Course name:
Growth and Characterization of Nano-electronic Materials (EE728)

Instructor: Apurba Laha

Department of Electrical Engineering, IIT Bombay

Contact: Tel: 022-2576 9408, email: laha@ee.iitb.ac.in

Etching

EE669 VLSI Technology

Reference: Textbook: Silicon VLSI Technology by Plummer, Deal and Griffin, Chapter 10

Outline

1. Introduction to etching.
2. Wet chemical etching: isotropic.
3. Anisotropic etching of crystalline Si.
4. Dry etching overview.
5. Plasma etching mechanism.
6. Types of plasma etch system.
7. Dry etching issues.
8. Dry etching method for various films.
9. Deep Si etching (can etch through a wafer).

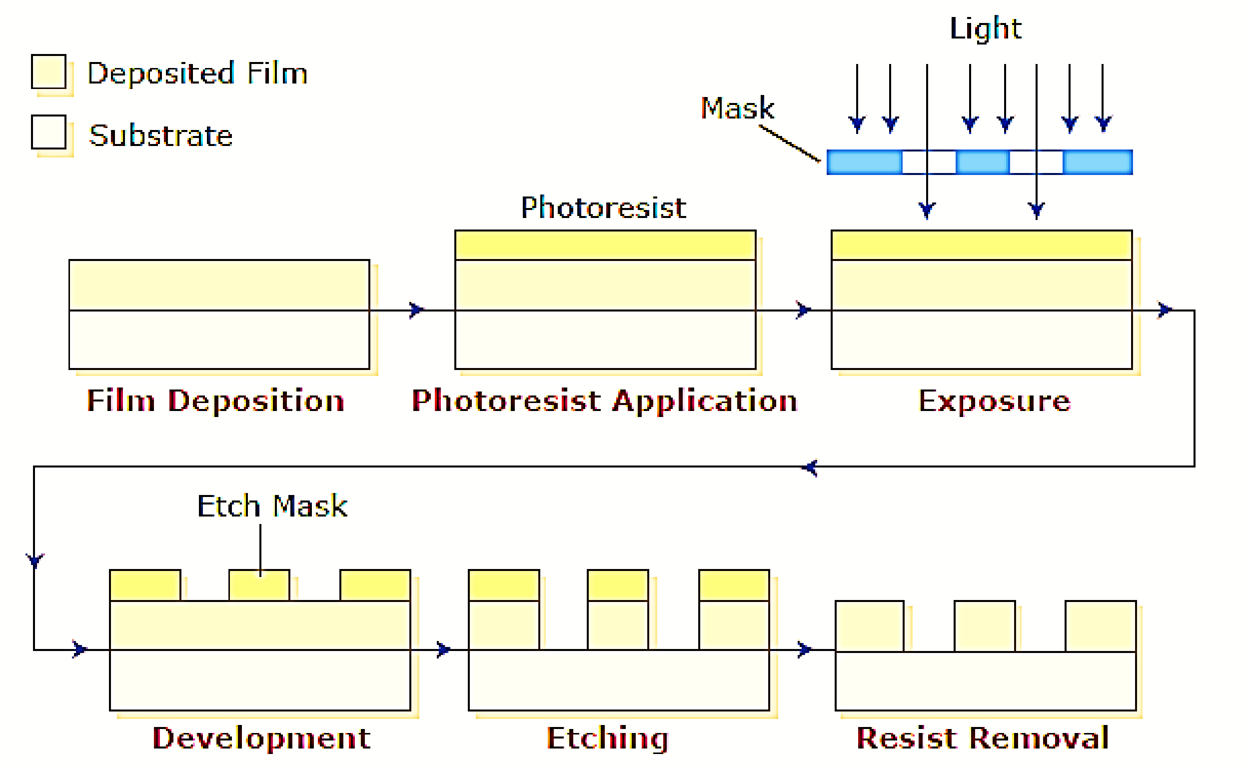
Etching

What is etching?

Etching is the selective removal of deposited films/layer

e.g.: HF dip to remove native oxide… but not Si

- **More often: through mask to realize a certain pattern required for specific device**

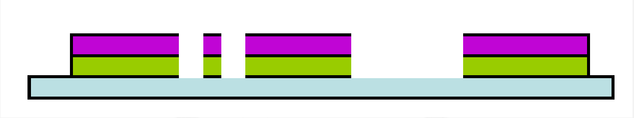


Etching

Etching usually done through a mask of

1. Photoresist(soft mask)

2. SiOx or SiN (hard mask)
(+ Photoresist to define hard mask)
More robust than PR alone



Etching must be done with consideration of prior processes(Material already present may inadvertently be affected by etching)

Mask, substrate

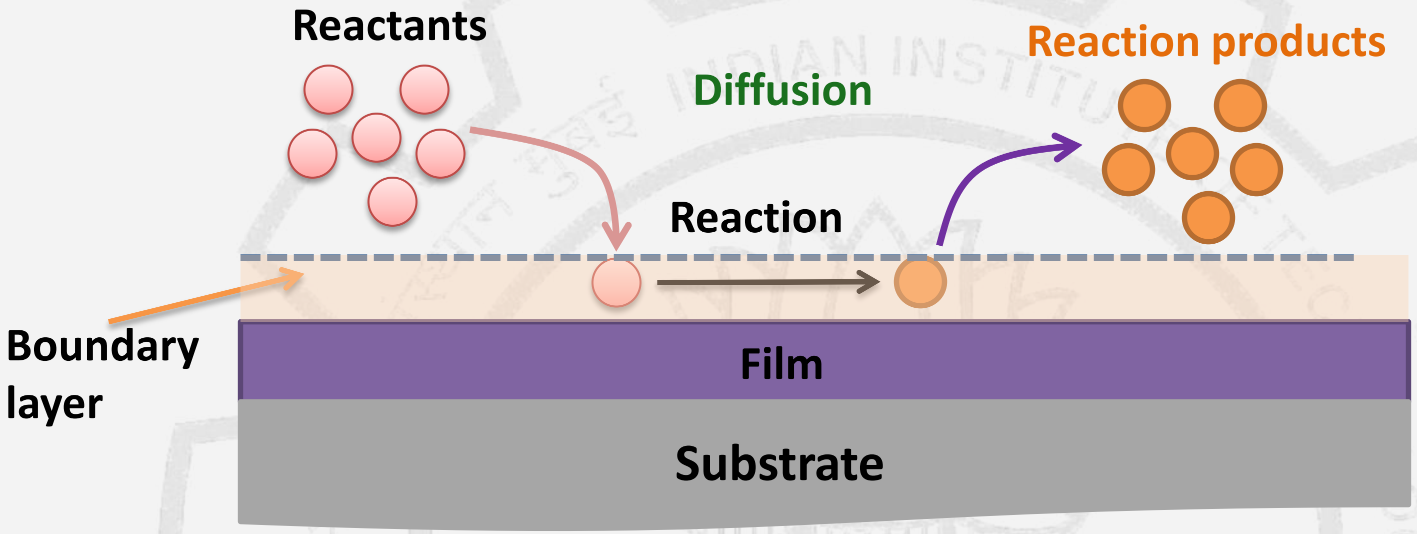
Etching processes

Two process: “dry” or “wet” methods

Wet etch	Dry etch
➢ Uses liquid etchants with wafers immersed in etchant solution. ➢ Is cheap and simple, but hard to control (not reproducible), not popular for nanofabrication for pattern transfer purpose.	➢ Uses gas phase etchants in plasma, both chemical and physical (sputtering process). ➢ Dry plasma etch works for many dielectric materials and some metals (Al, Ti, Cr, Ta, W…).

For other metals, ion milling (Ar^+) can be used, but with low etching selectivity. (as a result, for metals that cannot be dry-etched, it is better to pattern them using liftoff)

Etching processes



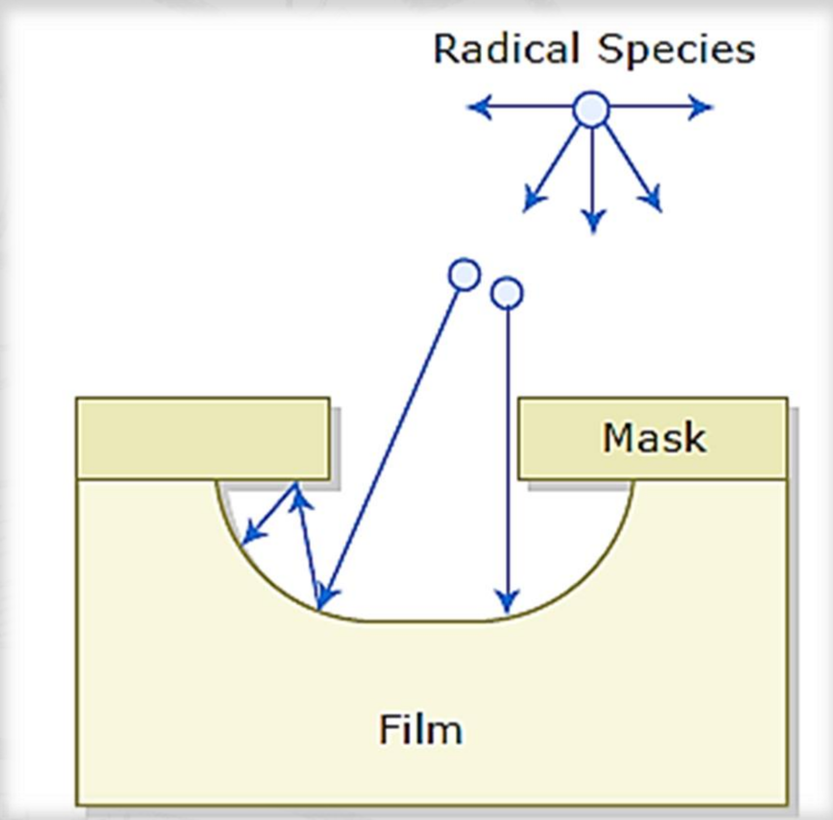
3 processes in etching:

- Mass transport of reactants (through a boundary layer) to the surface to be etched.
- Reaction between reactants and the film to be etched at the surface.
- Mass transport of reaction products from the surface through the surface boundary layer.

Figures of merit: etch rate, etch rate uniformity, selectivity, and anisotropy.

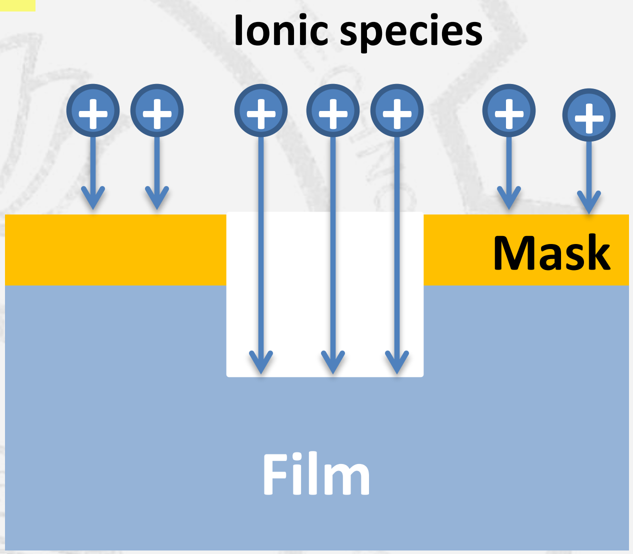
Chemical Etching

- Wafer in contact with liquid, reactive gas or plasma
- Etch is from chemical reaction acting isotropically
- Undercut is possible
- Highly selective
- Rate is thermally activated



Physical Etching

Wafer exposed to inert gas and/or plasma



- Etching: Momentum transfer of accelerated ions acting anisotropically
- Definition of good edge
- Low selectivity
- Rate is dependent on mass transport (byproduct)

Challenges and issues in etching

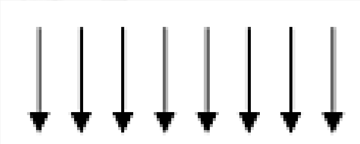
- ***Uniformity:*** *Must be uniform* across wafer, and across window
- ***Rate***: Fast enough to be practical, slow enough to be controllable
- ***Selectivity***: Rate of etching target material relative to mask-etch rate (should be large)
- ***Anisotropy***: Directional dependence of etch rate
- ***Byproducts***: Must be volatile or otherwise easily removed, and should be safe/easy to handle

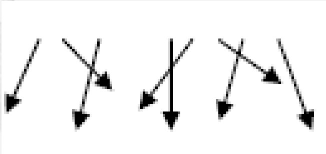
Selectivity

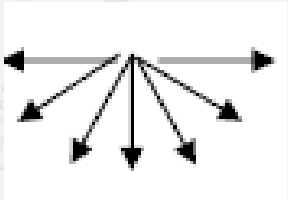
$$\textit{Selectivity} = \frac{\textbf{Etch rate of material intended to be removed}}{\textbf{Etch rate of mask}}$$

- ***Chemical*** **reactions can be highly selective (20 -50)**
- ***Physical*** **etch processes (sputter etch) less so (1 -5)**

Directionality: Anisotropic to Isotropic







	Wet etch (*Chemical*)
Selectivity	**25 - 50**
Directionality	**low**

	Dry etch (*Physical*)	Deposition techniques CVD	Sputtering
	1 - 5	high	(Sputter yield)
	high	good step	poor step

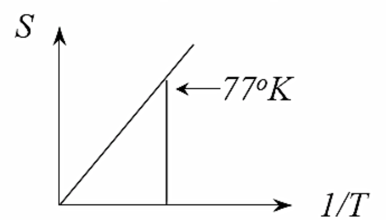
Figures of merit and selectivity

$$R_1 = A_1 e^{-Q_1/kT}$$

$$R_2 = A_2 e^{-Q_2/kT}$$

$$\therefore S = \frac{R_1}{R_2} = \frac{A_1}{A_2} e^{-(Q_1-Q_2)/kT}$$

R= etching rates
A = proportional constants
Q = activation energies



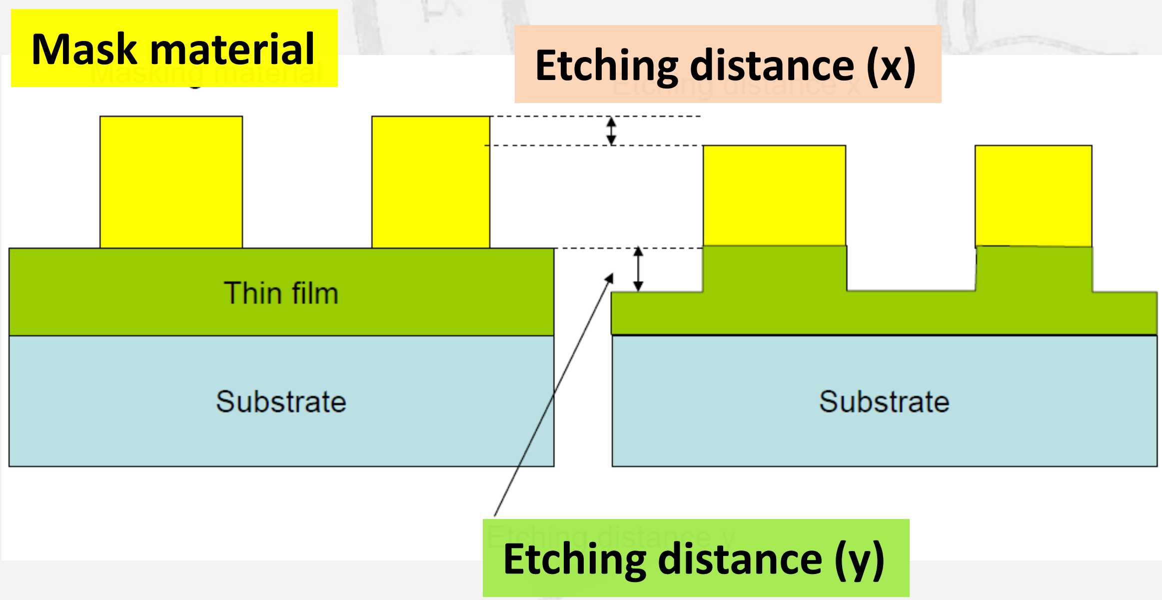
if $Q_1 < Q_2$

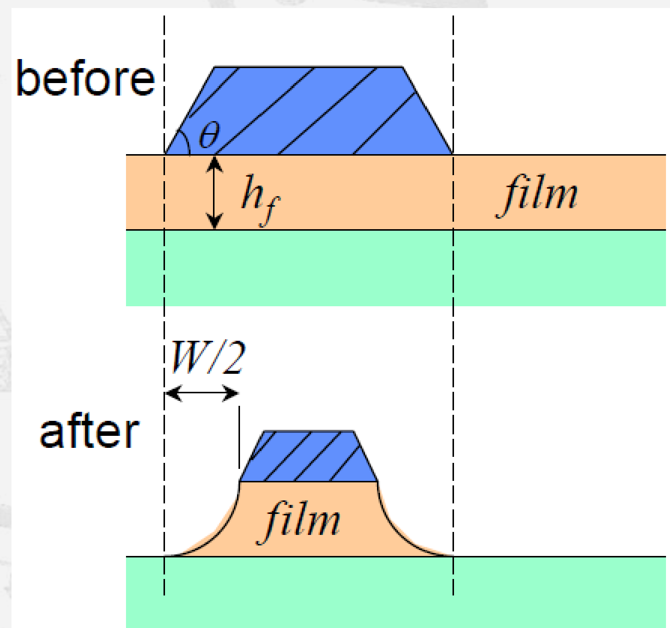
Temperature affects selectivity

Selectivity

$$S_{fm} \equiv \frac{V_{f\perp}}{V_{m\perp}} \left(\text{vertical components only} \right)$$

f: film; m: mask)





Etching with mask erosion

Figures of merit: anisotropy

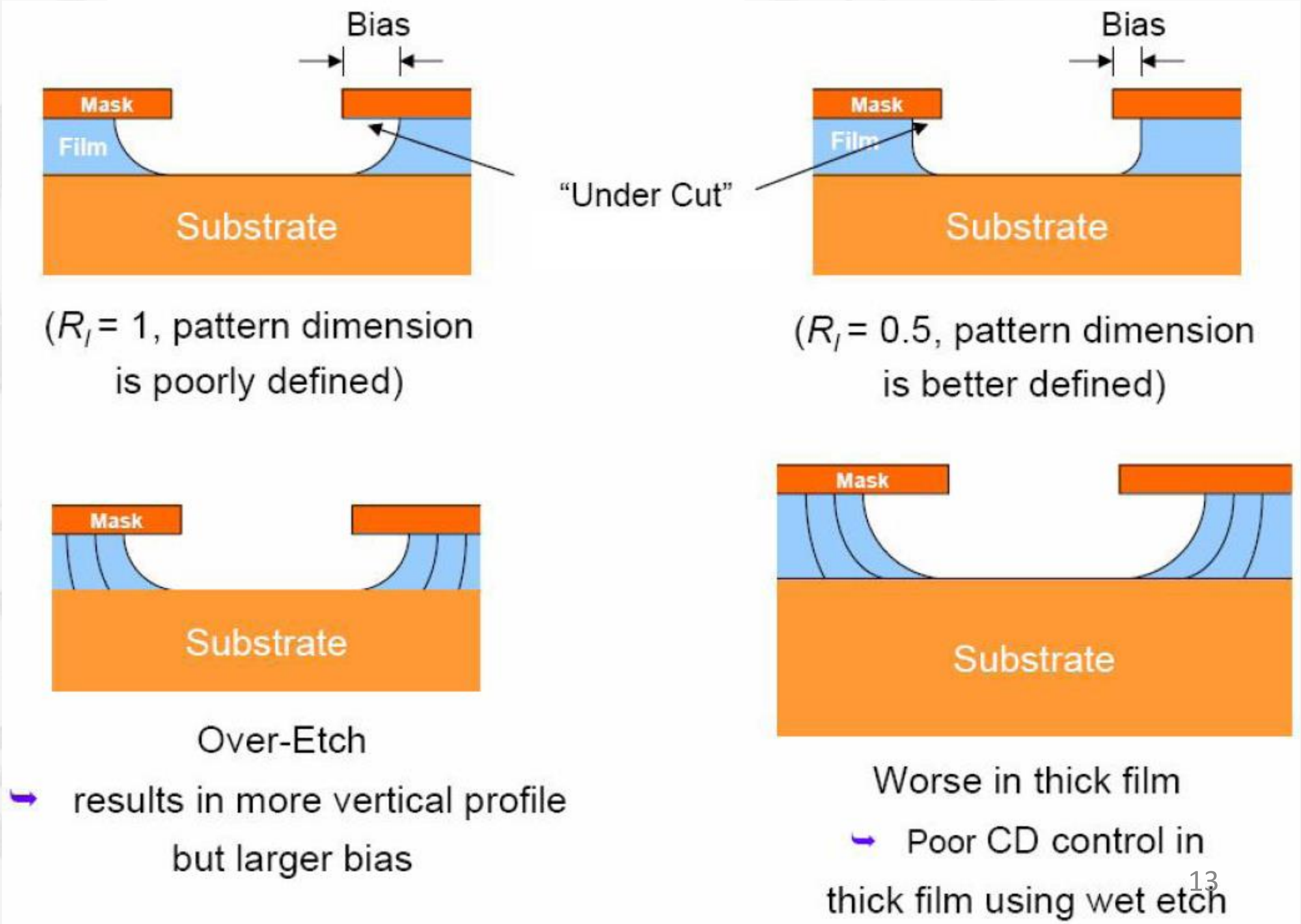
Isotropic: etch rate is the same along all directions.

Anisotropic: etch rate depends on direction, usually vertical vs. horizontal.

$$R_l = \frac{Horizontal\ Etch\ Rate(R_h)}{Vertical\ Etch\ Rate(R_v)}$$

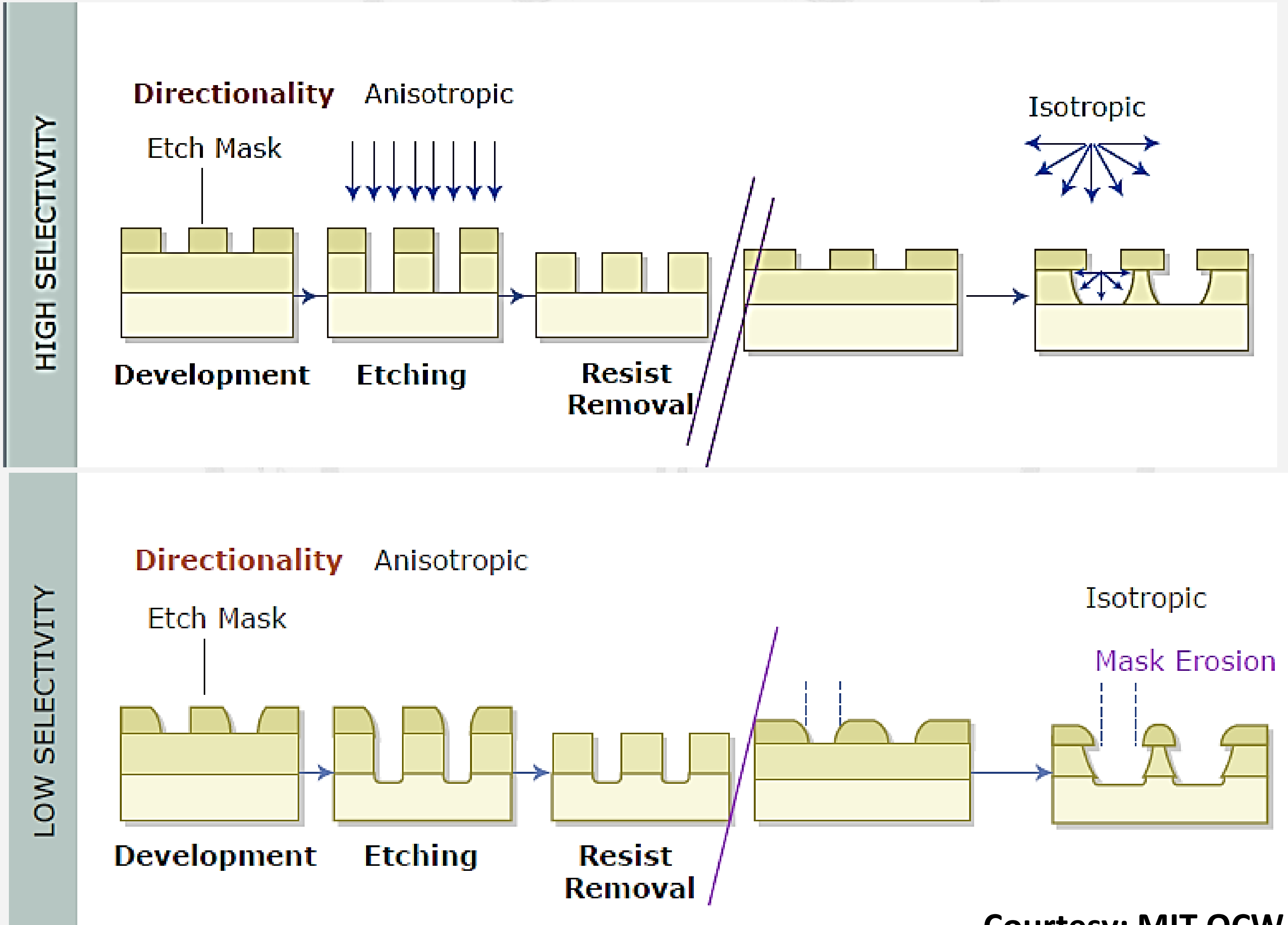
For isotropic, R_l=1.

For complete anisotropic, R_l=0.



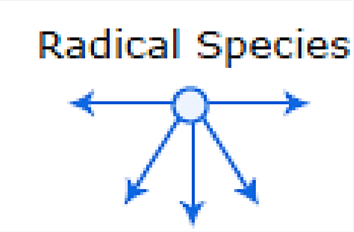
CD: critical dimension

Selectivity



Courtesy: MIT OCW

Etching

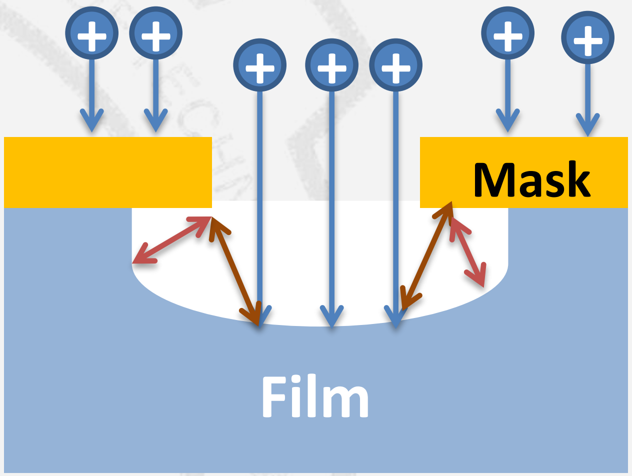


Wet etch (***Chemical***: *wet, vapor or in plasma*)
isotropic (*usually*), highly selective

HF dip: $\mathbf{SiO_2 + 6HF \Rightarrow H_2SiF_6(g) + 2H_2O}$

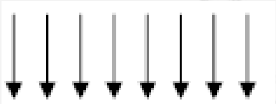
Used less for VLSI (poor feature size control)

Ionic species

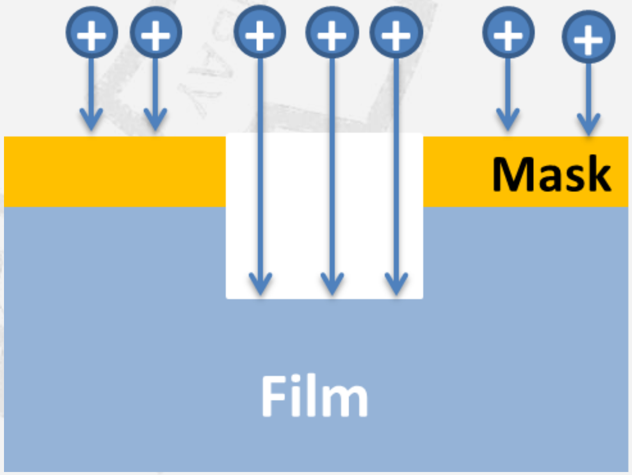


Dry Etch: (Physical: Ions, Momentum transfer)

Anisotropic, Not selective.
Sputter etching
More widely used for small feature



Ionic species

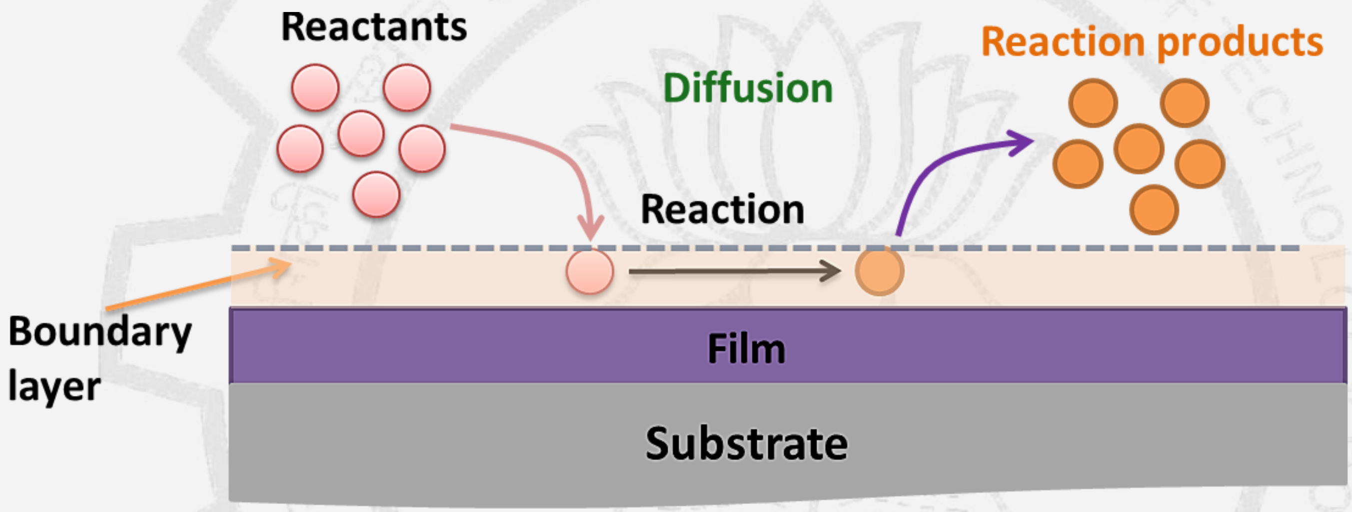


Combination (*Physical & Chemical*)
Ion-enhanced or
Reactive Ion Etching (RIE)

Blends best directionality and selectivity

Wet etching

Wafer in solution that attacks film to be etched, but not mask



- Reactive species *diffuse* through boundary layer to surface of wafer
- Thermally activated *reaction* at surface gives soluble species
- Products *diffuse* through boundary layer, transported away

Advantages: high *selectivity* due to chemical reactions

Disadvantages: *Isotropic (except for Si)*, poor *process control (can be transport or reaction limited, just like CVD),* strong *T*-dependence

Wet etching

Wet etching controlled by:	which affects:
Mass transport, boundary layer	***Uniformity, Rate*** $\delta(x) \propto \sqrt{x}$
Specific chemical reaction, ΔG	***Rate, Selectivity***
Temperature $\exp(-\Delta G/k_B T)$	***Rate***

Similar to CVD and Oxidation

Wet etching

HF dip removes native oxide from shipped wafers

Silicon Dioxide $$\boxed{SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O}$$

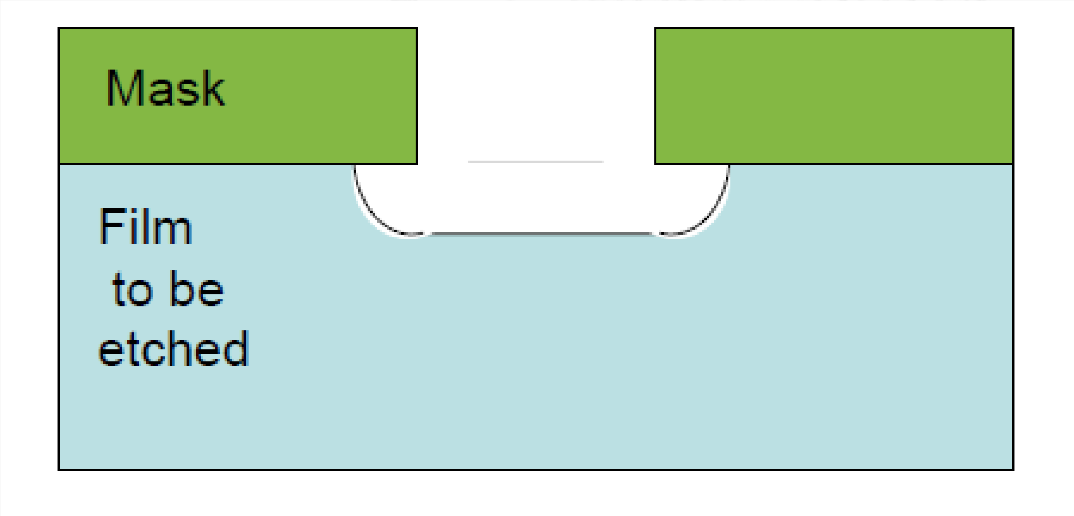
Rinse in DI water

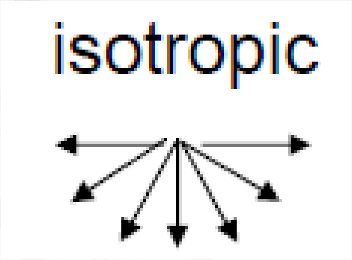
If you want no further oxide growth,
passivate surface with hydrogen

Crystallographic selectivity used to make cantilevers

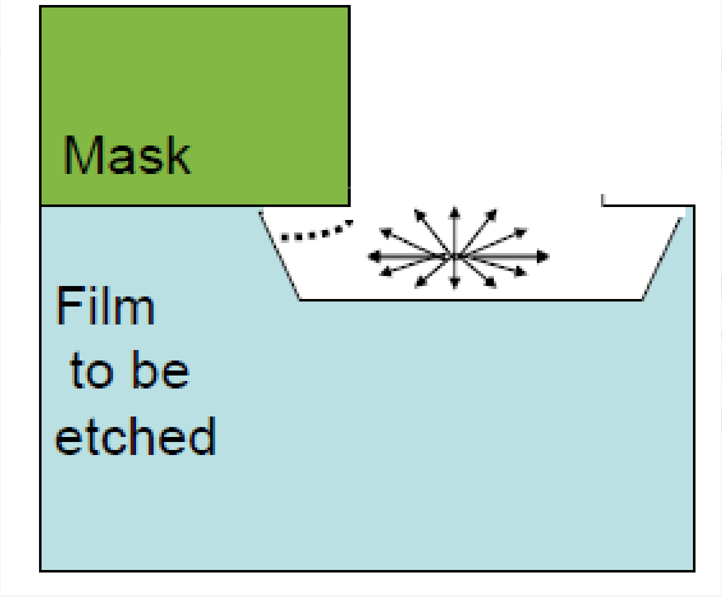
Silicon
$$\boxed{\begin{array}{l} Si + 2HNO_3 \rightarrow SiO_2 + 2HNO_2 \\ SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O \end{array}}$$

Wet etching





Boundary layer prevents growth from being Linear like this:



Boundary layer also retards removal of by-products

Wet etching of SiO_2

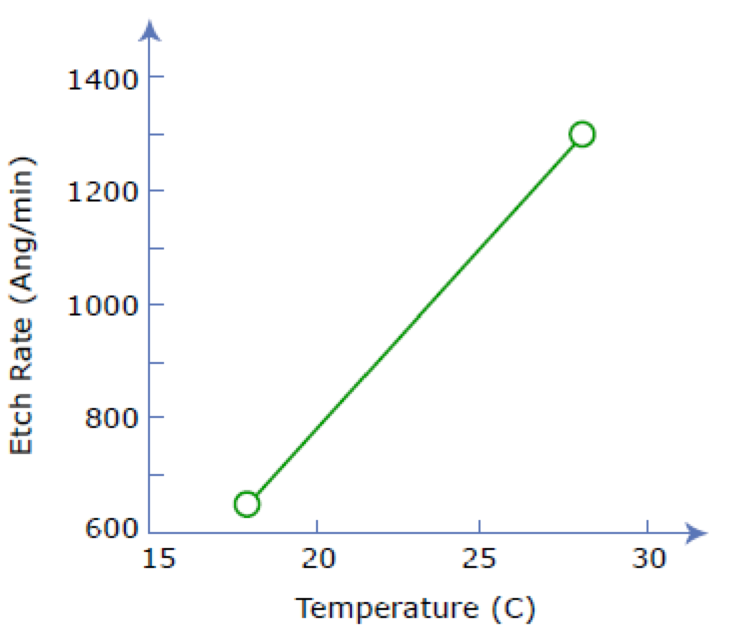
Immerse wafer in bath (HF dip)

or etch SiO_2 through photoresist mask

$$SiO_2(s) + 6HF(l) \rightarrow H_2SiF_6(g) + 2H_2O(l)$$

Reaction products must be gaseous or water soluble

- Slow reaction by diluting HF with H_2O
  - 120 nm/min in 6:1::H_2O:HF
  - 1000 nm/min in 1:1
- Doped or deposited oxide etches faster
- Selectivity relative to Si ≈ 100
- Buffered oxide etch (BOE) (add NH_4F)
  - improves consistency, maintains F



Wet etching of SiO_2

Common silicon wet etch: nitric (=>NO_2) + hydrofluoric acid

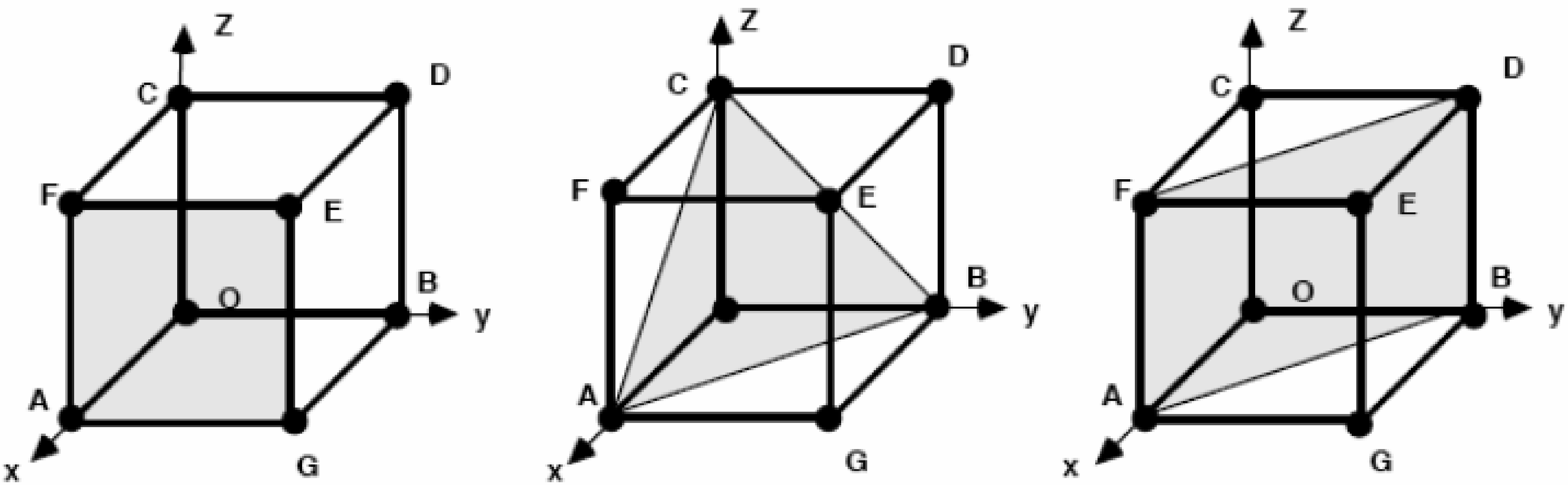
$$Si(s) + 2NO_2(g) + 2H_2O(l) \rightarrow SiO_2(s) + H_2 + 2HNO_2(l)$$

HF dissolves SiO_2 by reaction above. Total reaction:

$$Si(s) + HNO_3(l) + 6HF(l) \rightarrow H_2SiF_6(g) + 2H_2O(l) + HNO_2(l) + H_2$$

Buffered HF: Acetic acid (CH_3COOH) instead of H_2O,
NH_4F added to prevent depletion of F and retard etch of photoresist

Wet etching of Si

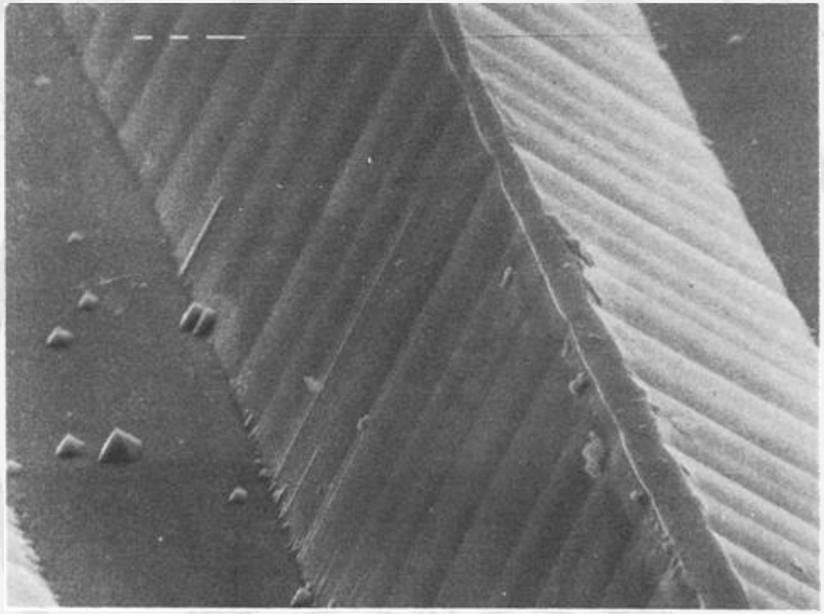


Bond coordination
in (111) is greatest

The family of planes AFEG (1,0,0), ABC (1,1,1) and ABDF (1,1,0)

(111) planes most stable

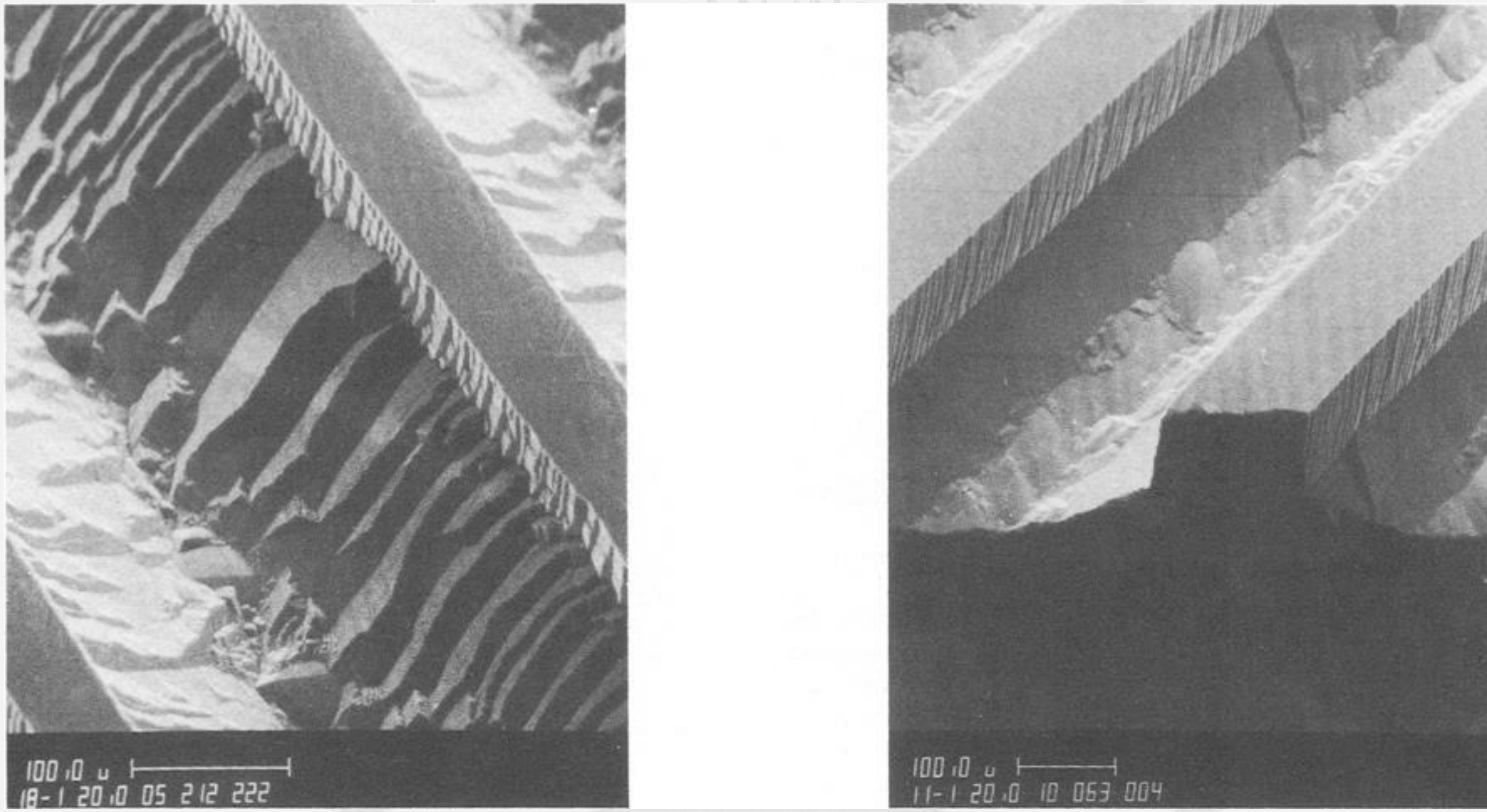
Wet etching of Si



Fast etching sidewalls on a <100> silicon wafer after exposure to an EDP solution
(ethylenediamine, water, and pyrocatechol)

See H. Seidel, L. Csepregi, A. Hueberger, and H. Baungärtel. *The Journal of the Electrochemical Society* 137 (1990): 3612-3626.

Wet etching of Si



Laterally underetched sidewall of a masked segment on a <110> wafer after exposure to a 50% KOH solution. The edges of the masked segment diagonally crossing the picture had an angular misalignment of (a, left) 32 ~ and (b, right) 42 ~ with respect to the [-110] direction, which is parallel to the *35.3* ~ inclined {111 } planes.

See H. Seidel, L. Csepregi, A. Hueberger, and H. Baungärtel. *The Journal of the Electrochemical Society* 137 (1990): 3612-3626.

Chapter 10 Etching

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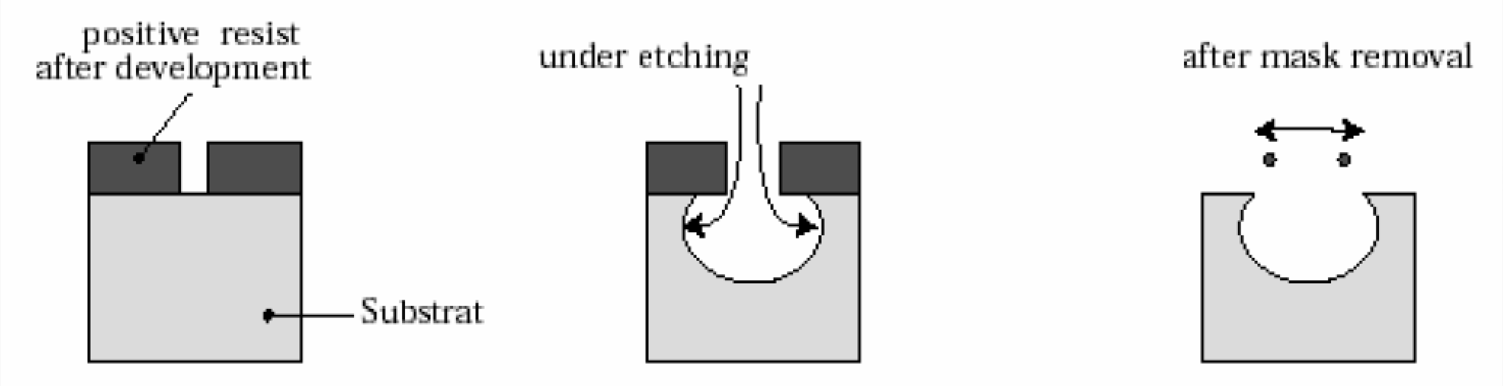
Wet etching

- Wet etching was used exclusively till 1970's when feature size >3um.
- For small scale features, large etch bias leads to significant CD (critical dimension) loss.
- For today's IC industry, wet etching is used for noncritical feature sizes.
- Advantages: high selectivity, relatively inexpensive equipment, batch system with high throughput, etch rate can be very fast (many µm/min).
- Disadvantages: generally isotropic profile, high chemical usage, poor process control (not so reproducible), excessive particulate contamination.



- The etch rate can be controlled by any of the three serial processes: reactants transport to the surface (depends on chemical concentration and stirring…), reaction rate (depends on temperature), reaction products transport from the surface (depends on stirring…).
- Preference is to have reaction rate controlled process because
  - Etch rate can be increased by temperature
  - Good control over reaction rate – temperature of a liquid is easy to control
- Mass transport control will result in non-uniform etch rate: edge etches faster.
- Etchant is often stirred to minimize boundary layer and make etching more uniform.

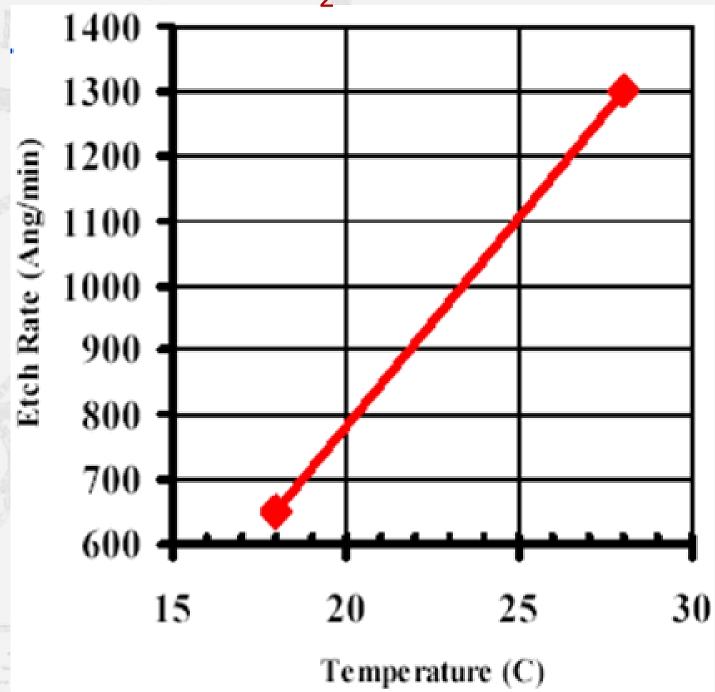
Isotropic wet etching (silicon dioxide)

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

- Etch is isotropic and easily controlled by dilution of HF in H_2O.
- Thermally grown oxide etches at
  - 120nm/min in $6H_2O$:1HF
  - ~1 µm/min in 49 wt% HF (i.e. undiluted as purchased HF).
- Faster etch rate for doped or deposited oxide.
- High etch selectivity (SiO_2/Si) > 100
- Buffered HF (BHF) or buffered oxide etchant (BOE) provides consistent etch rate
  - In regular HF etches, HF is consumed and the etch rate drops.
  - HF buffered with NH_4F to maintain HF concentration, typically $6NH_4F$: 1HF

$$NH_4F \rightarrow NH_3\uparrow + HF$$

SiO_2 etch rate



HF is very dangerous! Because:

- It is not a so strong acid (you don't feel the pain for diluted HF).
- Deceptive: it looks just like water.
- It penetrates skin and attacks slowly the flesh and the bone.
- It might be too late when you begin to feel the pain.

Isotropic etch (silicon)

- Silicon is etched by nitric acid and hydrofluoric acid mixtures (HNO_3 may be replaced by other strong oxidants like H_2O_2)
- HNO_3 partially decomposes to NO_2, which oxidizes the surface of Si.

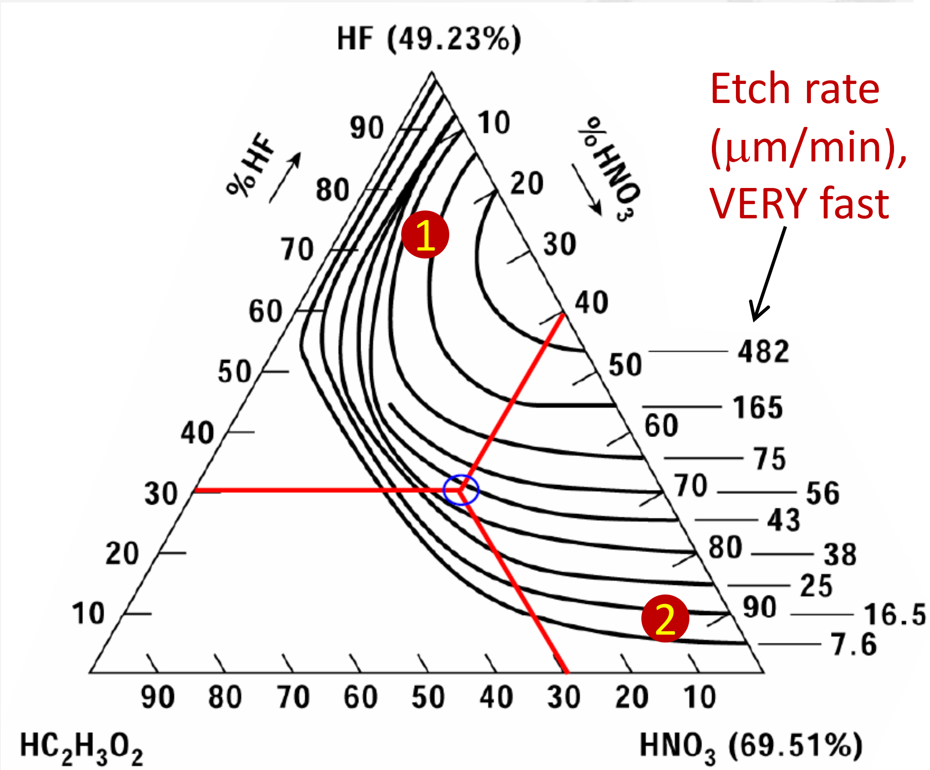
$$Si + 2NO_2 + 2H_2O \rightarrow SiO_2 + H_2 + 2HNO_2$$

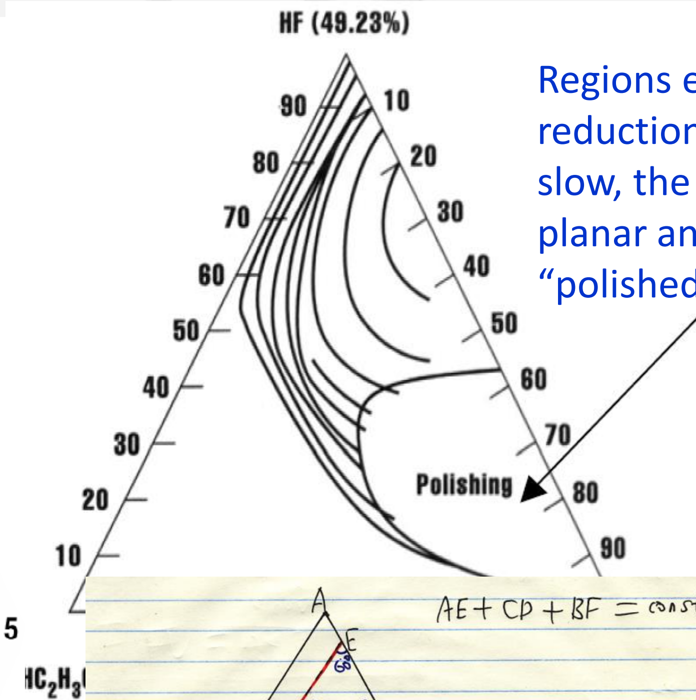
- The HF then dissolves the SiO_2. The overall reaction is:

$$Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2O + H_2$$

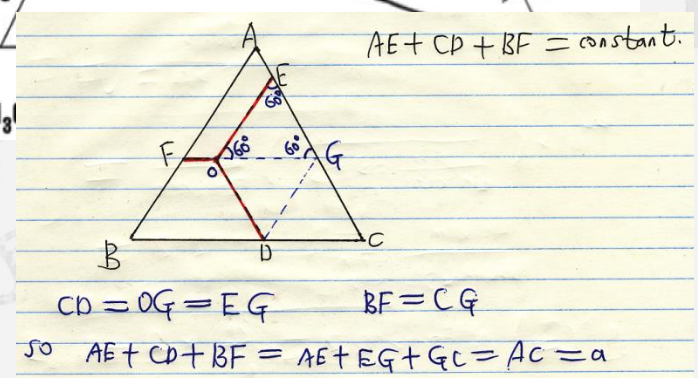
- Excess nitric acid results in a lot of silicon dioxide formation and etch rate becomes limited by HF removal of oxide (polishing).
- CH_3COOH (acetic acid) or H_2O can be added as diluent, but etch differently.
- Acetic acid is preferred because it prevents HNO_3 dissociation.

Si iso-etch curves





Regions exist where the reduction reaction is so slow, the surface is very planar and ends up being "polished" after the etch.



As-purchased HF is 49.23%, and HNO_3 69.51%)

Region 1:

High HF concentrations, reaction limited by HNO_3, follow constant HNO_3% lines.

Rate limited by oxidation, etched wafer surface have some oxide.

Region 2:

High HNO_3 concentrations, reaction limited by HF, follow constant HF % lines.

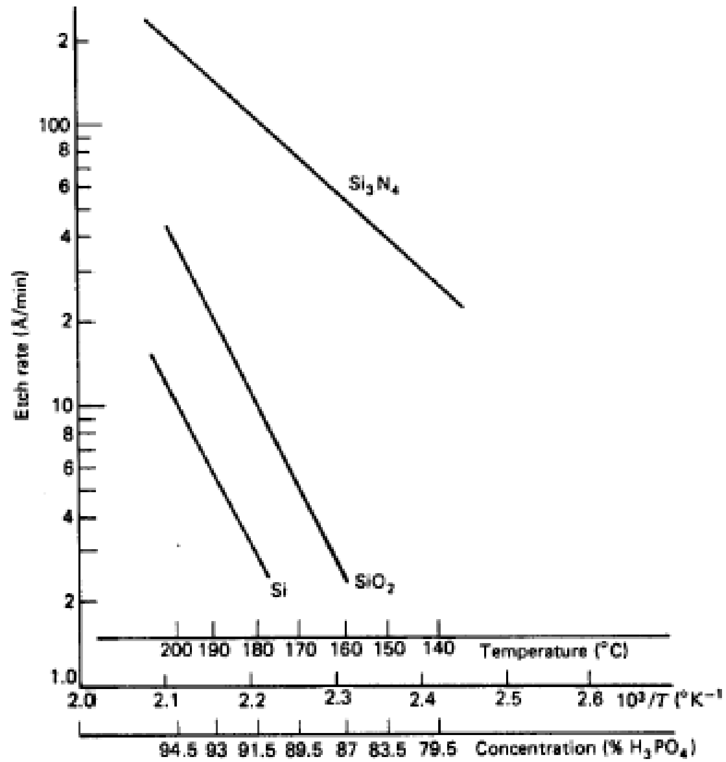
Rate limited by reduction, etched wafer surface have more oxide.

Isotropic etch (silicon nitride)

$$Si_3N_4 + H_3PO_4 + H_2O \rightarrow NO\uparrow + NO_3^- + H_2PO_4^- + H_2SiO_3$$

- Silicon Nitride is etched very slowly by HF solutions at room temperature, for example 20:1 BOE @20 C
  - Etch rate of SiO_2- 300 Å/min
  - Etch rate of Si_3N_4 – 5-15 Å/min
  - Very good selectivity of oxide to nitride
- Silicon nitride etches in 49% HF at room temperature at about 500 Å/min
- Phosphoric acid at 150 °C [140-200 °C] etches Si_3N_4 at fairly fast rate
  - Etch rate of Si_3N_4 – 100 Å/min
  - Etch SiO_2 – 10 Å/min
  - Selectivity of Si_3N_4 over SiO_2 : S = 10
  - Selectivity of Si_3N_4 over Si: S=30

Phosphoric Acid Etch Rate



Isotropic etching (aluminum)

$$50H_3PO_4 : 20H_2O : 1HNO_3 : 1CH_3COOH$$

$$6H^+ + 2Al \rightarrow 3H_2 + 2Al^{3+}$$

Al^{3+} is water-soluble

- Aluminum etches in water, phosphoric, nitric and acetic acid mixtures.
- Converts Al to $Al_2O_3$with nitric acid (evolves H_2).
- Dissolve Al_2O_3 in phosphoric acid.
- Gas evolution leading to bubbles.
- Local etch rate goes down where bubble is formed, leading to non-uniformity.
- Al can also be etched in (diluted) acid or base, such as HCl, HNO_3, H_2SO_4, NaOH or KOH, but less controllable (etch the native oxide slowly and un-controllably, then once oxide all etched away, etch Al metal very fast).
- The etch seems more repeatable in diluted HF (1:100 diluted), if one doesn't bother to mix the above mixture ($50H_3PO_4$…).

Summary

Etchant	Etches	Doesn't etch
H_3PO_4(19), Hac(1), HNO_3(1), H_2O(2)	Al, SiN, M	SiO_2, Si, PR
HF, BOE (HF + NH_4F)	SiO_2, M	Si, SiN, Au
H_2SO_4(3), H_2O_2(1) pirahna	Organics, M	Si, SiO_2, SiN
I_2(I),KI(2),H_2O(10)	Au, M	Si, SiO_2, SiN, M, PR
NH_4OH(5), H_2O_2(1)	Polymers, Al	Si, SiO_2, SiN, M
HNO_3(64), NH_4F(3), H_2O(33)	Si, M	SiN, PR
HCl(3), HNO_3(1) (aqua regia)	Au, other M	Cr, Si, SiN, SiO_2

M: metal;

PR: photoresist;

Hac: acetic acid

Those are just starting point, can use different ratios.

E.g. the ratio for the Al etchant is different from previous slide.

In addition, most metals can be etched by (diluted) acid, except Ti and Cr that form a dense stable oxide on top.

Ti can be etched by HF; Cr by ceric ammonium nitrate plus acid.

Table 10–1 Common wet chemical etchants for various thin films used in IC fabrication

Material	Etchant	Comments
SiO_2	HF (49% in water) "straight HF"	Selective over Si (i.e., will etch Si very slowly in comparison). Etch rate depends on film density, doping.
	NH_4F:HF (6:1) "Buffered HF" or "BOE"	About 1/20 th the etch rate of straight HF. Etch rate depends on film density, doping. Will not lift up photoresist like straight HF.
Si_3N_4	HF (49%)	Etch rate depends strongly on film density, O, H in film.
	H_3PO_4:H_2O (boiling @ 130–150°C)	Selective over SiO_2. Requires oxide mask.
Al	H_3PO_4:H_2O:HNO_3:CH_3COOH (16:2:1:1)	Selective over Si, SiO_2, and photoresist.
Polysilicon	HNO_3:H_2O:HF (+ CH_3COOH) (50:20:1)	Etch rate depends on etchant composition.
Single crystal Si	HNO_3:H_2O:HF (+ CH_3COOH) (50:20:1)	Etch rate depends on etchant composition.
	KOH:H_2O:IPA (23 wt. % KOH, 13 wt. % IPA)	Crystallographically selective; relative etch rates: (100): 100 (111): 1
Ti	NH_4OH:H_2O_2:H_2O (1:1:5)	Selective over $TiSi_2$.
TiN	NH_4OH:H_2O_2:H_2O (1:1:5)	Selective over $TiSi_2$.
$TiSi_2$	NH_4F:HF (6:1)	
Photoresist	H_2SO_4:H_2O_2 (125°C)	For wafers without metal.
	Organic strippers	For wafers with metal.

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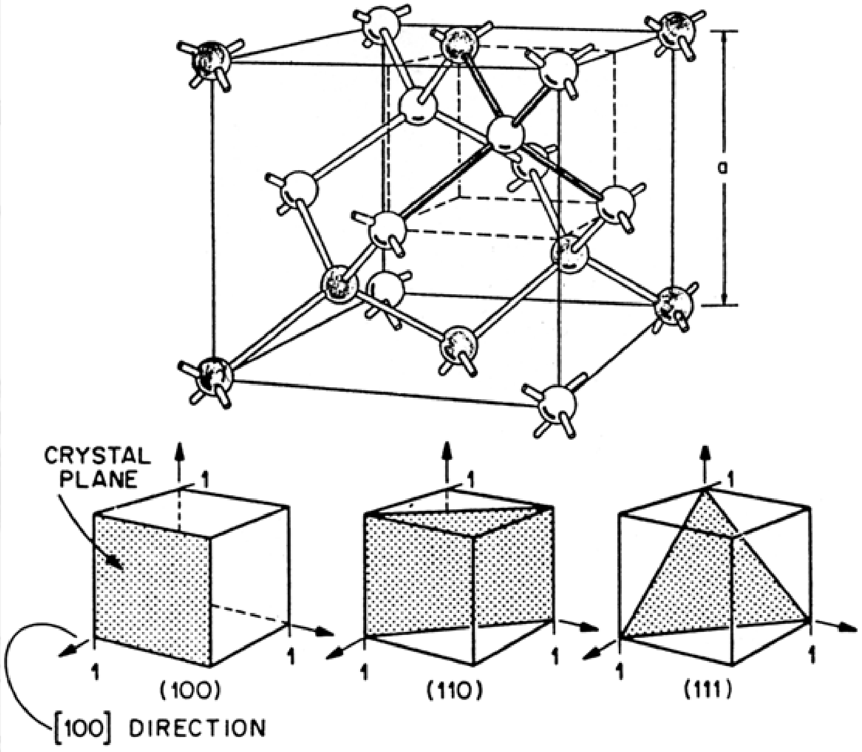
3. Anisotropic etching of crystalline Si.
4. Dry etching overview.
5. Plasma etching mechanism.
6. Types of plasma etch system.
7. Dry etching issues.
8. Dry etching method for various films.
9. Deep Si etching (can etch through a wafer).

An-isotropic wet etching of Si: overview

- Orientation selective etch of silicon occur in hydroxide solutions partly because of the closer packing of some orientations relative to other orientations
  - Density of planes: <111> > <110>, <100>
  - Etch rate: R(111) << R(110), R(100)
- <100> direction etches faster than <111> direction, with etch rate
  - R(100) = few 100 × R(111)
  - It is reaction rate limited
- Used very widely in MEMS (micro electro mechanical systems), since it is inexpensive, fast etching and easy to control.



{100} and {110} have 2 bonds below surface & 2 dangling bonds that can react.

{111} plane has three of its bonds below surface & only one dangling bond to react → much slower etch rate.

An-isotropic wet etching of Si

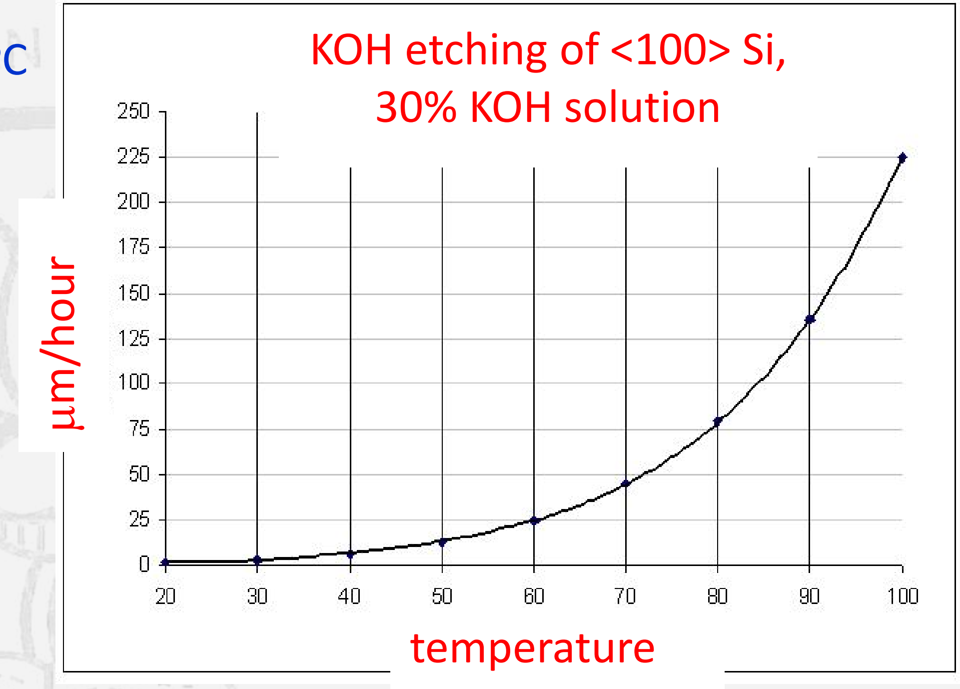
KOH etch example:

250 g KOH: 200 g 2-propanol, 800 g H_2O at 80^oC

1000 nm/min of [100]

Etch stops at p++ layers

Selectivity: {111}:{110}:{100} ~ 1:600:400



Seidel's etching model:

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

$Si(OH)_2^{2+} + 2OH^- \rightarrow Si(OH)_4 + 2e^-$

$Si(OH)_4 + 4e^- + 4H_2O \rightarrow Si(OH)_6^{2-} + 2H_2$

This is a model, real reaction is complicated.

$Si(OH)_4$ is soluble.

H_2 is generated and form bubbles.

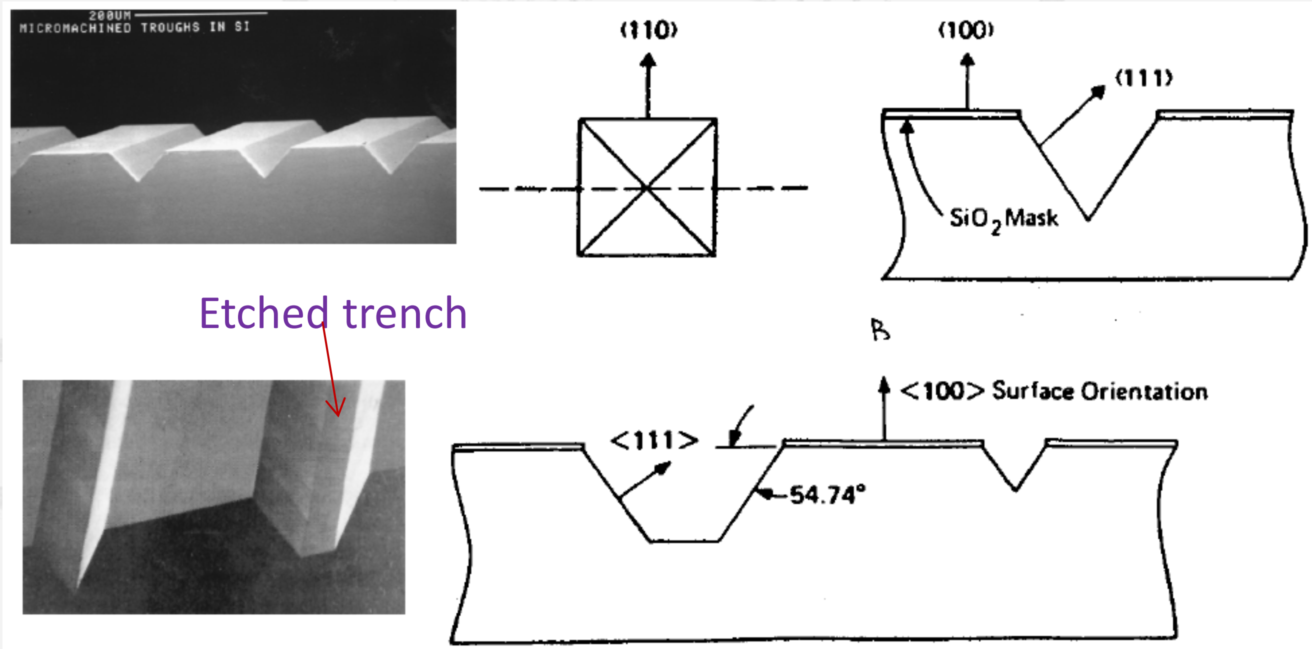
Materials	Etchants	Etch Rates
Silicon in <100> Silicon in <100>	KOH EDP	0.25 – 1.4 μm/min 0.75 μm/min
Silicon dioxide Silicon dioxide	KOH EDP	40 – 80 nm/hr 12 nm/hr
Silicon nitride Silicon nitride	KOH EDP	5 nm/hr 6 nm/hr

Rate drops
Harder to etch

EDP: see later slides

Examples: for (100) wafer

Effect of slow {111} etching with KOH: etching virtually stops at {111} plane.

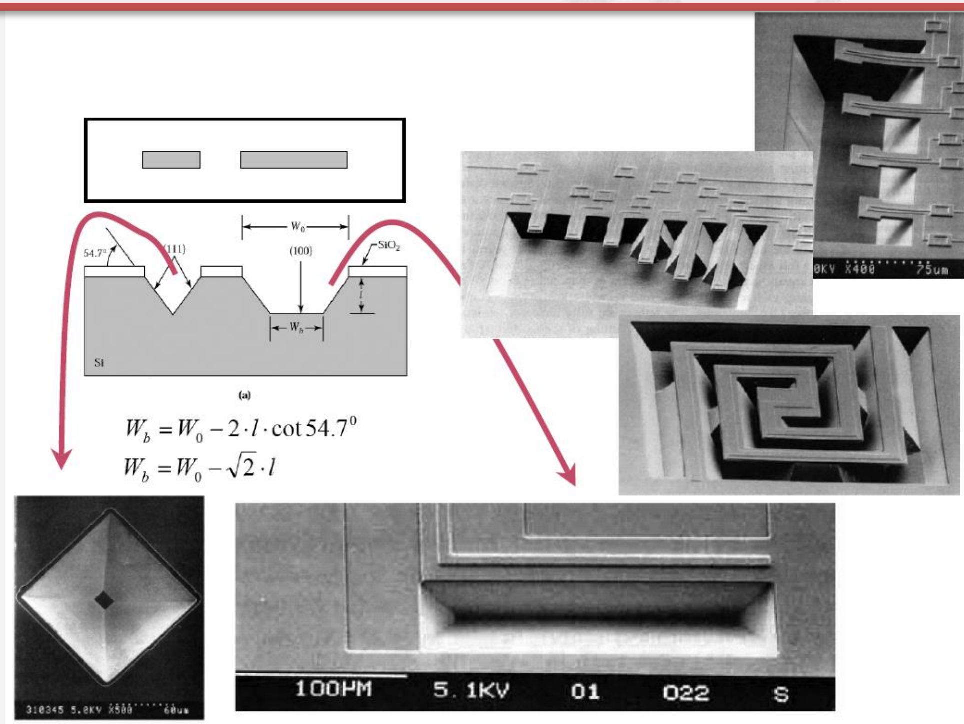


Etching selectivity to thermal oxide ~1000,
to *LPCVD* nitride ~infinity (>10⁴!).

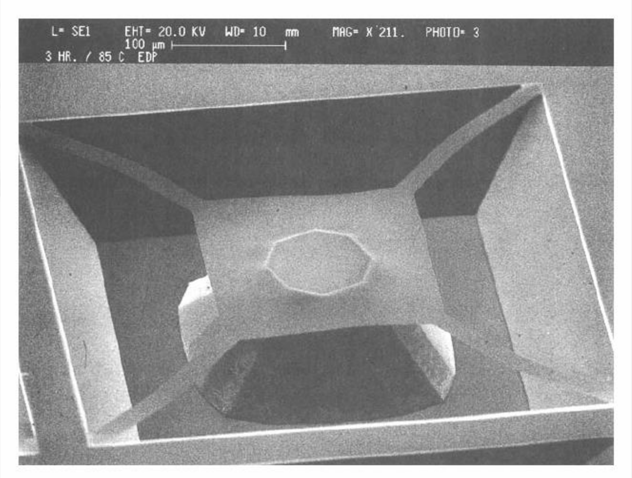
But KOH attacks *PECVD* oxide and nitride.

Etch mask: SiO_2 or Si_3N_4 or Cr/Au

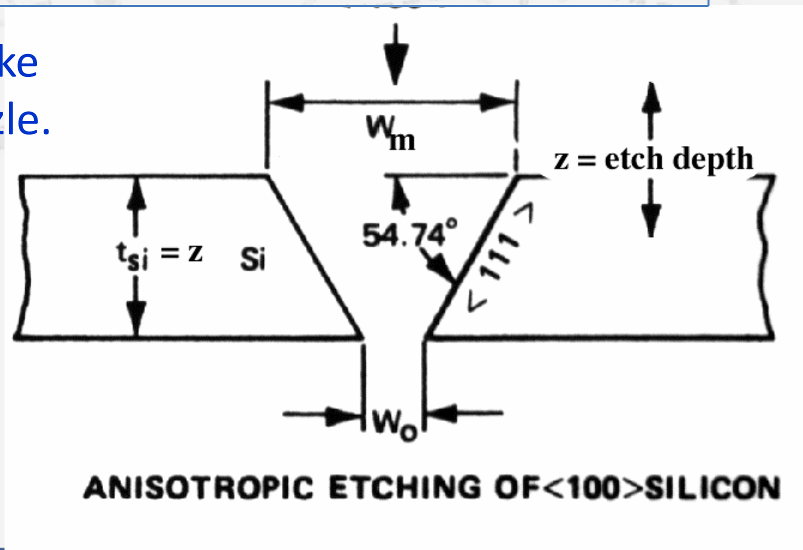
Examples: for (100) wafer

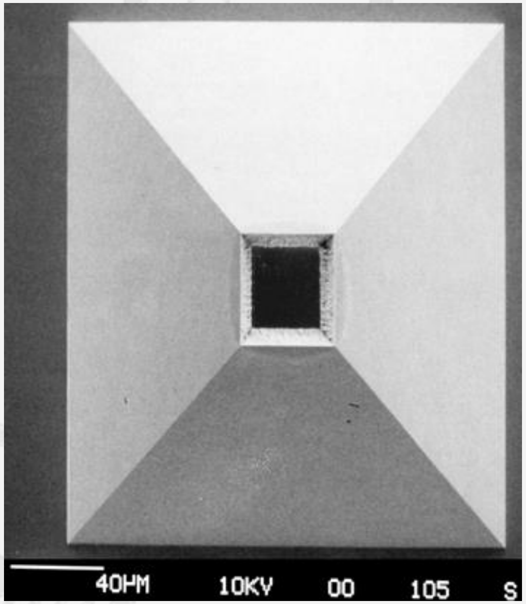


$$W_b = W_0 - 2 \cdot l \cdot \cot 54.7^0$$
$$W_b = W_0 - \sqrt{2} \cdot l$$

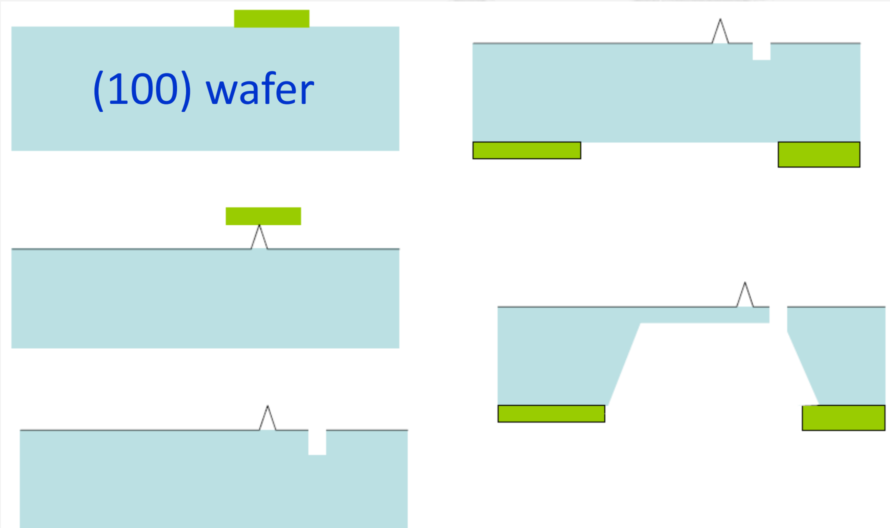


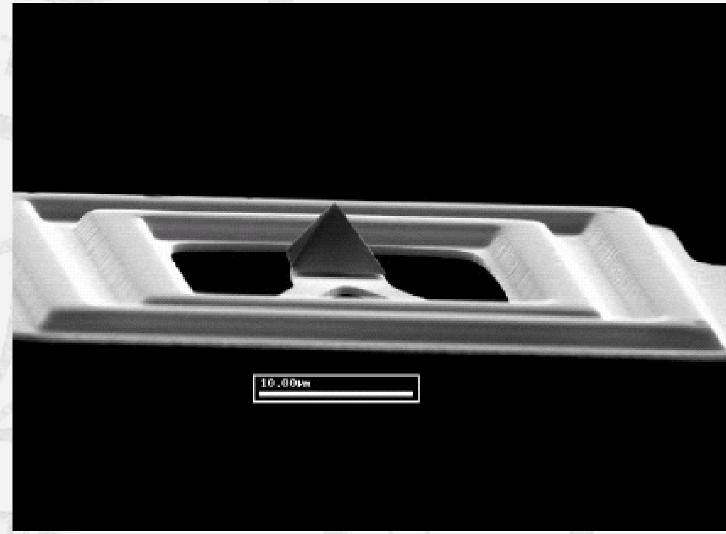
Have been used to make bubble-jet printer nozzle.



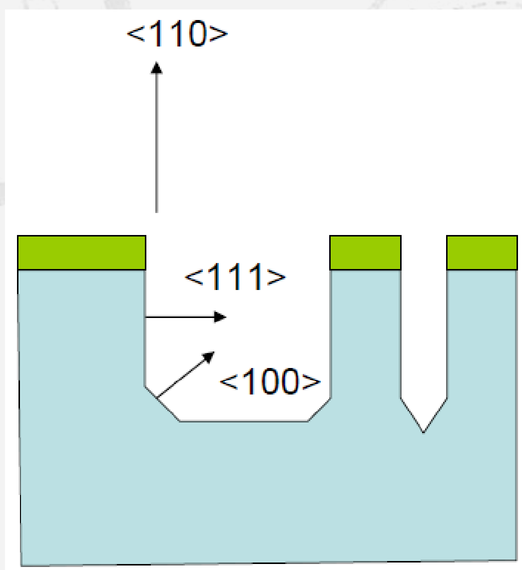


AFM (atomic force microscope) tips

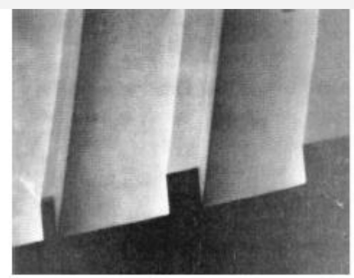


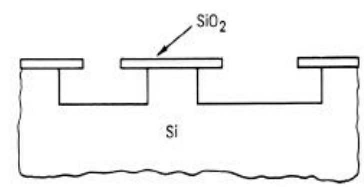


For (110) (not (100)) wafer, vertical (not tapered) trench possible.



What is the direction along the grating lines?





Bottom of pits are

- flat ({110} plane) if KOH is used
  {100} etches slower than {110}
- V-shaped ({100} planes) if EDP is used
  {110} etches slower than {100}

Other anisotropic silicon etchants

Tetramethyl Ammonium Hydroxide (TMAH)

- Used widely as positive photoresist developer (since it contains no metal like K or Na, which are harmful for device.)
- Typical etching at 80-90°C.
- Etching rate ~0.5-1.5 µm/min (10-40%w.t)
- Selectivity <100> : <111> ~ 10 - 35, much lower than KOH.
- Result in rough surface(H_2 bubble), KOH etch is smoother.
- Like KOH, attacks aluminum
- Like KOH, can use boron-stop-etching technique (etching rate decreases 40 times for $10^{20}/cm^3$ boron doping).
- Excellent selectivity of <100>Si : oxide/nitride (1: 5000-50000)

Ethylene Diamine Pyrochatechol (EDP)

- Typical etching temperature 115°C.
- Etching rate 1µm/min.
- Selectivity of <100>Si : oxide/nitride ~ 3000-7000.
- Doesn't attack metal (Au, Cr, Cu, Ta) but attacks Al.
- Selectivity <100> : <111> ~35; (100) etches faster than (110), ((110) etches faster for KOH).
- Excellent for boron stop technique, etching rate drops 50 times for $7 \times 10^{19}/cm^3$ boron doping.
- Carcinogenic.

http://en.wikipedia.org/wiki/Ethylenediamine_pyrocatechol

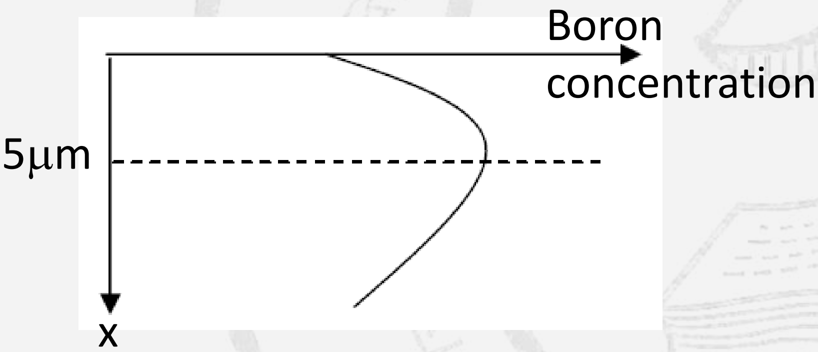
Etch stop

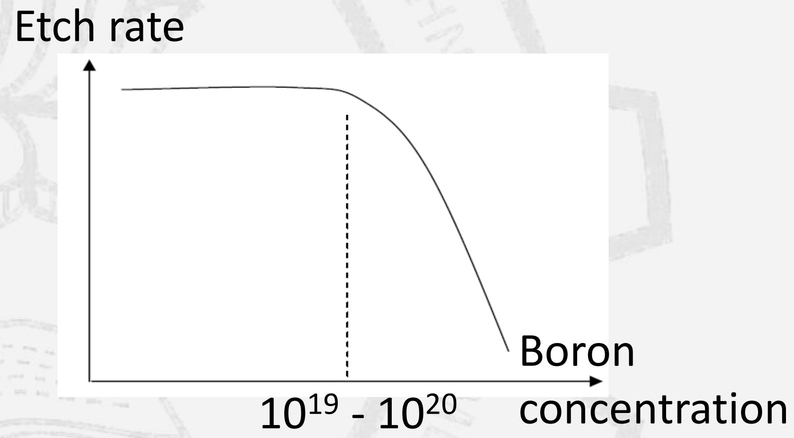
In wet etching process, etching depth is hard to control, so need etch stop layer.

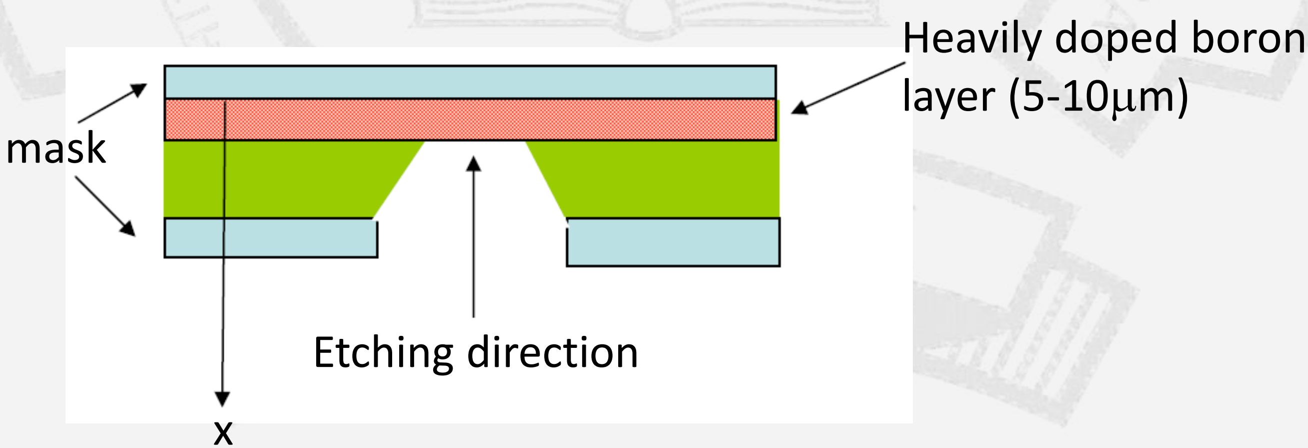
Besides oxide and nitride, etching may be stopped by the following two methods, both related to doping of the silicon substrates.

- Controlled by doping: doped Si dissolved slower than pure Si.
- Controlled by electrochemical etch stop.

Etching stop by boron doping

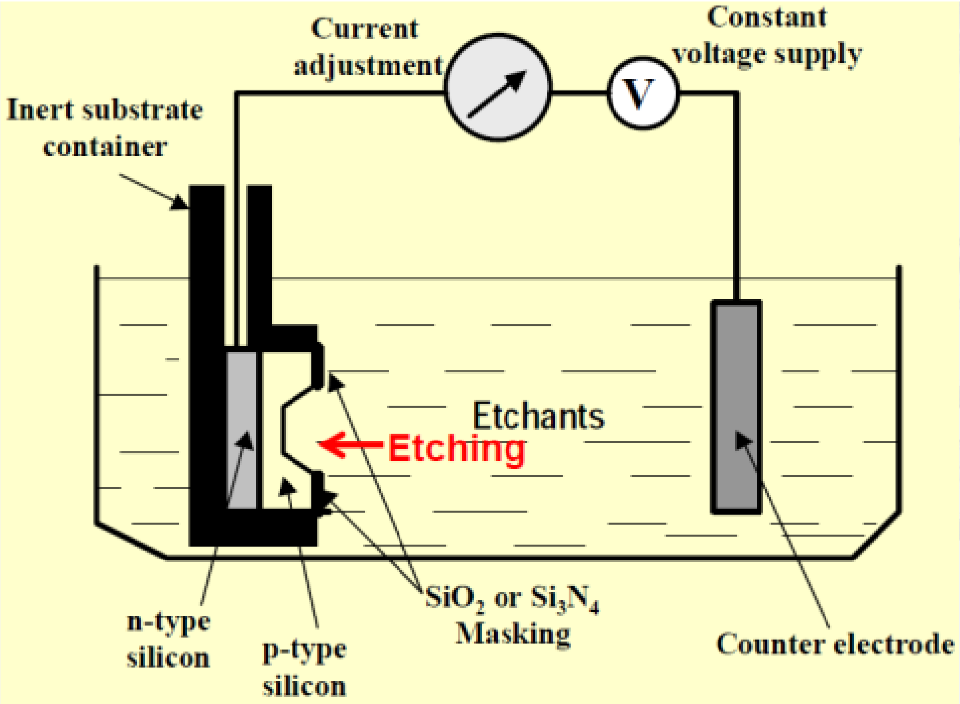


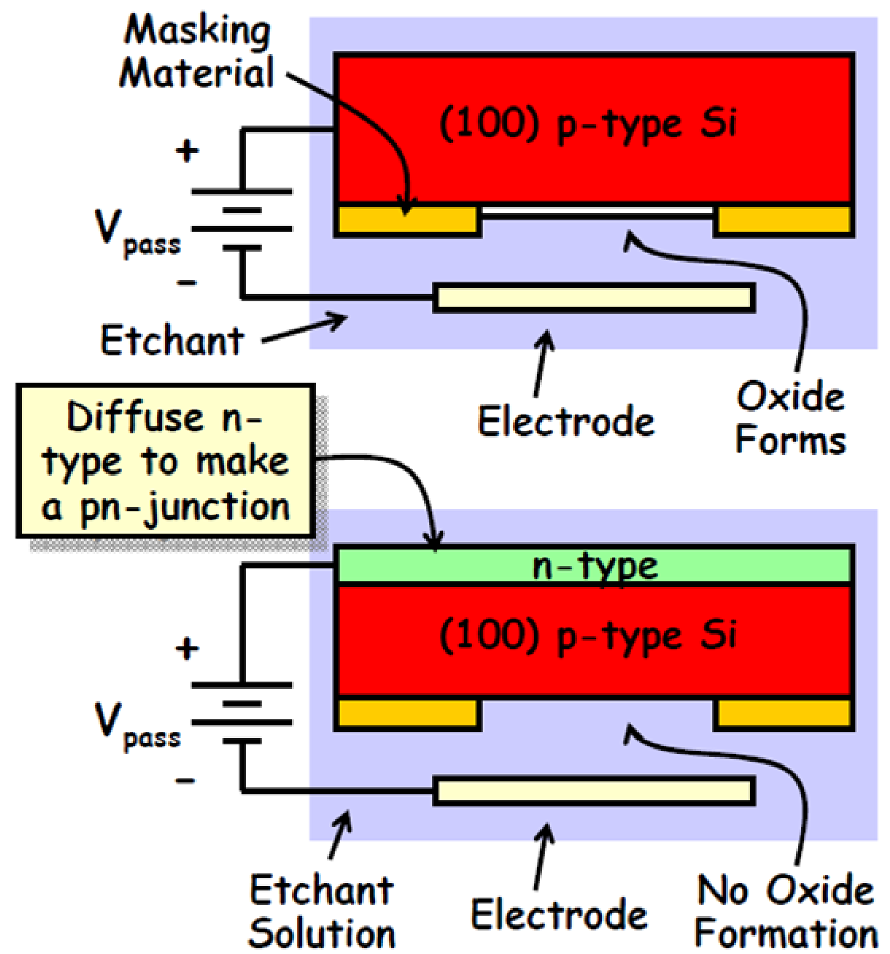




Electrochemical etch stop

- When silicon is biased with a sufficiently large anodic potential relative to the etchant, it get oxidized due to electrochemical passivation, which then prevents etching.
- For passivation to occur, current flow is required.
- So if current flow can be prevented, there will be no oxide growth and etching can proceed.
- Current flow can be prevented by adding a reverse-biased diode structure.





When n-type exposed to solution, oxide forms and etch stops.

Selective over-etch of different materials

The film is etched through to the bottom, plus over-etch to etch laterally for under-cut profile.