EE-527: MicroFabrication

Wet Etching

Outline

- Isotropic Si etching
- Anisotropic Si etching
- Anisotropic GaAs etching
- Isotropic etching of SiO_2, Al, and Cr
- General features of wet chemical etching
- Selective etching and etch stops
- Interesting etch techniques
  - Junction diode etch stops
  - Field assisted etching
  - CMOS post processing

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

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: H_2O_2, HNO_3
  - Acid or base to dissolve oxidized surface
    - examples: H_2SO_4, NH_4OH
  - Dillutent media to transport reactants and products through
    - examples: H_2O, CH_3COOH

Redox Reactions

- Etching is inherently an electrochemical process:
  - It involves electron transfer processes as part of the surface reactions.
- The <u>oxidation number</u> is the net positive charge on a species.
- <u>Oxidation</u> is the process of electron loss, or increase in the oxidation number.
- <u>Reduction</u> 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:
  - $Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2O + H_2$
  - 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/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.

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:
  - $Si^0 + 2h^+ \rightarrow Si^{2+}$
- NO_2 from the nitric acid is simultaneously reduced at a cathode site which produces free holes:
  - $2NO_2 \rightarrow 2NO_2^- + 2h^+$
- The Si^{2+} combines with OH^- to form SiO_2:
  - $Si^{2+} + 2OH^- \rightarrow Si(OH)_2 \rightarrow SiO_2 + H_2O$
- The SiO_2 is then dissolved by HF to form a water soluble complex of H_2SiF_6:
  - $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

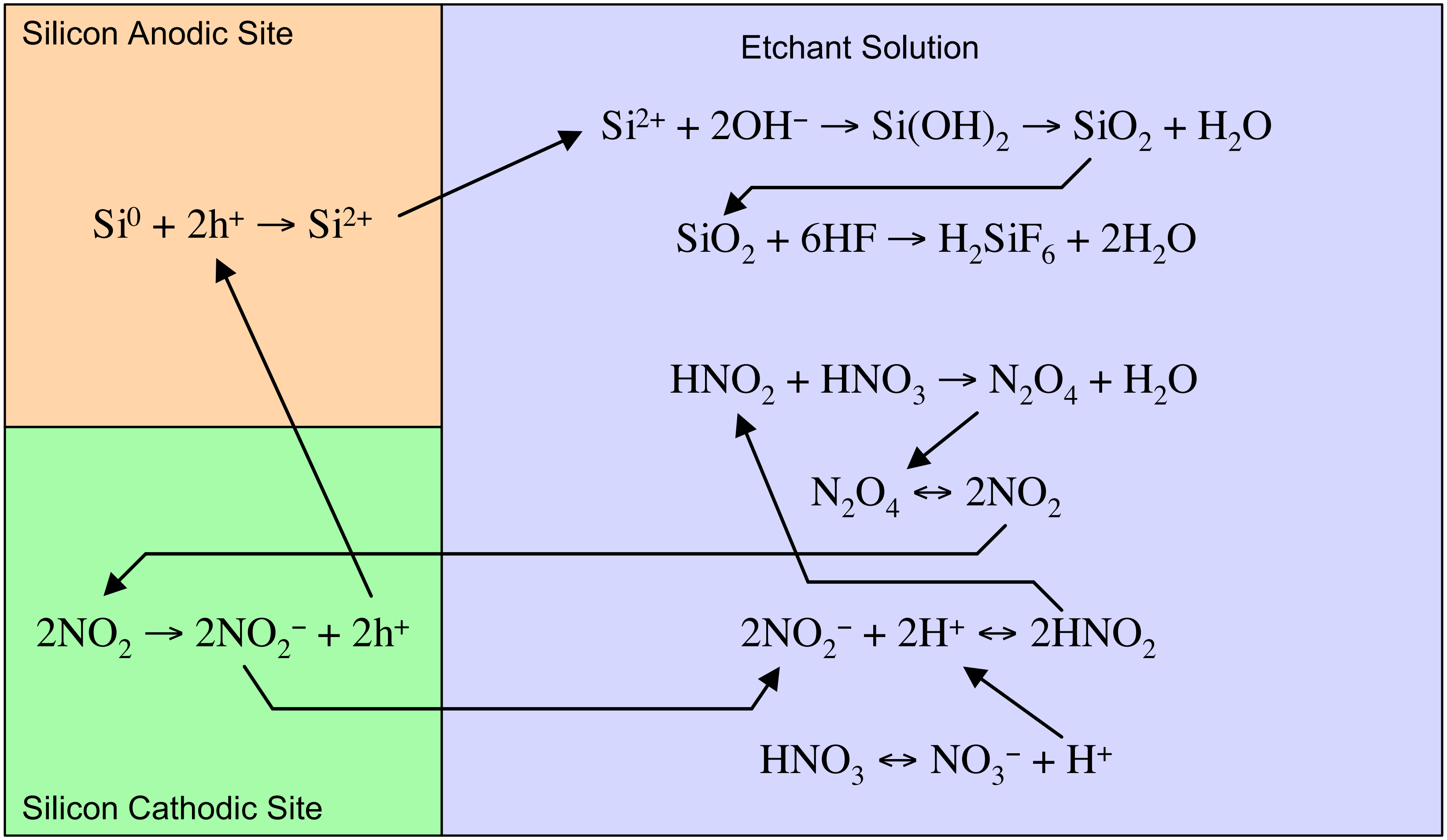
HNA Etching of Silicon - 3

- Nitric acid has a complex behavior:
  - Normal dissociation in water (deprotonation):
    - $HNO_3 \leftrightarrow NO_3^- + H^+$
  - Autocatalytic cycle for production of holes and HNO_2:
    - $HNO_2 + HNO_3 \rightarrow N_2O_4 + H_2O$
    - $N_2O_4 \leftrightarrow 2NO_2 \leftrightarrow 2NO_2^- + 2h^+$
    - $2NO_2^- + 2H^+ \leftrightarrow 2HNO_2$
  - NO_2 is effectively the oxidizer of Si
    - Its reduction supplies holes for the oxidation of the Si.
  - HNO_2 is regenerated by the reaction (autocatalytic)
  - Oxidizing power of the etch is set by the amount of undissociated HNO_3.

HNA Etching of Silicon - 4

- Role of acetic acid (CH_3COOH):
  - Acetic acid is frequently substituted for water as the dilutent.
  - Acetic acid has a lower dielectric constant than water
    - 6.15 for CH_3COOH versus 81 for H_2O
    - This produces less dissociation of the 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 - 5



Silicon Anodic Site

Etchant Solution

$Si^{2+} + 2OH^- \rightarrow Si(OH)_2 \rightarrow SiO_2 + H_2O$

$Si^0 + 2h^+ \rightarrow Si^{2+}$

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

$HNO_2 + HNO_3 \rightarrow N_2O_4 + H_2O$

$N_2O_4 \leftrightarrow 2NO_2$

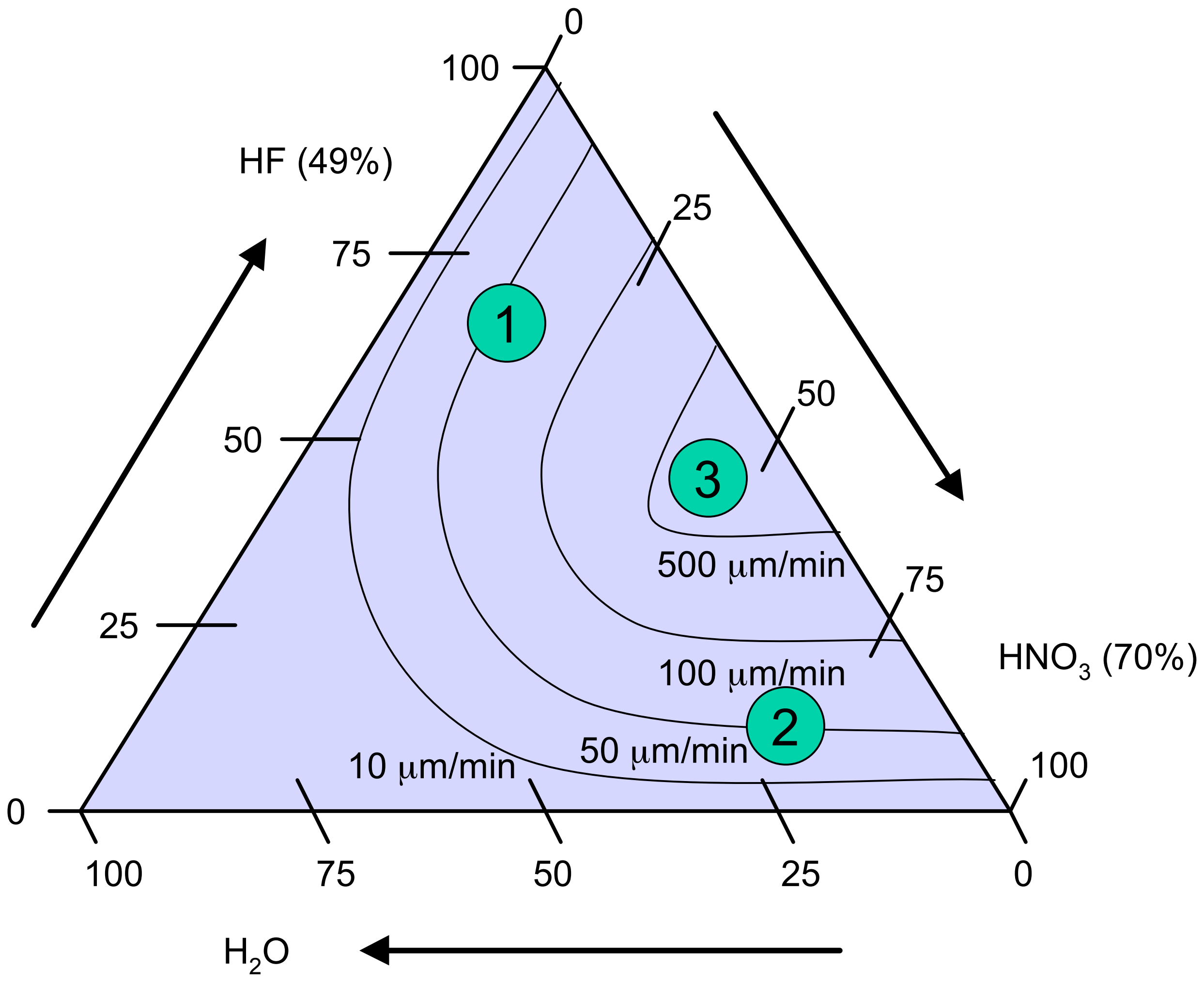
$2NO_2 \rightarrow 2NO_2^- + 2h^+$

$2NO_2^- + 2H^+ \leftrightarrow 2HNO_2$

$HNO_3 \leftrightarrow NO_3^- + H^+$

Silicon Cathodic Site

HNA Etching of Silicon - 6

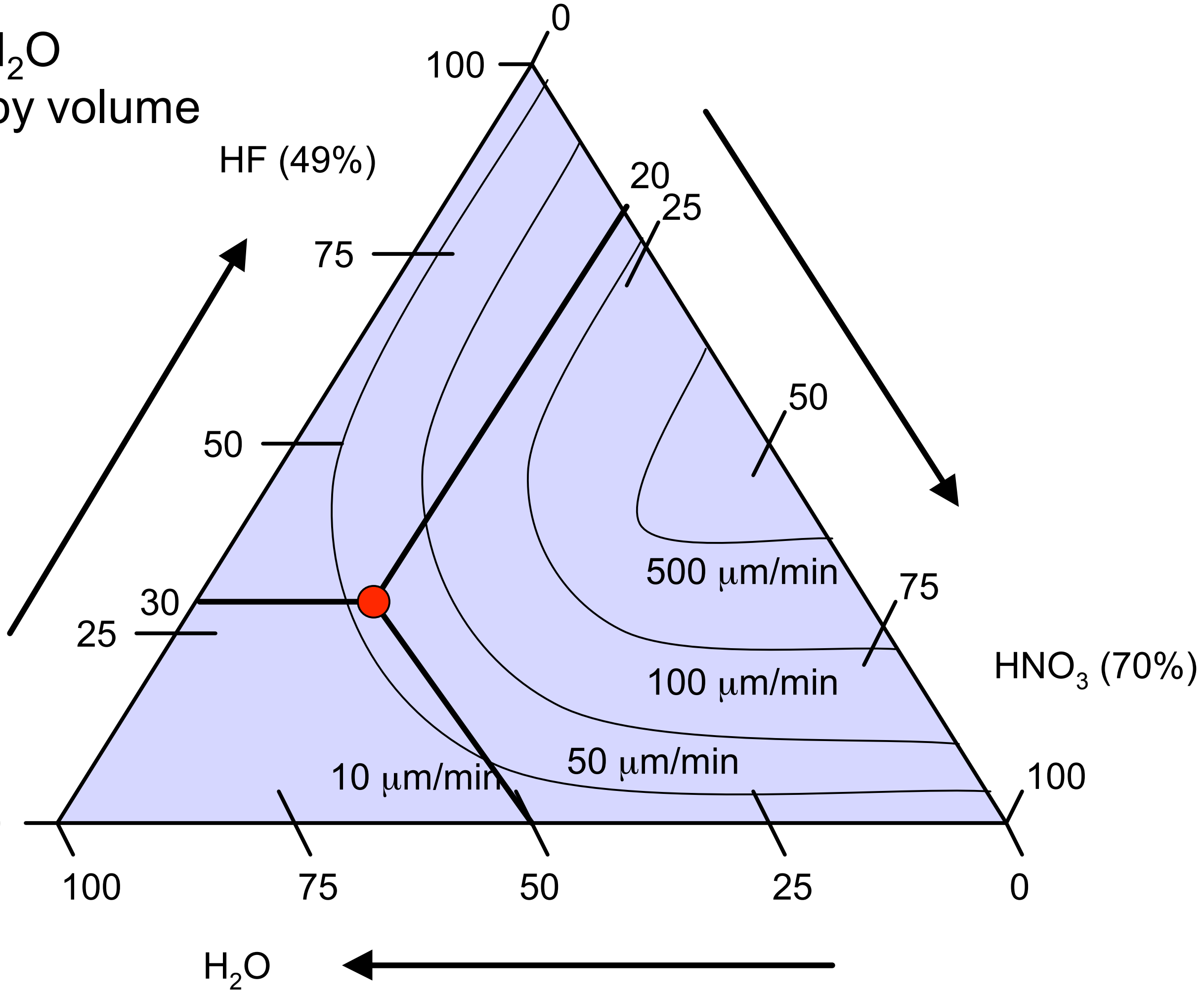


HNA Etching of Silicon - 7

- 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_2O, then etch rate falls of sharply for 1:1 HF:HNO_3 ratios.

Isoetch Contours

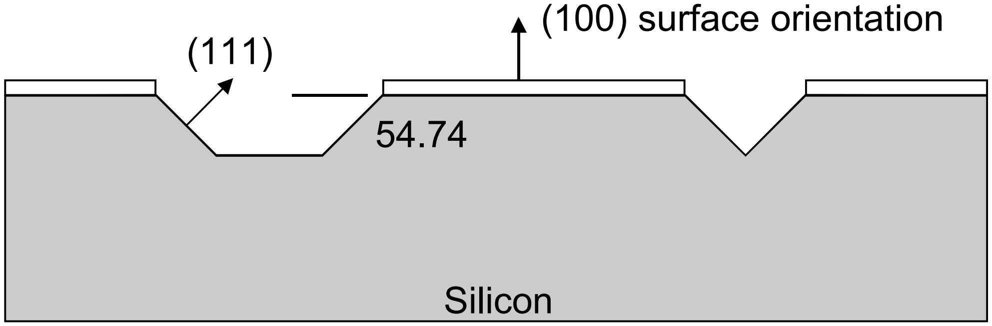
EXAMPLE:
$HF:HNO_3:H_2O$
3:2:5 ratio by volume

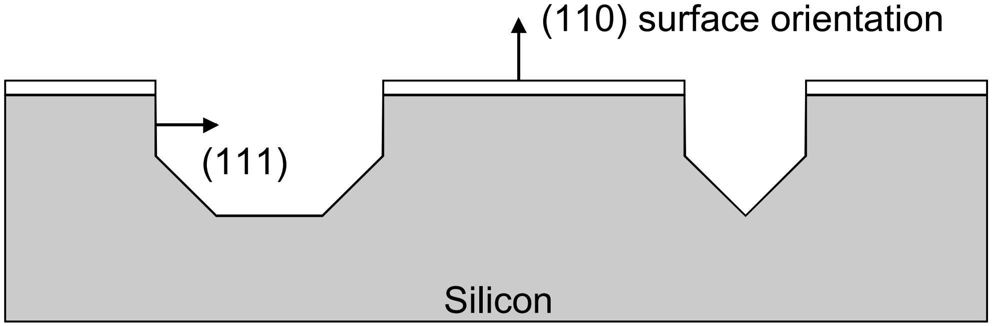


Anisotropic Etching of Silicon - 1

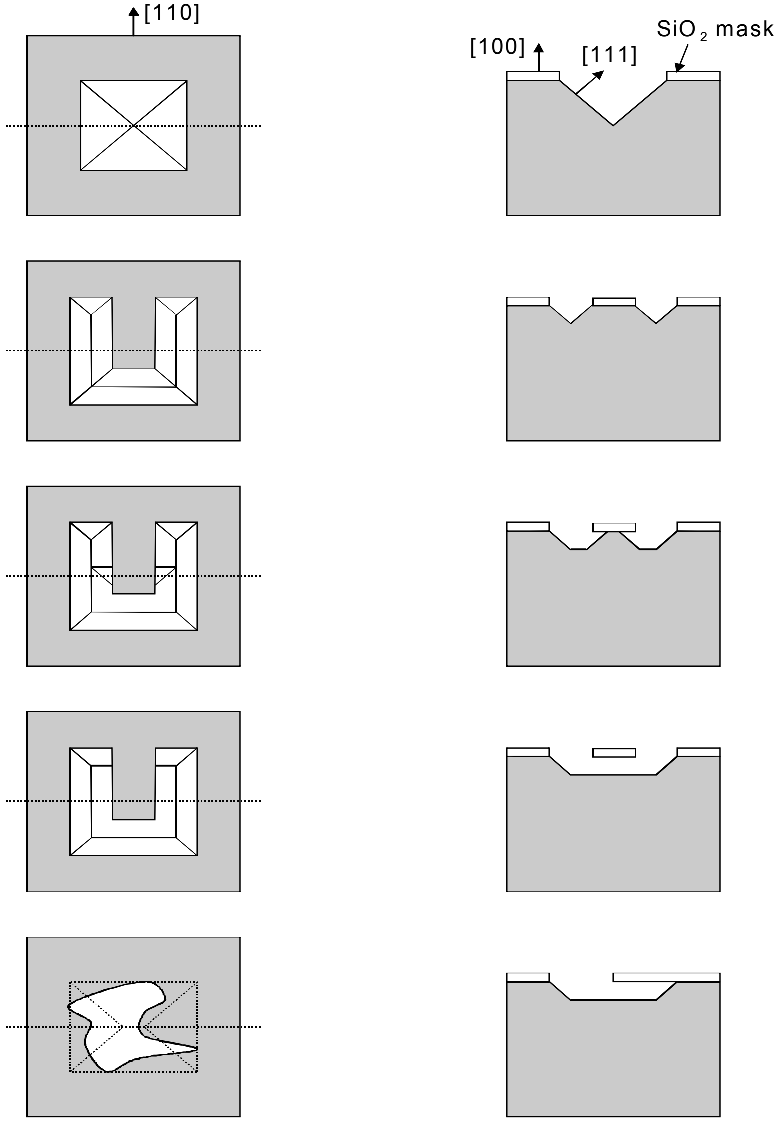
- Differing hybridized (sp^3) orbital orientation on different crystal planes causes drastic differences in etch rate.
- Typically, etch rates are: (100) > (110) > (111).
- The (111) family of crystallographic planes are normally the "stop" planes for anisotropic etching.
- There are 8 (111) planes along 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

Anisotropic Etching of Silicon - 2





Anisotropic Etching of Silicon - 3



Hydroxide Etching of Silicon

- Several hydroxides are useful:
  - KOH, NaOH, CeOH, RbOH, NH_4OH, TMAH: $(CH_3)_4NOH$
- Oxidation of silicon by hydroxyls to form a silicate:
  - $Si + 2OH^- + 4h^+ \rightarrow Si(OH)_2^{++}$
- Reduction of water:
  - $4H_2O \rightarrow 4OH^- + 2H_2 + 4h^+$
- Silicate further reacts with hydroxyls to form a water-soluble complex:
  - $Si(OH)_2^{++} + 4OH^- \rightarrow SiO_2(OH)_2^{2-} + 2H_2O$
- Overall redox reaction is:
  - $Si + 2OH^- + 4H_2O \rightarrow Si(OH)_2^{++} + 2H_2 + 4OH^-$

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 H_2O
  - Use at 80°C with agitation
- Etch rates:
  - ~1 μm/min for (100) Si planes; stops at p^{++} layers
  - ~14 Angstroms/hr for Si_3N_4
  - ~20 Angstroms/min for SiO_2
- Anisotropy: (111):(110):(100) ~ 1:600:400

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.

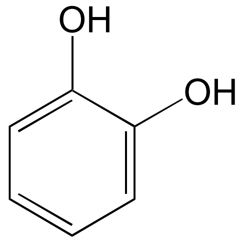
EDP Etching of Silicon - 1

- Ethylene Diamine Pyrocatechol
- Also known as Ethylene diamine - Pyrocatechol - Water (EPW)
- EDP etching is readily masked by SiO_2, Si_3N_4, 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:

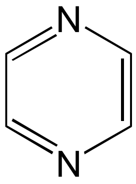
70°C	14 μm/hr
80°C	20 μm/hr
90°C	30 μm/hr = 0.5 μm/min
97°C	36 μm/hr

EDP Etching of Silicon - 2

- Typical formulation:
  - 1 L ethylene diamine, NH_2-CH_2-CH_2-NH_2
  - 160 g pyrocatechol, $C_6H_4(OH)_2$
  - 6 g pyrazine, $C_4H_4N_2$
  - 133 mL H_2O

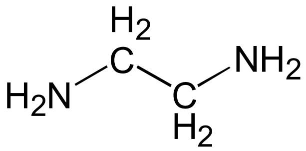


catechol



pyrazine

- Ionization of ethylene diamine:
  - $NH_2(CH_2)_2NH_2 + H_2O \rightarrow NH_2(CH_2)_2NH_3^+ + OH^-$



ethylene diamine

- Oxidation of Si and reduction of water:
  - $Si + 2OH^- + 4H_2O \rightarrow Si(OH)_6{}^{2-} + 2H_2$
- Chelation of hydrous silica:
  - $Si(OH)_6{}^{2-} + 3C_6H_4(OH)_2 \rightarrow Si(C_6H_4O_2)_3{}^{2-} + 6H_2O$

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

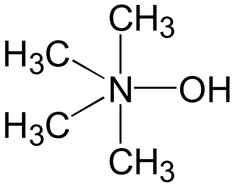
- EDP etching can result in deposits of polymerized $Si(OH)_4$ on the etched surfaces and deposits of $Al(OH)_3$ on Al pads.
- Moser’s post EDP protocol to eliminate this:
  - 20 sec. DI water rinse
  - 120 sec. dip in 5% ascorbic acid (vitamin C) and H_2O
  - 120 sec. rinse in DI water
  - 60 sec. dip in hexane, C_6H_{14}

Amine Gallate Etching of Silicon

- Much safer than EDP
- Typical recipe:
  - 100 g gallic acid
  - 305 mL ethanolamine
  - 140 mL H_2O
  - 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

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 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 H_2O
  - 22 g Si dust dissolved into solution
  - Use at 90°C
  - Gives about 1 µm/min etch rate



tetramethyl ammonium hydroxide
(TMAH)

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 (NH_4OH) 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: $(CH_3)_4NOH$
  - Tetraethyl ammonium hydroxide: $(C_2H_5)_4NOH$

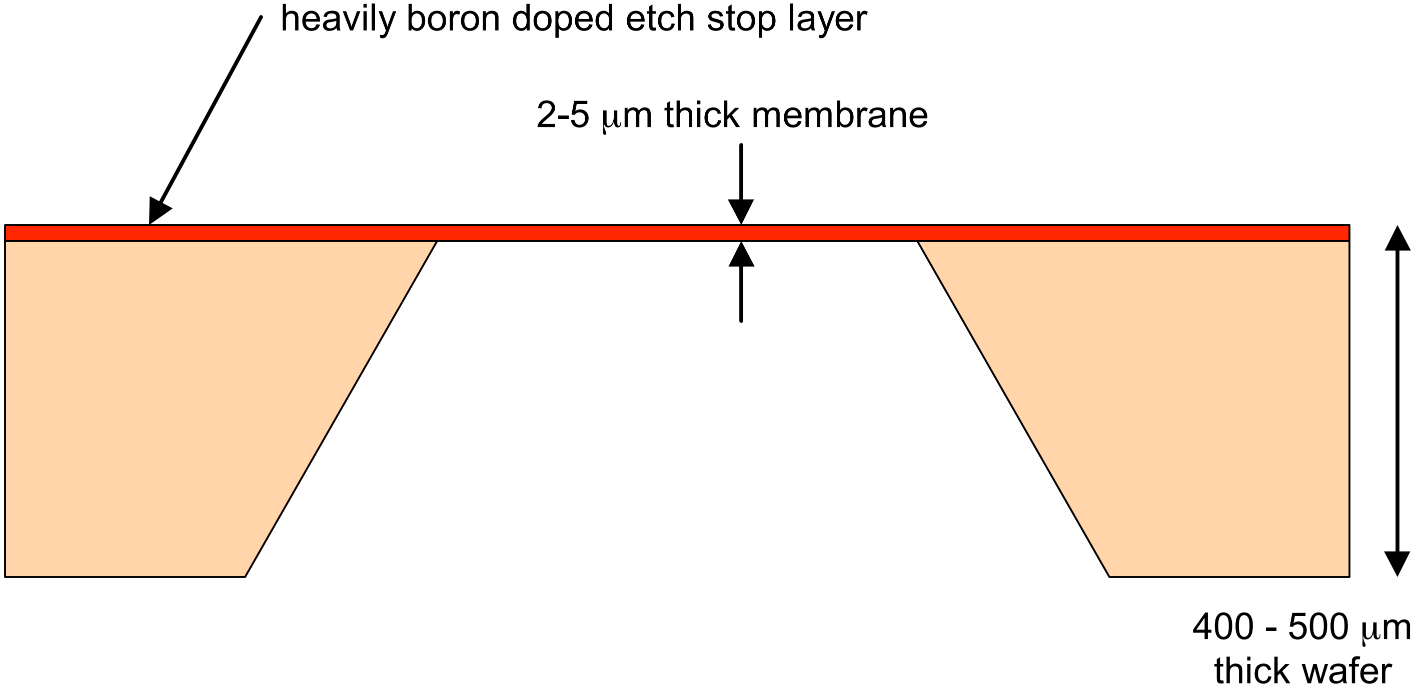
Hydrazine and Water Etching of Silicon

- Produces anisotropic etching of silicon, also.
- Typical recipe:
  - 100 mL N_2H_4
  - 100 mL H_2O
  - ~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: $N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O$ (explosively)
  - Pyrophoric: $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$ (explosively)
  - Flash point = 52°C = 126°F in air.

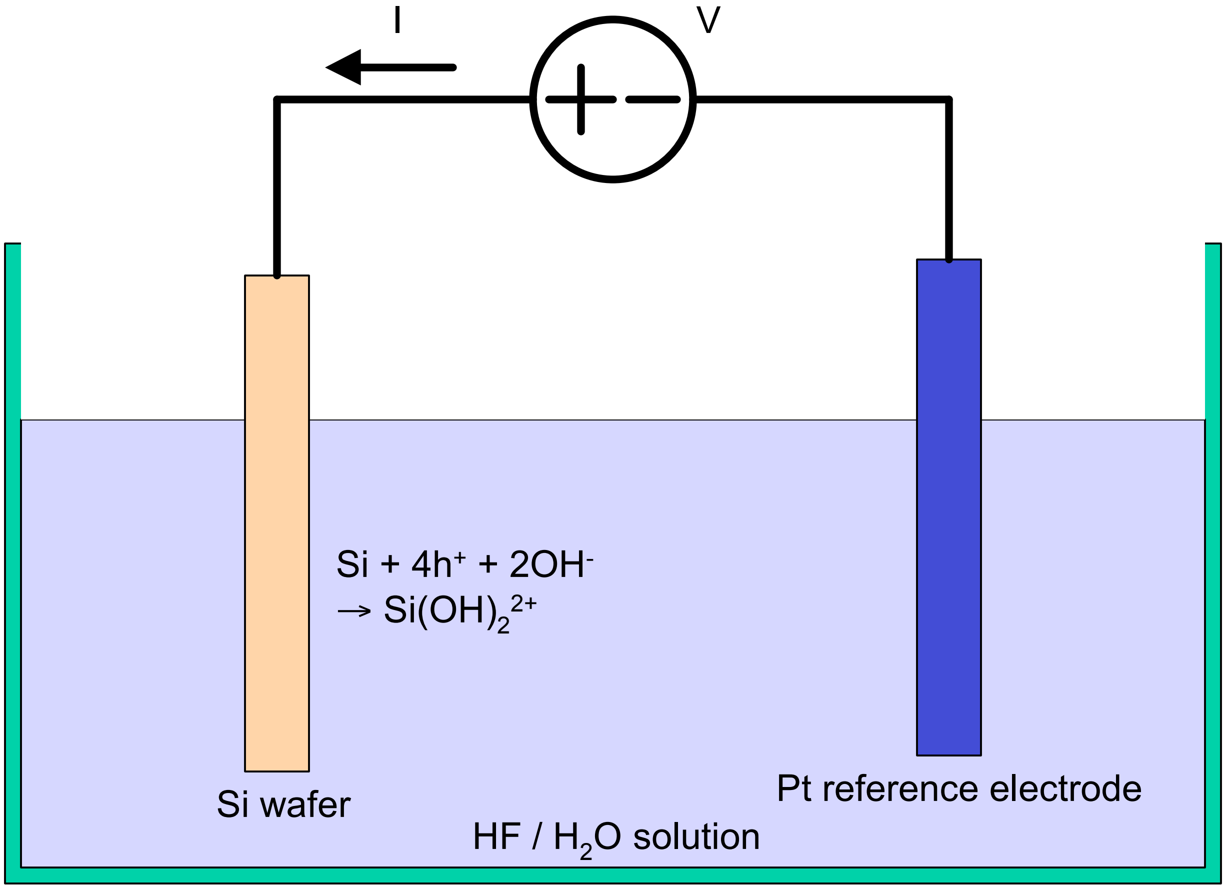
Anisotropic Etch Stop Layers - 1

- 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 20× for boron doping $> 10^{20}$ cm^{-3}
  - NaOH etch rate reduces by 10× for boron doping $> 3 \times 10^{20}$ cm^{-3}
  - EDP etch rate reduces by 50× for boron doping $> 7 \times 10^{19}$ cm^{-3}
  - TMAH etch rate reduces by 10× for boron doping $> 10^{20}$ cm^{-3}

Anisotropic Etch Stop Layers - 2



Electrochemical Etch Effects - 1

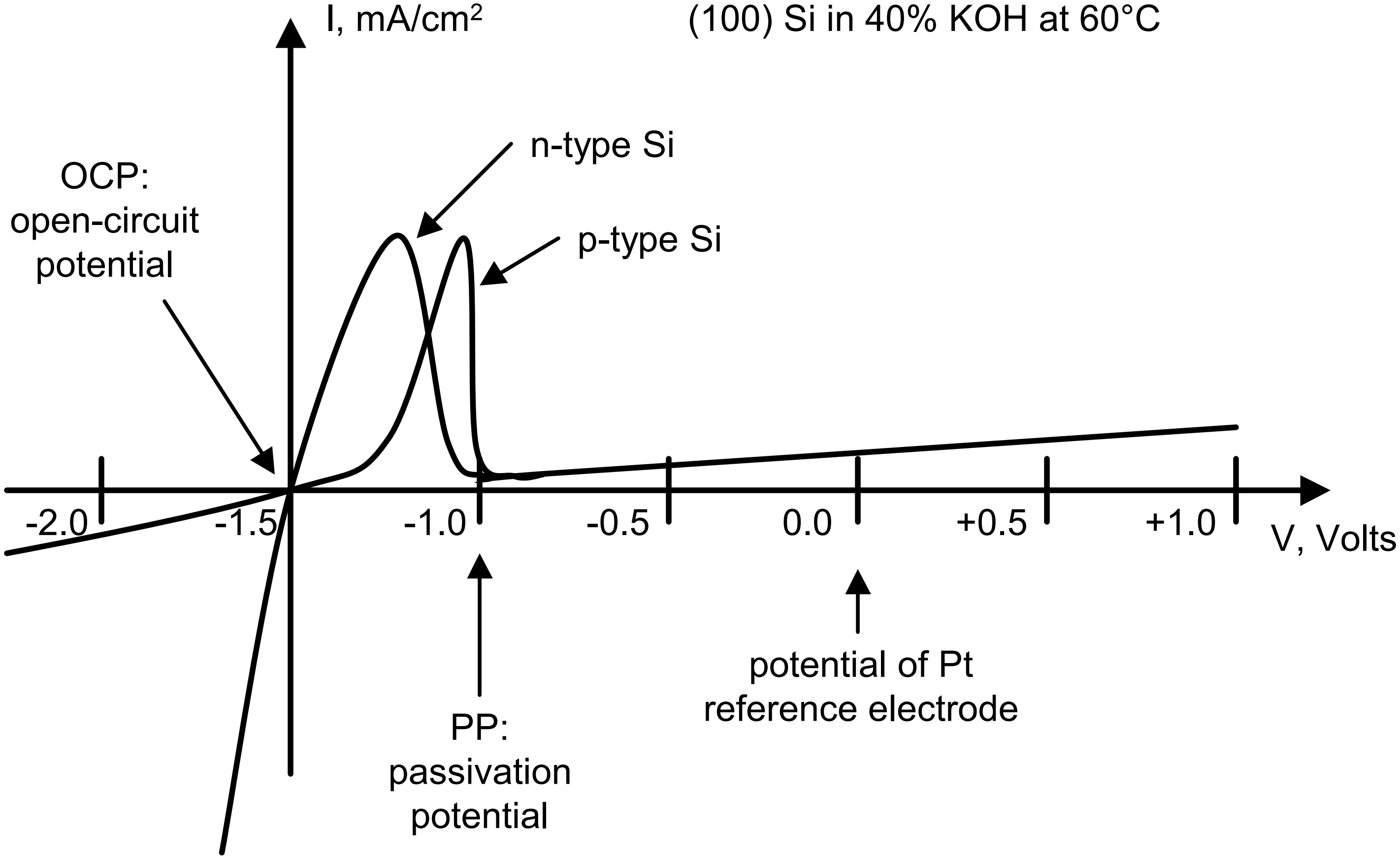


$Si + 4h^+ + 2OH^-$
$\rightarrow Si(OH)_2^{2+}$

Electrochemical Etch Effects - 2

- HF normally etches SiO_2 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 Si_3N_4.
- 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 - 3



(100) Si in 40% KOH at 60°C

n-type Si

p-type Si

OCP:
open-circuit
potential

PP:
passivation
potential

potential of Pt
reference electrode

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.