Flash point = 52°C = 126°F in air.

TMAH Etching of Silicon - 2

- Hydroxide etches are generally safe and predictable, but they usually involve an alkali metal which makes them incompatible with MOS or CMOS processing.
- Ammonium hydroxide (NH₄OH) is one hydroxide which is free of alkali metal, but it is really ammonia which is dissolved into water. Heating to 90°C for etching will rapidly evaporate the ammonia from solution.
- Ballasting the ammonium hydroxide with a less volatile organic solves the problem:
  - Tetramethyl ammonium hydroxide: (CH₃)₄NOH
  - Tetraethyl ammonium hydroxide: (C₂H₅)₄NOH

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 > 10²⁰ cm⁻³
  - NaOH etch rate reduces by 10x for boron doping > 3 × 10²⁰ cm⁻³
  - EDP etch rate reduces by 50x for boron doping > 7 × 10¹⁹ cm⁻³
  - TMAH etch rate reduces by 10x for boron doping > 10²⁰ cm⁻³
Electrochemical Etch Effects - 2

- 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.

Anisotropic Etch Stop Layers - 2

Electrochemical Etch Effects - 3

- (100) Si in 40% KOH at 60°C
- PP: passivation potential
- OCP: open-circuit potential
- n-type Si
- p-type Si
- potential of Pt reference electrode

Electrochemical Etch Effects - 1

- Si + 4H⁺ + 2OH⁻ → Si(OH)₄⁺
- Pt reference electrode
Various issues

- safety hazards
  - EDP, hydrazine potentially quite hazardous
  - ammonia released from TMAH at elevated temperatures
- hydrogen bubbles
  - all the reactions tend to produce $H_2$
    - bubble formation can locally “mask” etch leading to rough surfaces
    - bubbles trapped inside sacrificial regions can stop etch or cause breakage

Electrochemical Etch Effects - 4

- 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 $SiO_2$ forms.
  - This passivates the surface and terminates the etch.
  - The HF / $H_2O$ solution does not exhibit a PP, since the $SiO_2$ is dissolved by the HF.

Silicon Etching---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.

Other formulations

- similar: ammonium hydroxide $NH_3OH$
  - $3.7\text{wt}\%$ @ $75^\circ C$, (100) : (111) of $8,000 : 1$, but $< 0.1\ \mu m/min$ etch rate
  - hillock formation also a problem
- TMAH (tetramethyl ammonium hydroxide (CH$_3$)$_3$NOH)
  - $90^\circ C$, 10-40%, $\sim 1\ \mu m/min$; surface roughness can be problem
  - (100) : (111) selectivity 10:35 : 1
  - boron doping stop
  - selectivity against oxide $>1000$
  - low aluminum etch rate
- EDP (ethylene diamine / pyrochatechol / water)
  - $115^\circ C$, $\sim 1\ \mu m/min$, (100) : (111) selectivity 35 : 1
  - oxide selectivity $>1000:1$, etches aluminum
- hydrazine
HNA Etching of Silicon - 3

- 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 $\text{HNO}_2$:
    - $\text{HNO}_2 + \text{HNO}_3 \rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O}$
    - $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2 \leftrightarrow 2\text{NO}_2^- + 2\text{H}^+$
    - $2\text{NO}_2^- + 2\text{H}^+ \leftrightarrow 2\text{HNO}_2$
  - $\text{NO}_2$ is effectively the oxidizer of Si
    - Its reduction supplies holes for the oxidation of the Si.
  - $\text{HNO}_2$ is regenerated by the reaction (autocatalytic)
  - Oxidizing power of the etch is set by the amount of undissociated $\text{HNO}_3$.

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 ~100 A/cm² (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.

HNA Etching of Silicon - 4

- Role of acetic acid ($\text{CH}_3\text{COOH}$):
  - Acetic acid is frequently substituted for water as the diluent.
  - Acetic acid has a lower dielectric constant than water
    - 6.15 for $\text{CH}_3\text{COOH}$ versus 81 for $\text{H}_2\text{O}$
    - This produces less dissociation of the $\text{HNO}_3$ 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.

HNA Etching of Silicon - 2

- Silicon is promoted to a higher oxidation state at an anodic site which supplies positive charge in the form of holes:
  - $\text{Si}^0 + 2\text{H}^+ \rightarrow \text{Si}^{4+}$
- $\text{NO}_3$ from the nitric acid is simultaneously reduced at a cathode site which produces free holes:
  - $2\text{NO}_2^- \rightarrow 2\text{NO}_2^- + 2\text{H}^+$
- The $\text{Si}^{2+}$ combines with $\text{OH}^-$ to form $\text{SiO}_2$:
  - $\text{Si}^{2+} + 2\text{OH}^- \rightarrow \text{Si(OH)}_2 \rightarrow \text{SiO}_2 + \text{H}_2\text{O}$
- The $\text{SiO}_2$ is then dissolved by HF to form a water soluble complex of $\text{H}_2\text{SiF}_6$:
  - $\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$
Silicon Nitride and Silicon Dioxide Etching

**Si$_3$N$_4$ Etching**
- 1% HF etches about 600 Å/min
- 10% HF etches about 5000 Å/min
- BHF etches 5-10 Å/min
- H$_3$PO$_4$ etches 100 Å/min at 180 °C

**SiO$_2$ Etching**
- BHF etches 1000-2500 Å/min
- HF etches very quickly

Etch rates for both SiO$_2$ and Si$_3$N$_4$ vary greatly depending on film quality

HNA Etching of Silicon

- **Region 1**
  - For high HF concentrations, contours are parallel to the lines of constant HNO$_3$; therefore the etch rate is controlled by HNO$_3$ in this region.
  - Leaves little residual oxide; limited by oxidation process.

- **Region 2**
  - For high HNO$_3$ concentrations, contours are parallel to the lines of constant HF; therefore the etch rate is controlled by HF in this region.
  - Leaves a residual 30-50 Angstroms of SiO$_2$; self-passivating; limited by oxide dissolution; area for polishing.

- **Region 3**
  - Initially not very sensitive to the amount of H$_2$O, then etch rate falls of sharply for 1:1 HF:HNO$_3$ ratios.
Metal Etching

**Copper and Nickel**
(1) 30% FeCl₃  
(2) 5% Piranha (30% H₂O₂:70% H₂SO₄)  
(3) KI:I₂:H₂O (Not transparent)

**Chromium** - usually requires depassivation
(1) Aqua Regia (75% HCl: 25% HNO₃)  
(2) HCl:Glycerin

**Gold (Au)**
(1) Aqua Regia  
(2) Iodine  
(3) Alkali Cyanide w/Hydrogen Peroxide

**Silver (Ag)**
(1) Iodine  
(2) HNO₃