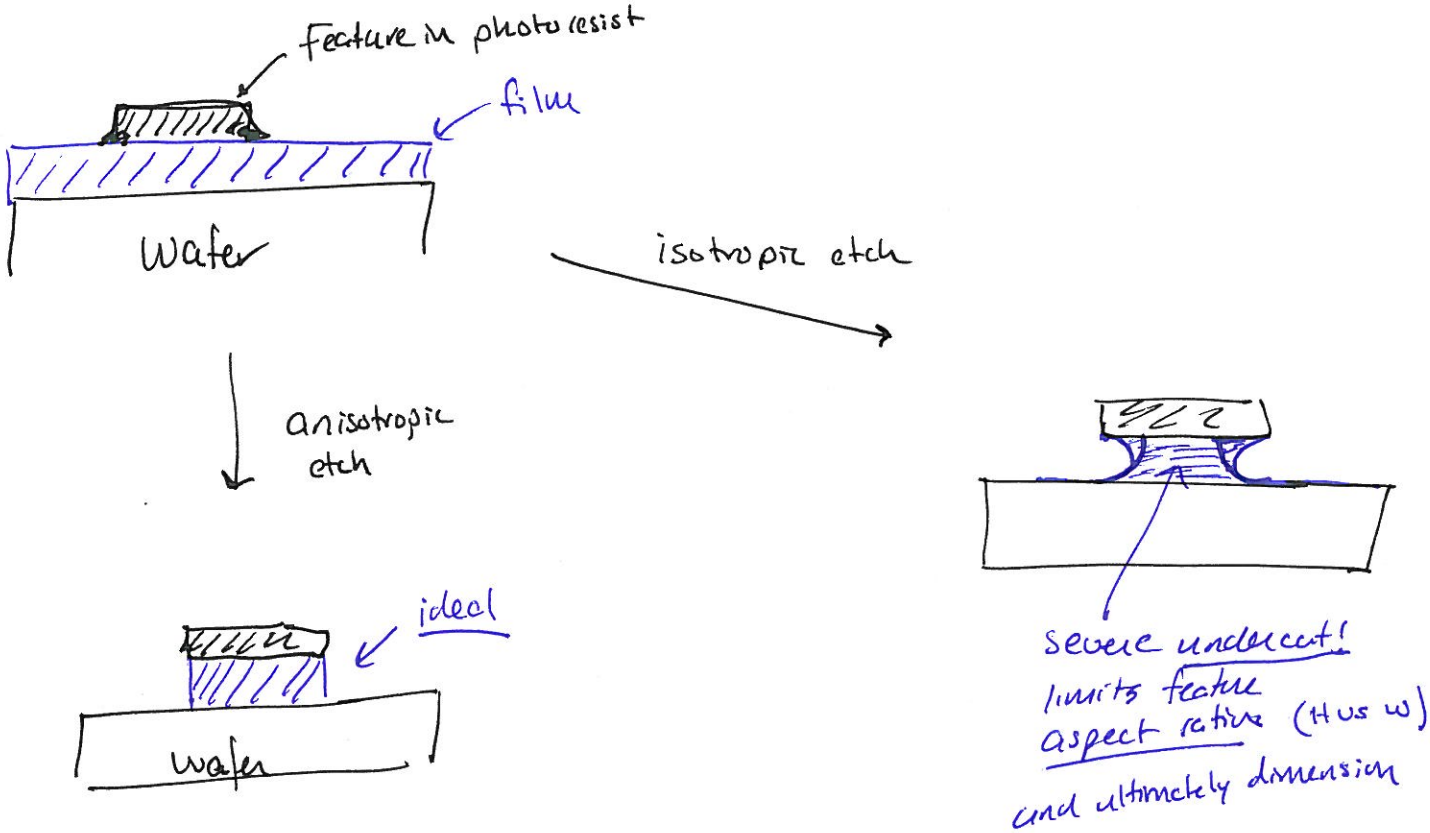
15 Etching (Wet, CMP, Dry)

Def. → Process by which material is removed from film or substrate by etchant

Mask layer used to precisely transfer features into exposed regions of underlying material

Wet etching (typically isotropic) and Dry (Plasma, gasphase) Etching (typically more anisotropic)



Reality: somewhere in between.

Ideal etching process for ULSI manufacture

(ULSI = ultra-large scale integration)

Criteria

(1) selective against etching: mask material

(2) "selective against etching": underlying layer

(3) rapid etch rate (i.e. machine throughput high)

(4) uniform wafer to wafer and within wafer

(5) safe

(6) minimal damage to substrate (e.g. plasma or sputter damage)

(7) process clean

(8) mask removeable

(9) full automation

Parameters that characterize an Etching process:

bias → difference between lateral mask dimension and etched dimension

tolerance → statistical distribution of bias value

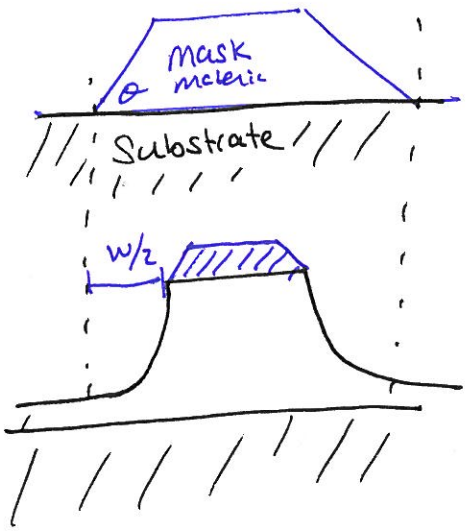
etch rate (ie nm/min, Å/min μm/min)

Lateral etch ratio $L_R = \frac{\text{horizontal etch rate}}{\text{vertical etch rate}}$

degree of anisotropy, $A = 1 - L_R$

Smaller than ~3μm patterns, need anisotropic etches

a. S_{fm} → Selectivity w/ respect to mask material

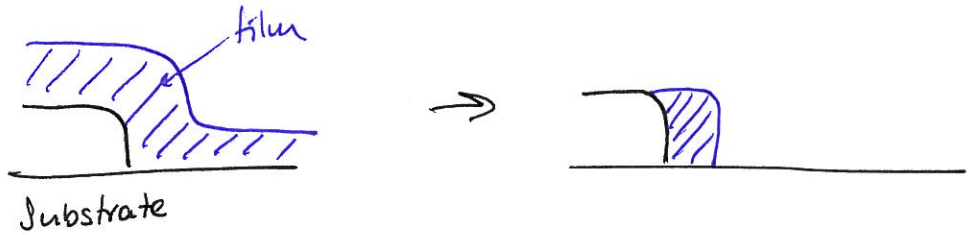


Critical to characterize and consider geometry of resist and worst case scenario when designing process.

b. S_{fs} → Selectivity w/ respect to substrate

→ very important when different heights!

↓ ↓ ↓ ↓ anisotropic etch

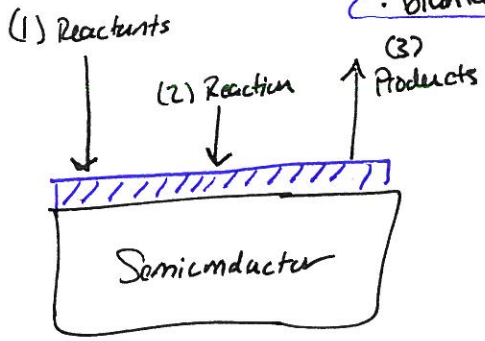


- need to overetch when material is deposited onto surfaces with steps!
- must have selectivity.

higher anisotropy requires higher selectivity!

Wet Etching (put on "chemistry" hat)

- used for: . polishing/cleaning sawed wafers
  . cleaning
  . blanket etches



Process affected by:

- agitation
- temperature
- concentration

- typically sprayed or immersion

Silicon Etching

Ask | What chemical processes are required to etch material?

a. $Si + 4HNO_3 \rightarrow \underbrace{SiO_2}_{\text{oxidized}} + 2H_2O + \underbrace{4NO_2}_{\text{reduced!}}$

Si^0 N^{+5} Si^{+4} N^{+4}

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$ etches SiO_2 formed.

Acetic acid used to dilute: **HNA etch**

→ AA. less polar than H_2O = better wetting.
($\varepsilon = 6.15$ vs 81)

→ less dissociation of HNO_3 → higher oxidative power

(Nitrate anion is a weaker oxidant than HNO_3!)

Mechanism Aside

HNO_3 has complex behavior!
Auto catalytic decomposition w/ HNO_2...
h^+ generated in semiconductor

High HNO_3 + Low HF = polishing regime

high HF/low HNO_3 → little residual oxide... etching?

b. Hydroxide Etching of Silicon

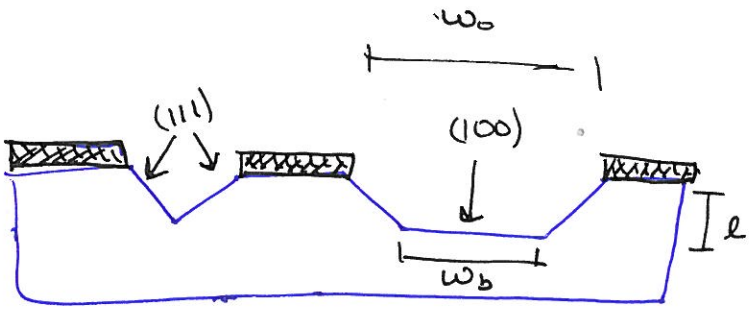
(eg. KOH in H_2O + IPA)

~20 wt% KOH at 80°C

TMAOH → used for IC manufacture since no metal contamination.

→ etch rate (100):(110):(111) = 100:16:1

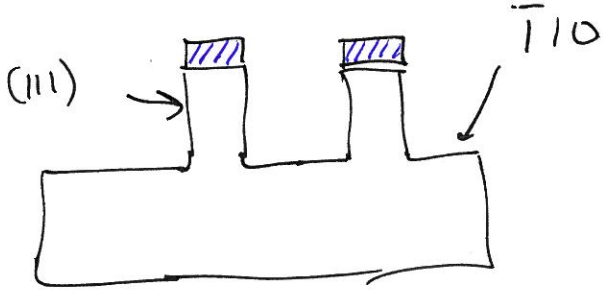
i. 100-oriented Si wafer



• etching can result in precise <u>V-shaped grooves</u>.

$$w_b = w_o - \sqrt{2}\, l$$

ii $\bar{1}10$-oriented wafer



111 is ⊥ to $\bar{1}10$ in cubic system $\alpha = \beta = \gamma = 90°$

$111 \cdot \bar{1}10 = -1 + 1 + 0 = \emptyset$

orthogonal

$$Si + H_2O + 2OH^- \rightarrow SiO_3^{2-} + 2H_2 \text{ (generates heat)}$$

- SiO_2 is etched slowly in base
- Si is thermodynamically unstable in water! Because in strong base Si oxide is soluble, solution etches.

(etch masks can be made w/ Si_3N_4 or SiO_2)

SiO_2 Etching

Bond energies:

Si-H	3-4 eV
Si-Si	3-4 eV
Si-F	6-7 eV ← !

Overall reaction:

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

Note: what is oxidized? :)

reactions

$$SiO_2 + 4F^- + 4H^+ \rightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2F^- \rightarrow SiF_6^{2-} \qquad K = 1.5 \times 10^6$$

dominant stable species in solution

Etch rate is controlled by the free fluorine/proton concentration in the solution!

$$K_a = \frac{[F^-][H^+]}{[HF]} = 10^{-3.18}!$$

$$pKA = 3.18 = -\log(K_a)$$

weak acid... most undissociated!

$$HF \rightarrow F^- + H^+$$

dissociation is pH dependent

high pH = no etching by this mechanism (no H^+)

low pH = no etching (no F^-)

→ want to buffer pH.

Add $NH_4F \rightarrow NH_4^+ + F^-$ fully dissociates

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$pH = 3.18 + \log\frac{[F^-]}{[HF]}$$

← determined by NH_4F concentration

← what you put in

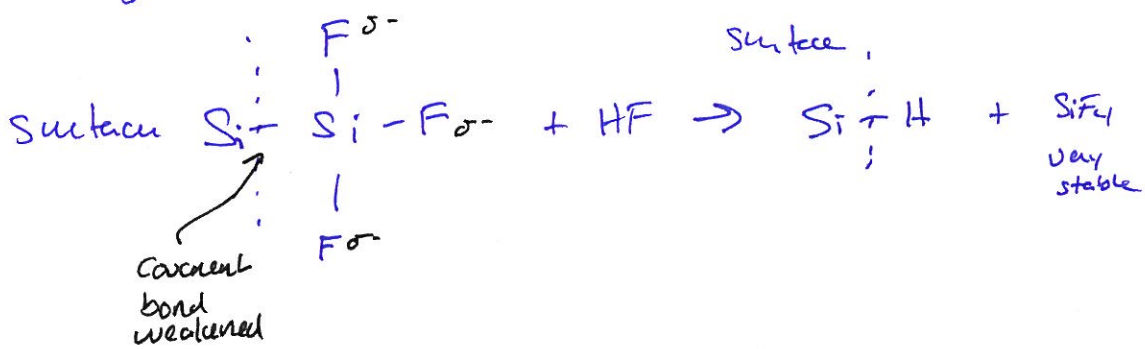
now $[HF] \sim [F^-]$

must have large changes in $[F^-]$ to affect pH ⇒ etch rate constant! as F^- depletes.

So, if Si-F bond is very strong,

Why is the silicon surface H-terminated after etching and not F-terminated?

Polarization of Si-F bond leads to preferential etching of remaining Si-Si bond:



GaAs etching

→ surface activities of 111-Ga and 111-As very different!

→ etches anisotropic

→ typical chemistry is

$H_2SO_4 - H_2O_2 - H_2O$

$H_3PO_4 - H_2O_2 - H_2O$

General idea to wet etch something: convert to something soluble! often via oxidation.

A. Silicon Nitride Etching

a. 85% H_3PO_4 at 180°C – selective over SiO_2

→ typically use a hard mask (eg SiO_2) as resist doesn't hold up to these conditions

$$3Si_3N_4 + 27H_2O + 4H_3PO_4 \rightleftharpoons 4(NH_4)_3PO_4 + 9H_2SiO_3$$

hydrolysis of Si-Ni bonds to form ammonia....

Examples of how etches are designed chemistries and work.

B. Al etch

4 ml HNO_3 ← oxidant

3.5 ml CH_3COOH

73 ml H_3PO_4

14.5 ml H_2O

Solvents

30 nm/min

H_3PO_4 ← stabilizes and etches aluminum oxides!

C. Au etch

4g KI ← forms soluble AuI complexes AuI_3

1g I_2 ← oxidant $I_2^0 \rightarrow 2I^- + 2h^+$

40 ml H_2O

1000 nm/min

D. Pt etch (dilute aqua regia)

Oxidizes $Pt^0 \rightarrow Pt^{4+}$ → 1 ml HNO_3

7 ml HCl

8 ml H_2O

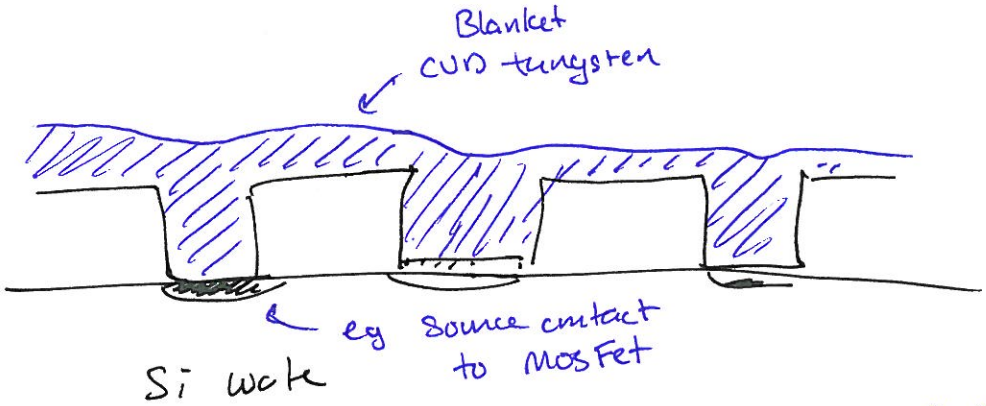
50 nm/min

Pt-chloride

Chemo-mechanical Polishing (Wolf 742)

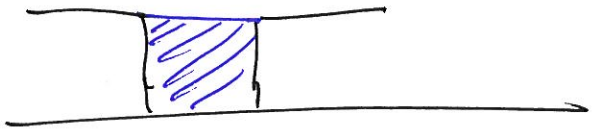
- planarization of dielectric and metal layers critical
- selectively remove high elevation features

Ex.



* need to isolate contacts, obtain smooth layer so that second lithographic step can be used to wire everything together correctly.

CMP → uses chemical etchants along w/ abrasive slurries to precisely remove material w/ nm precision.



→ planar structure results.

II. Plasma Etching (Dry Etch)

↳ ionized gas w/ equal + and −

3 basic mechanisms

(1) physical sputter (low Press < 100mtorr)
- anisotropic (directional due to ion momentum)
- low selectivity (same mechanism discussed in previous)

(2) Plasma Etching
- chemical, fast!
- can be selective
- isotropic, high pressure

(3) Reactive Ion etching
- physical and chemical etch processes
- can be <u>selective</u> and <u>anisotropic</u>!
- ~100mtorr pressure (intermediate)

<u>physical / chemical processes</u>

a. plasma gases used in sputtering → inert, atomic eg Ar^+

b. in selective etching gas used react chemically
eg. Cl_2 or CF_4 → $F^\cdot$, $CF_3^\cdot$, CF_3^+ etc
all highly reactive species.

→ primary role of plasma is to generate highly reactive species.

C. Plasma Etch Mechanism (Based solely on chemical mechanisms) (in RF Plasma)

(1) reactive species generated in plasma

(2) species transported via diffusion (RF, high Pressure)

(3) species absorbed

* (4) chemical reaction. – must form volatile product

(5) by product desorbed and pumped from chamber

Example: $CF_4 + e^- \rightarrow CF_3^+ + F\cdot + 2e^-$ ↗ O_2 (reacts w/ CF_3^+, reduces recombination $F\cdot + CF_3\cdot$)

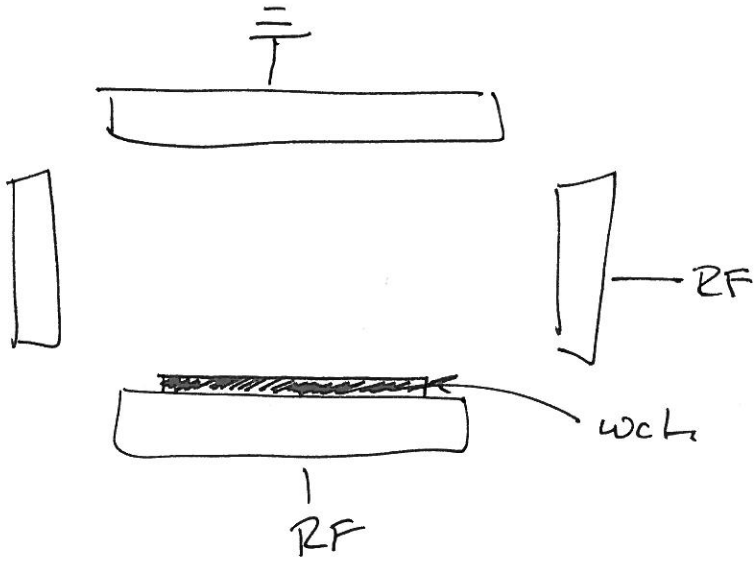
Si/SiO_2 etch. ⇒ Adding O_2 enhances Si etch rate (over SiO_2) by increasing conc. F. radicals.

⇒ H_2 enhances SiO_2 etch rate, increases CF_3^+ conc. (causes CFx polymer film to grow)

Examples of Etch Chemistries:

Solid	Etch Gas	Product
Si, SiO_2, Si_3N_4	CF_4, SF_6, NF_3	SiF_4
Si	Cl_2, CCl_2F_2	$SiCl_2$, $SiCl_4$
Al	BCl_3, CCl_4, Cl_2	$AlCl_3$, Al_2Cl_6
Organic Solids	O_2	CO_2, H_2O, CO
W, Ta, Mo etc	CF_4	WF_6...

Triode configuration RIE Etcher



→ RF generates plasma

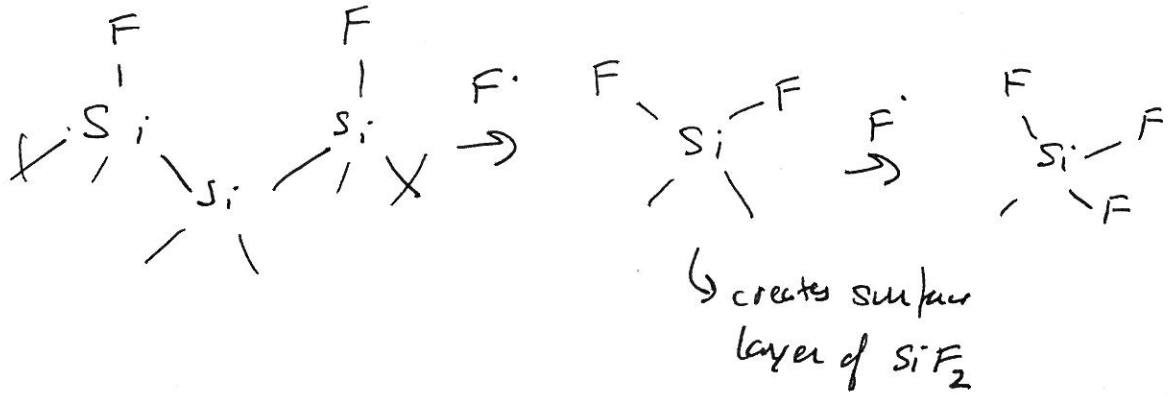
→ DC bias can be use to control ion energy, turn etching.

ion bombardment of substrate enhances etching rate → more anisotropy.

Example: CF_4 etching of Silicon

→ no plasma → no etching by CF_4

→ F• radicals bombard surface



↳ creates surface layer of SiF_2

→ SiF_4 etc...

Plasma chemistry not well understood... skip this?

Copper Electroplating

- Mechanism?
- use in CMOS fab.
- basic electrochemistry
- electrodeposition <u>versus</u> electroless deposition

Interconnects, low-k dielectrics, high K dielectrics

* Materials limit performance of CMOS besides Semiconductor mobility.