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).

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

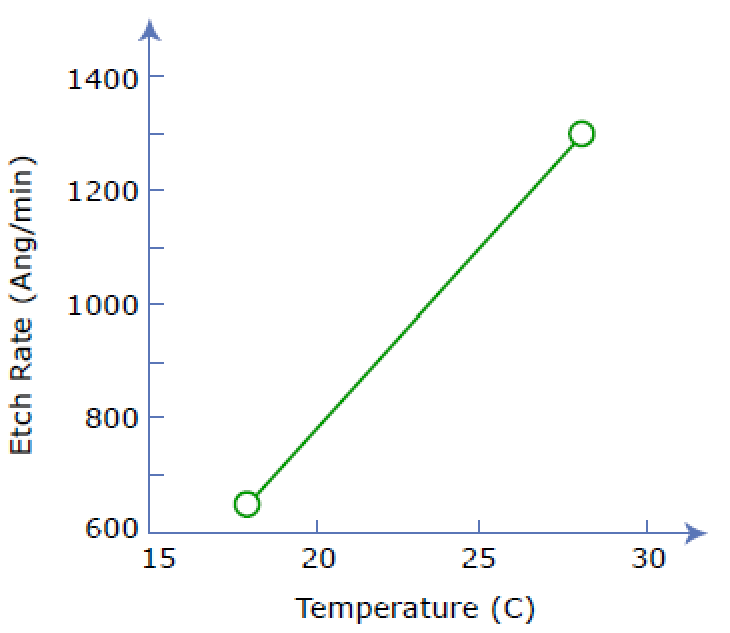
120 nm/min in 6:1::H_2O:HF

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

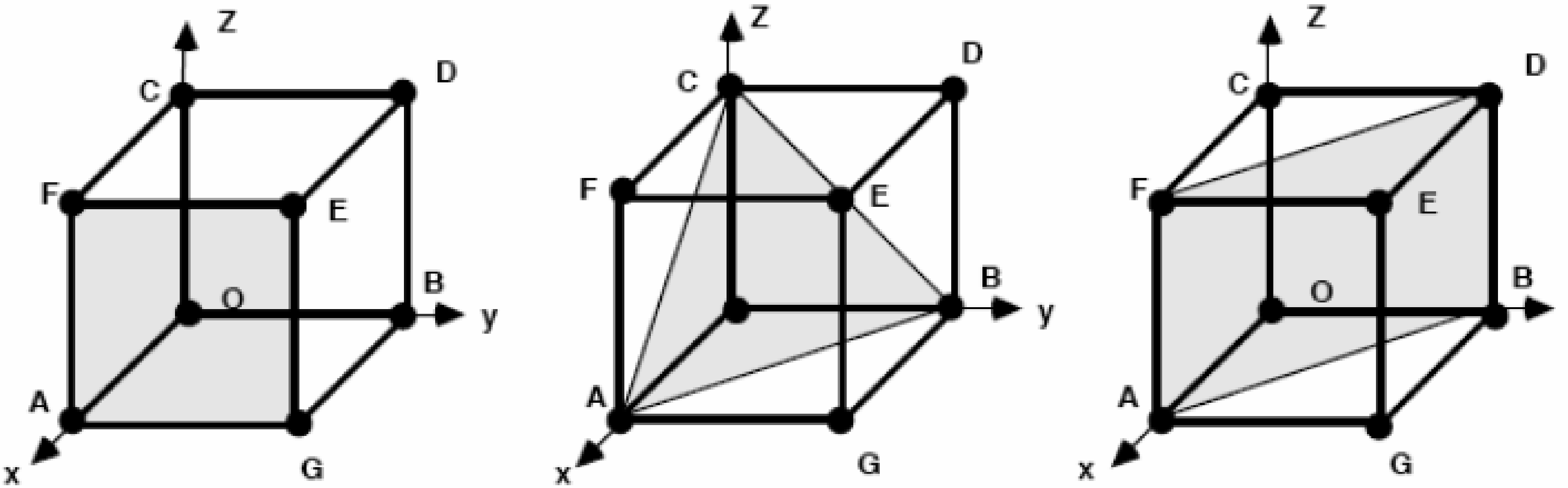
$$Si(s) + 2NO_2(g) + 2H_2O(l) \rightarrow SiO_2(s) + H_2 + 2HNO_2(l)$$

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

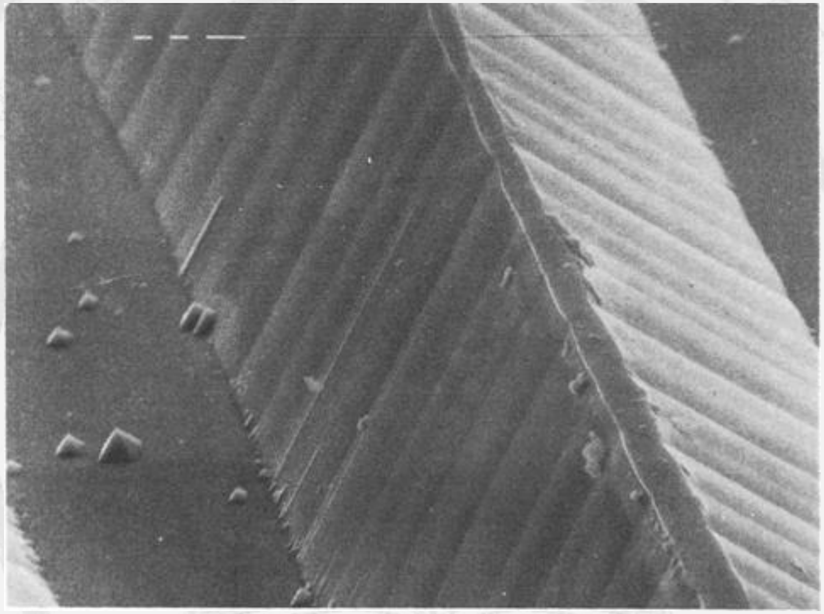


Bond coordination
in (111) is greatest

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

(111) planes most stable

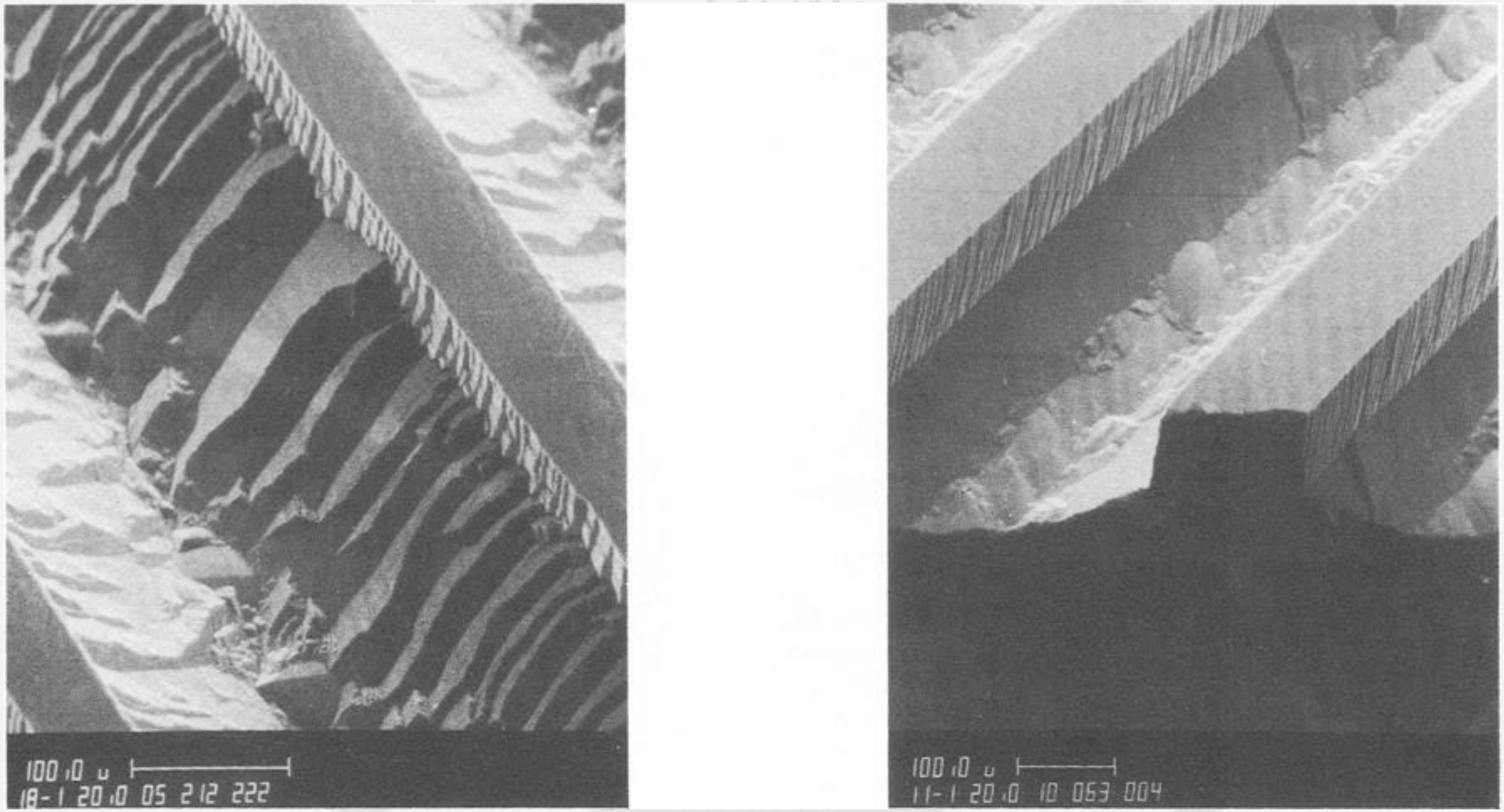
Wet etching of Si



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.

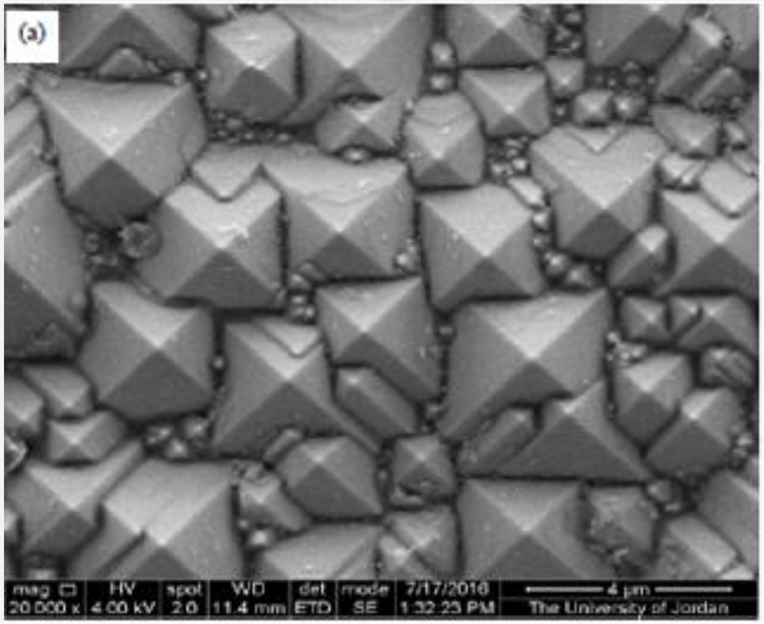
Wet etching of Si

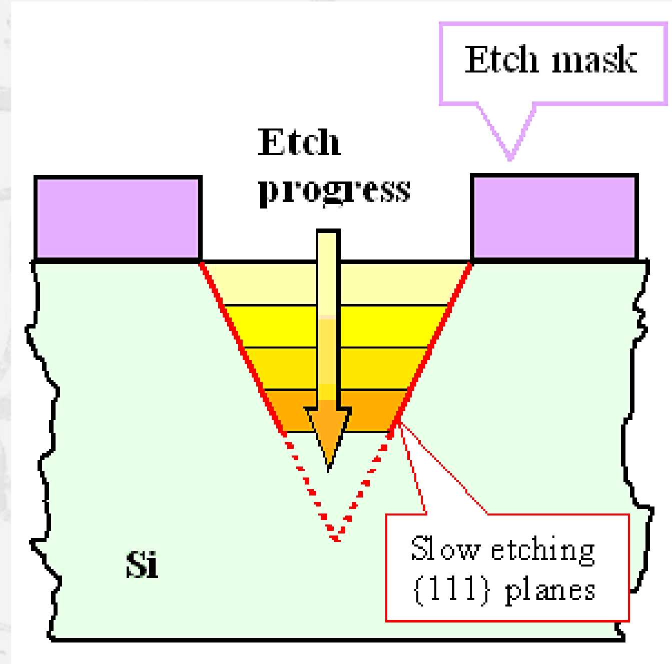


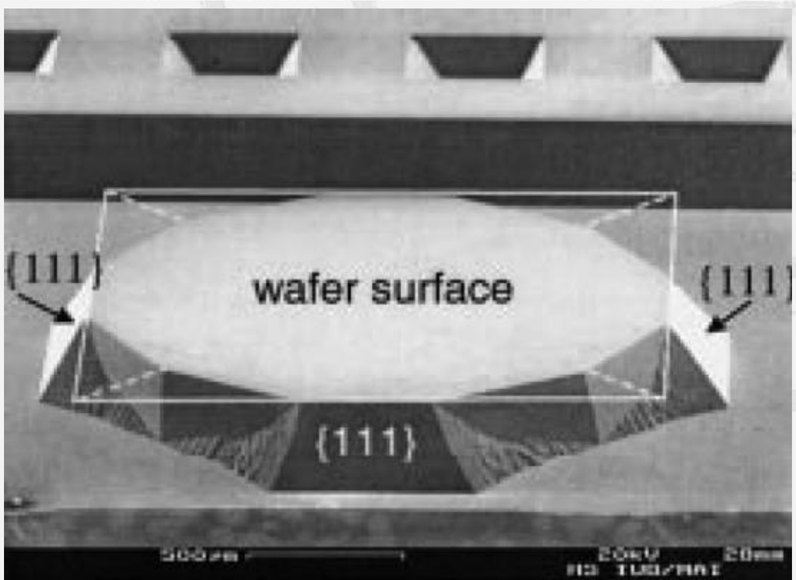
Laterally underetched sidewall of a masked segment on a <110> wafer after exposure to a 50% KOH solution. The edges of the masked segment diagonally crossing the picture had an angular misalignment of (a, left) 32 ~ and (b, right) 42 ~ with respect to the [-110] direction, which is parallel to the *35.3*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

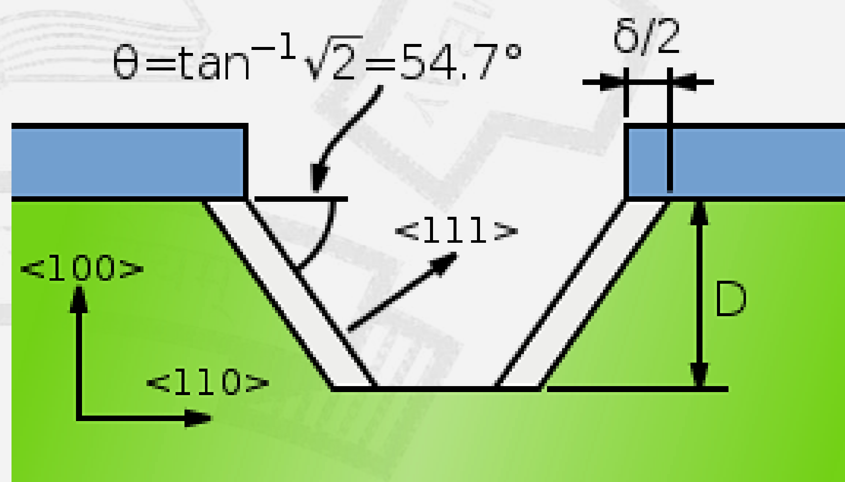
See H. Seidel, L. Csepregi, A. Hueberger, and H. Baungärtel. *The Journal of the* Electrochemical Society 137 (1990): 3612-3626.

Anisotropic Etching of Si surface: KOH

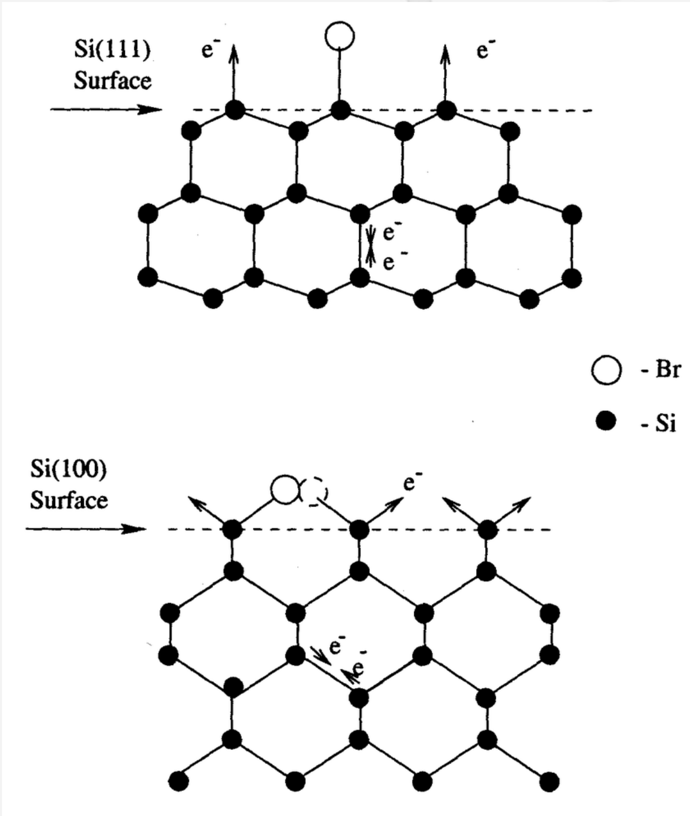


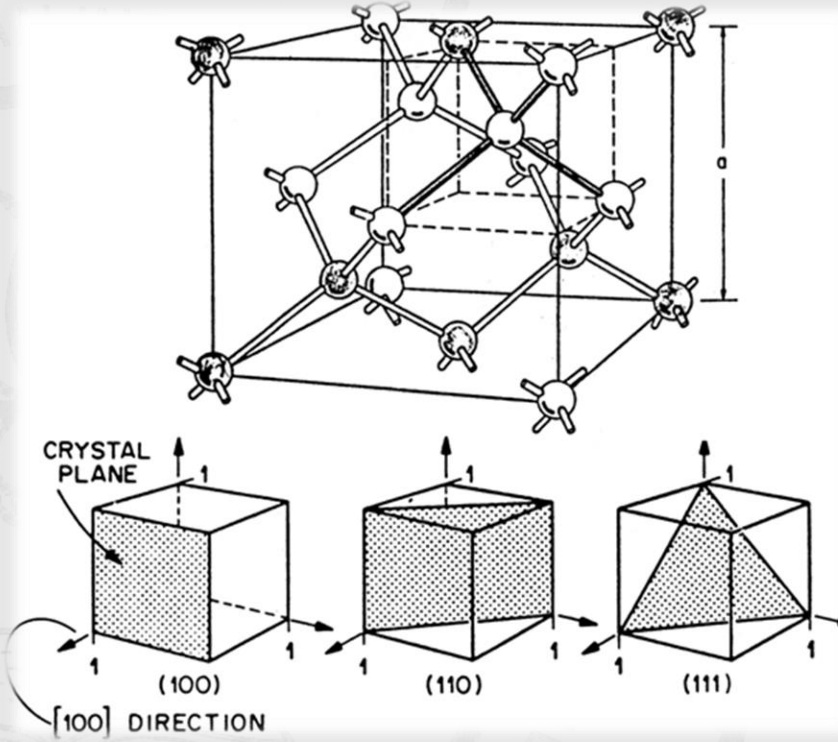






An-isotropic wet etching of Si: overview





- {100} and {110} have 2 bonds below surface & 2 dangling bonds pointing out of the surface that can react. **Reacts very fast.**
- {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: 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.**

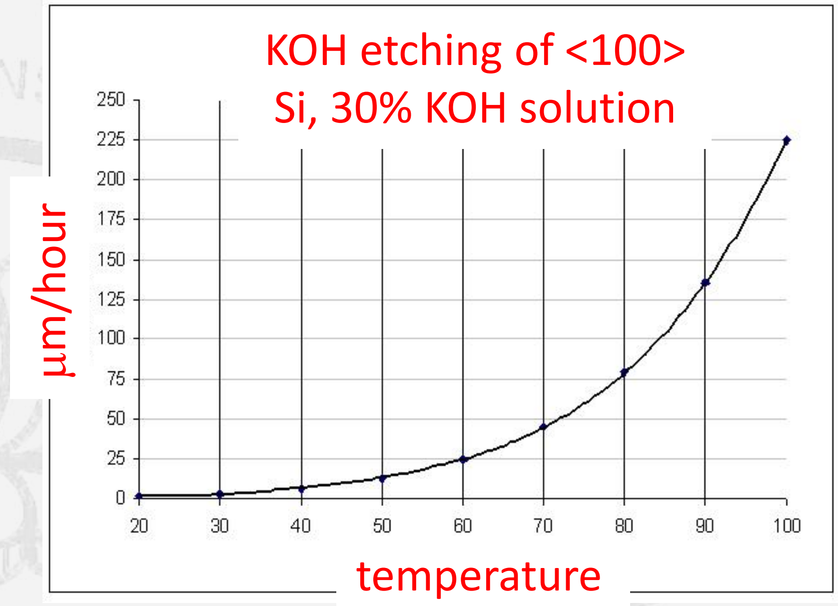
An-isotropic wet etching of Si

KOH etch example:

250 g KOH: 200 g 2-propanol, 800 g H_2O at 80°C

1000 nm/min of [100]

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.

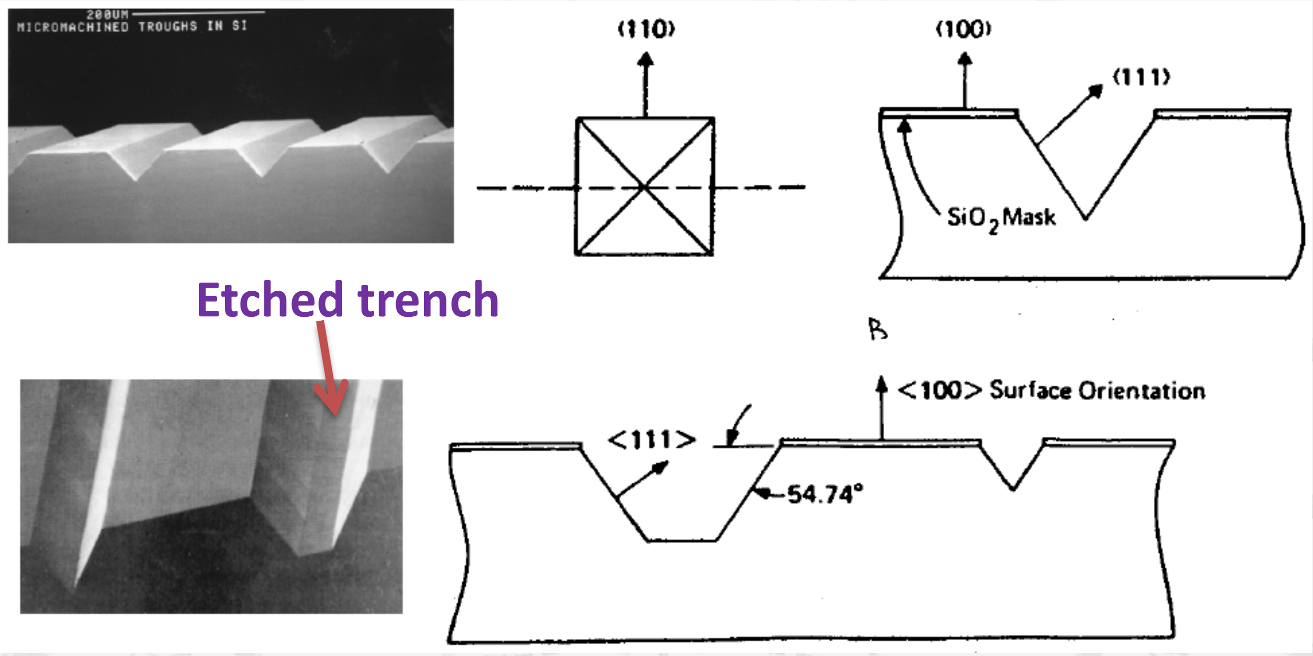
Materials	Etchants	Etch Rates
⟨100⟩ Si **⟨100⟩ Si**	**KOH** **EDP**	**~0.26 – 1.4 µm/min** **~0.75 µm/min**
SiO_2 **SiO_2**	**KOH** **EDP**	**~40– 80 nm/hr** **~12 nm/hr**
Silicon Nitride **Silicon Nitride**	**KOH** **EDP**	**~5 nm/hr** **~6 nm/hr**

Harder to etch

Rate drops

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 (>10^4!).

But KOH attacks *PECVD* oxide and nitride.

Etch mask: SiO_2 or Si_3N_4 or Cr/Au

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.

Summary

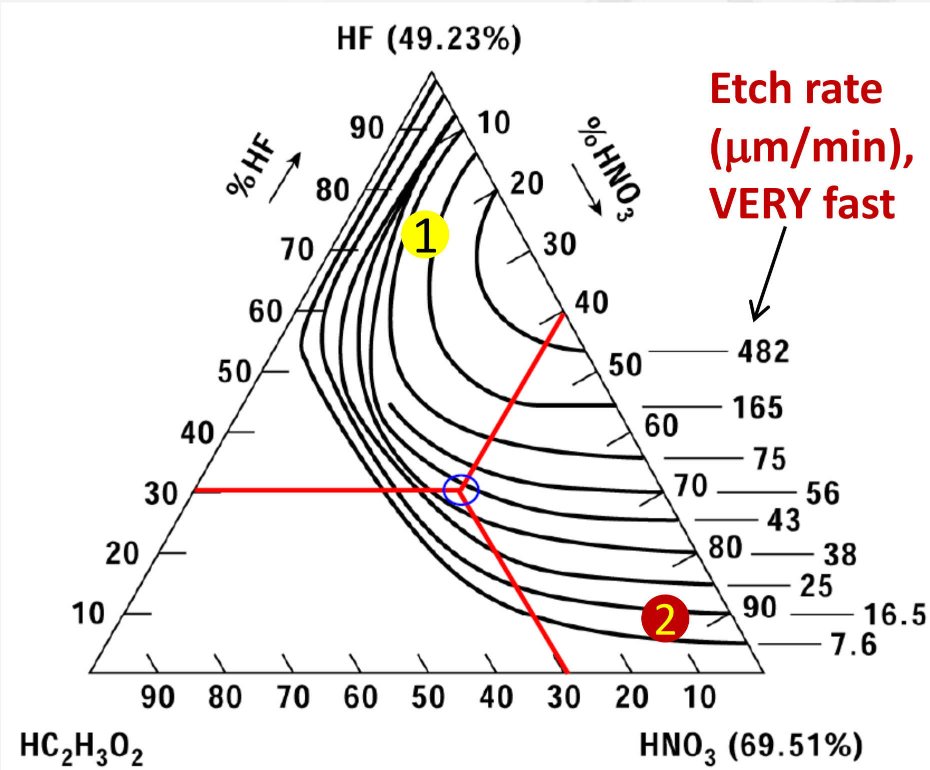
Etchant			Etches	Doesn't etch
H_3PO_4(19), CH3COOH, HNO_3(1), H_2O(2)			Al, SiN, M	SiO_2, Si, PR
HF, BOE (HF + NH_4F)			SiO_2, M	Si, SiN, Au
H_2SO_4(3), H_2O_2(1) pirahna			Organics, M	Si, SiO_2, SiN
I_2(I),KI(2),H_2O(10)			Au, M	Si, SiO_2, SiN, M, PR
NH_4OH(5), H_2O_2(1)			Polymers, Al	Si, SiO_2, SiN, 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;

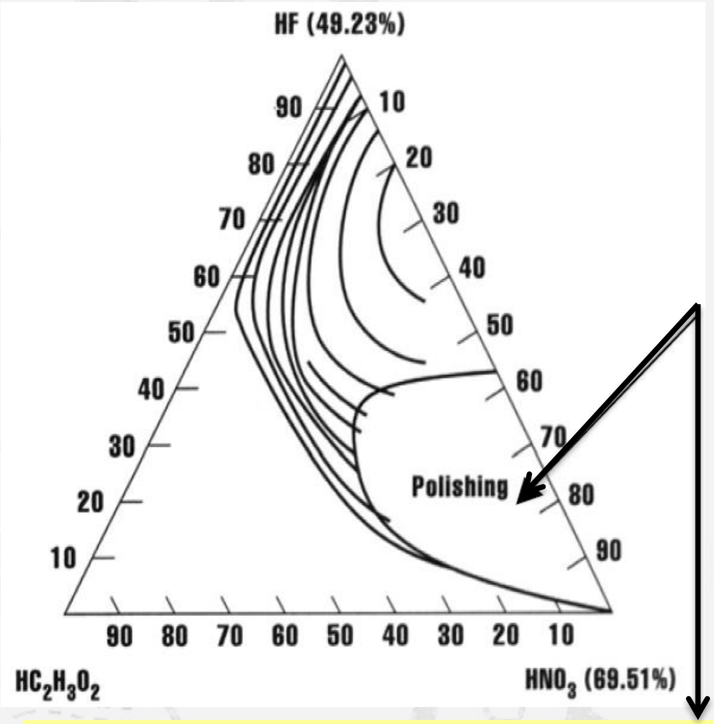
In addition, most metals can be etched by (diluted) acid, except Ti and Cr that form a dense stable oxide on top.

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

Si iso-etch curves



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



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

Region 1:

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

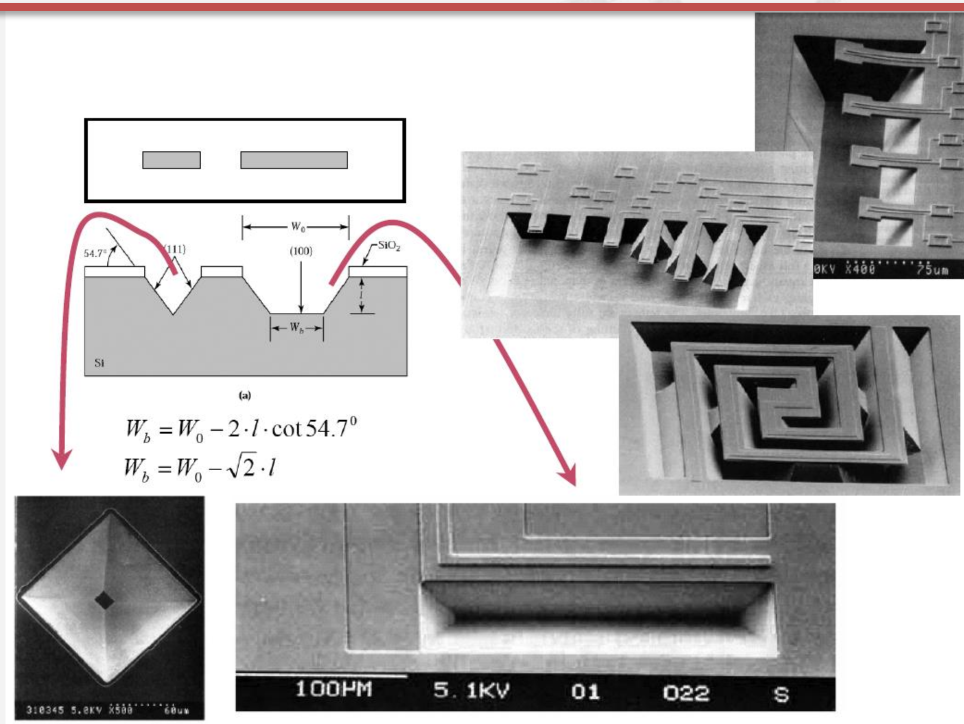
Rate limited by oxidation, etched wafer surface have some oxide.

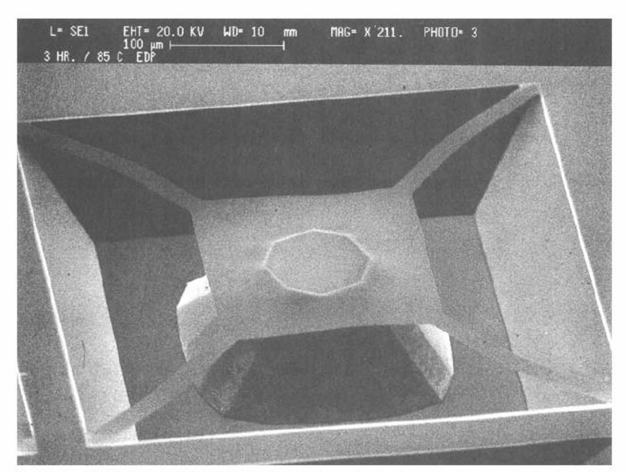
Region 2:

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

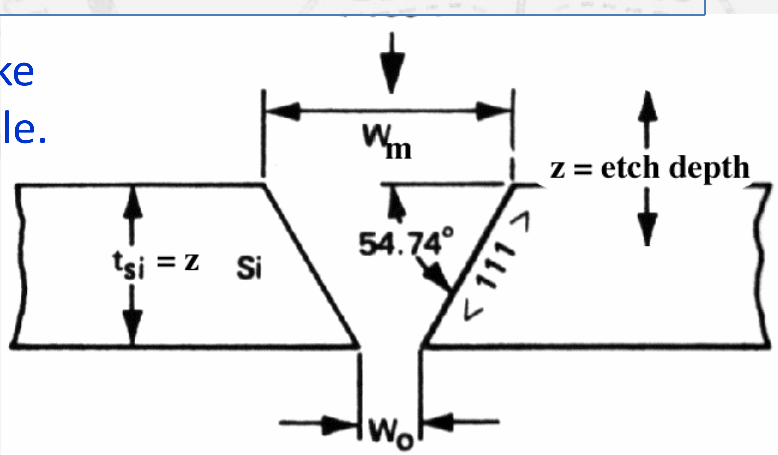
Rate limited by reduction, etched wafer surface have more oxide.

Examples: for (100) wafer

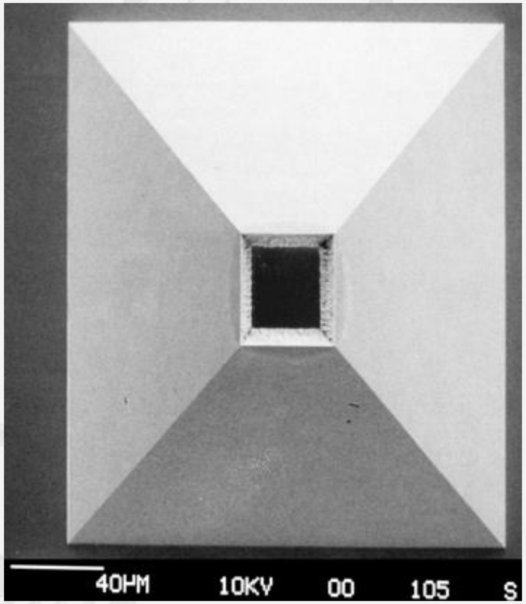




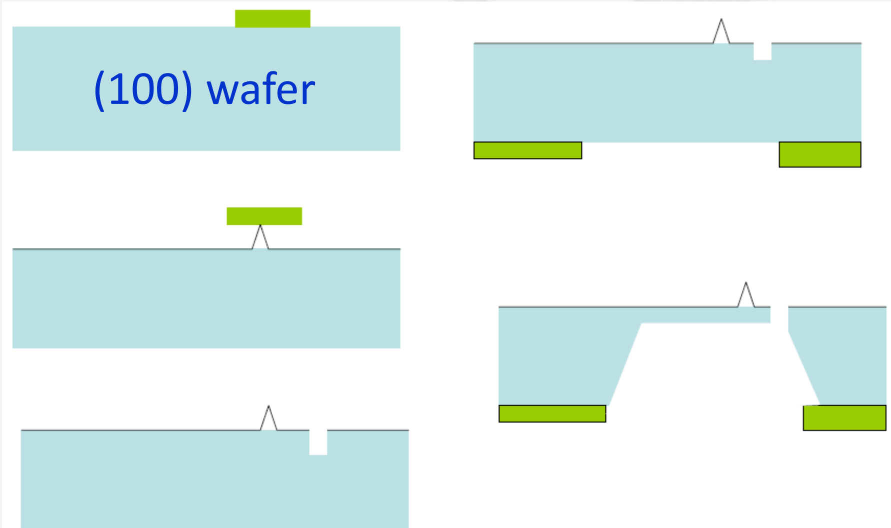
Have been used to make bubble-jet printer nozzle.

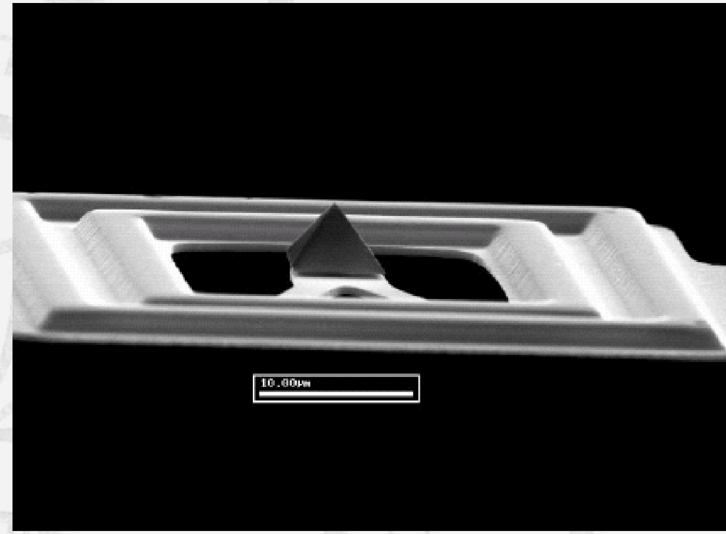


ANISOTROPIC ETCHING OF<100>SILICON



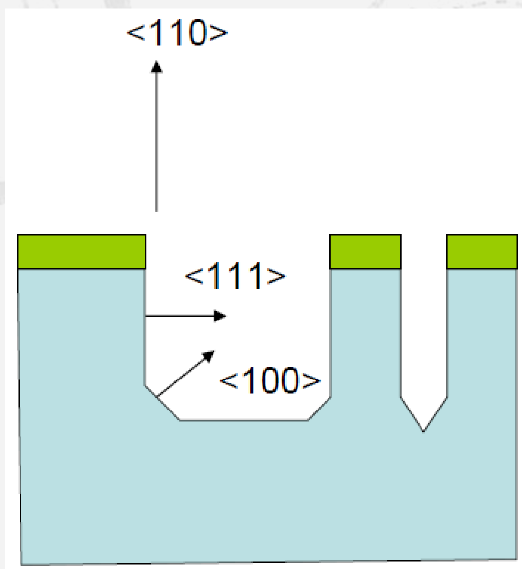
AFM (atomic force microscope) tips

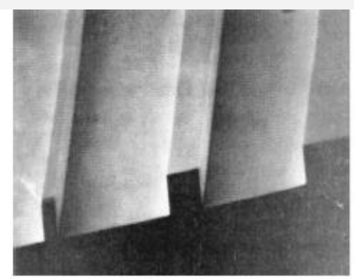


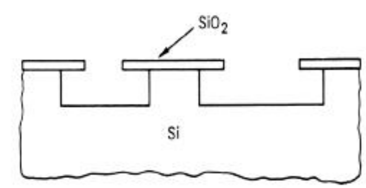


For (110) (not (100)) wafer, vertical (not tapered) trench possible.

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) ($C_4H_{13}NO$)

- 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^{o}C.
- Etching rate ~0.5-1.5 µm/min (10-40%w.t)
- Selectivity <100> : <111> ~ 10 - 35
- 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 (~ 5000-50000)

Ethylene Diamine Pyrochatechol (EDP)

- Typical etching temperature 115^{o}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 $7x10^{19}/cm^3$ boron doping.
- Carcinogenic.

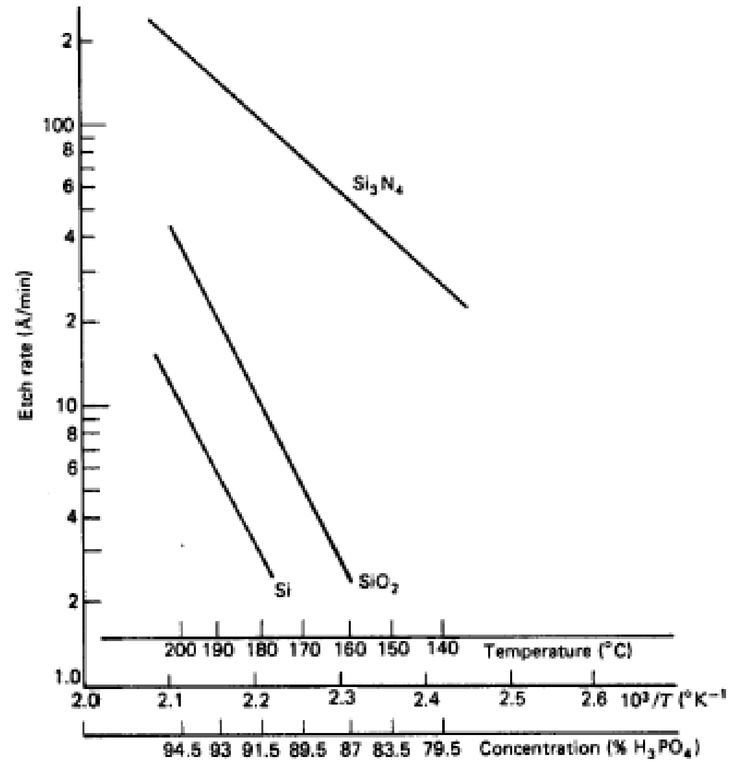
http://en.wikipedia.org/wiki/Ethylenediamine_pyrocatechol

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),**

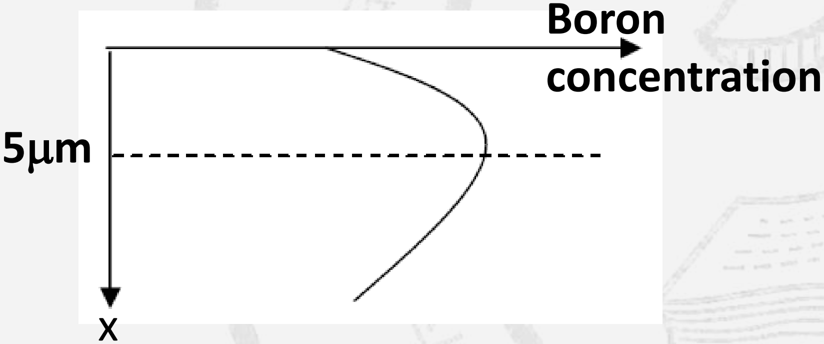
Etch stop

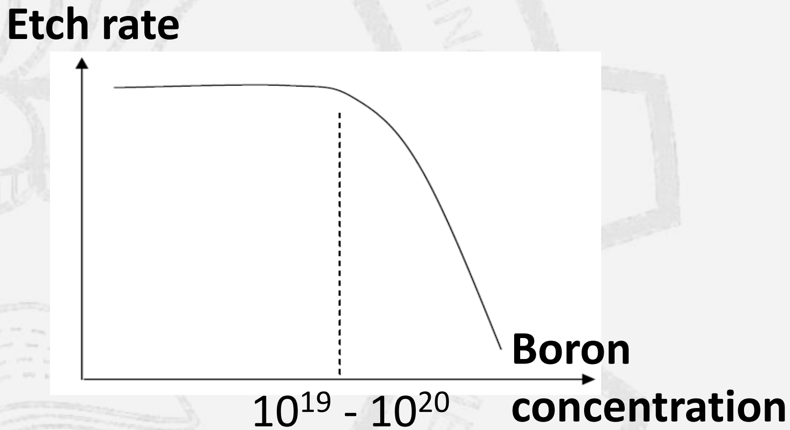
It’s hard to control the etching depth in wet etching. Therefore, a need to have a “stop layer”.

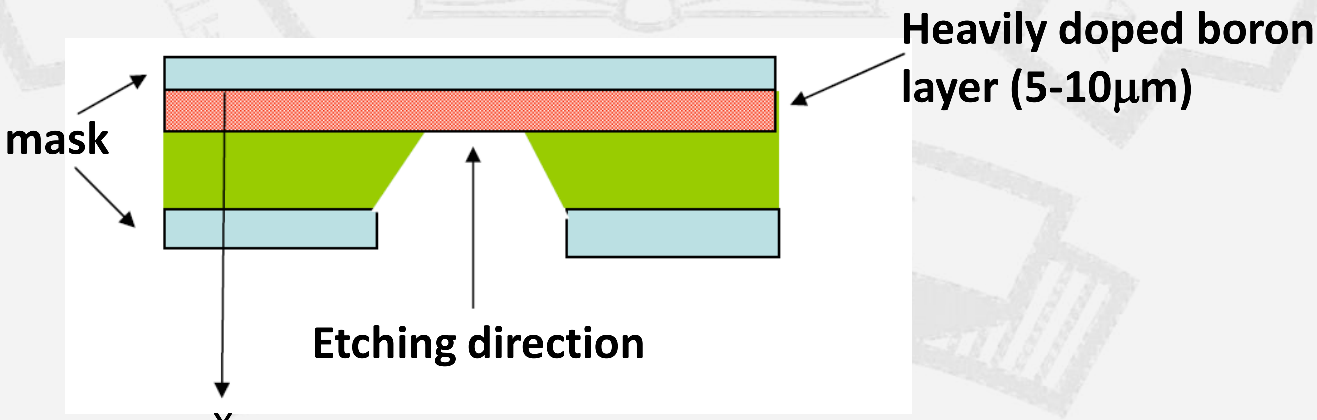
Besides oxide and nitride, etching may be stopped by the following two methods, both related to doping of the silicon substrates.

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

Etching stop by boron doping





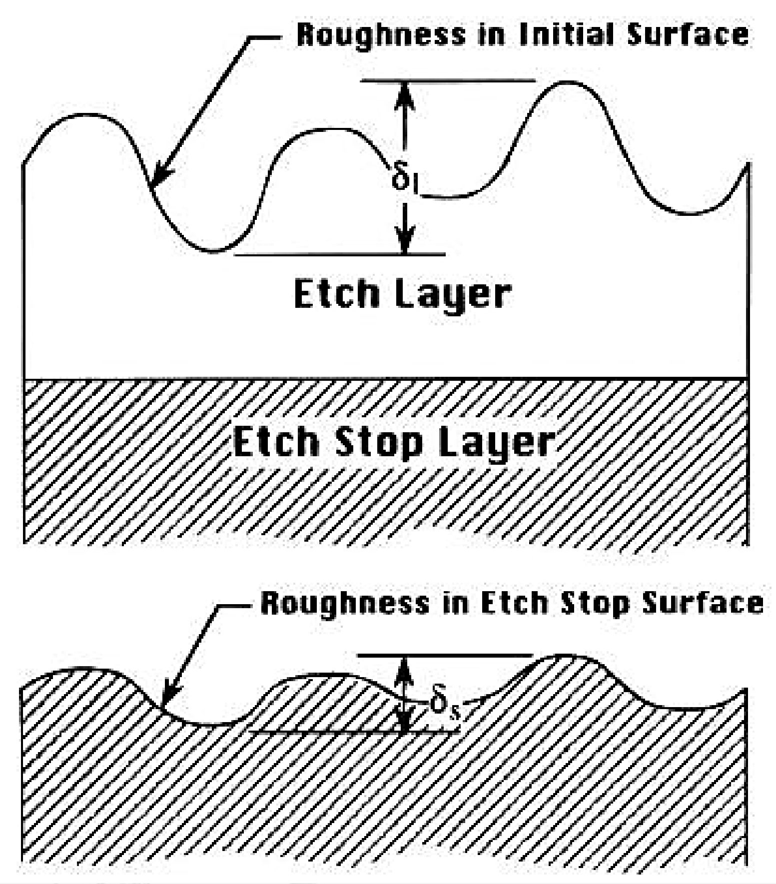


Introducing an etch stop

What is an Etch-Stop?

Etch-stop is defined as a technique that allows termination of the etching process at a controllable depth

` Selectivity: S = $\delta 1 / \delta s$

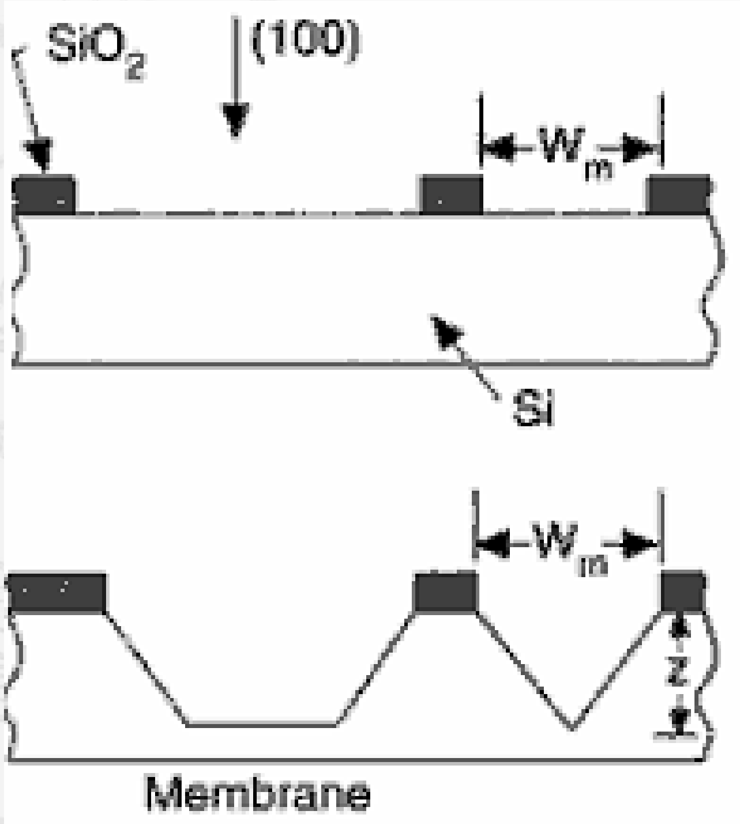


Etch-Stop Techniques

- **Timing Method**
- **Boron Etch-Stop**
- **Electrochemical Etch-Stop**

Timing Method: V-Groove

- Method to control depth of etch
- At the precise moment the V-groove develops, the membrane has reached the correct thickness



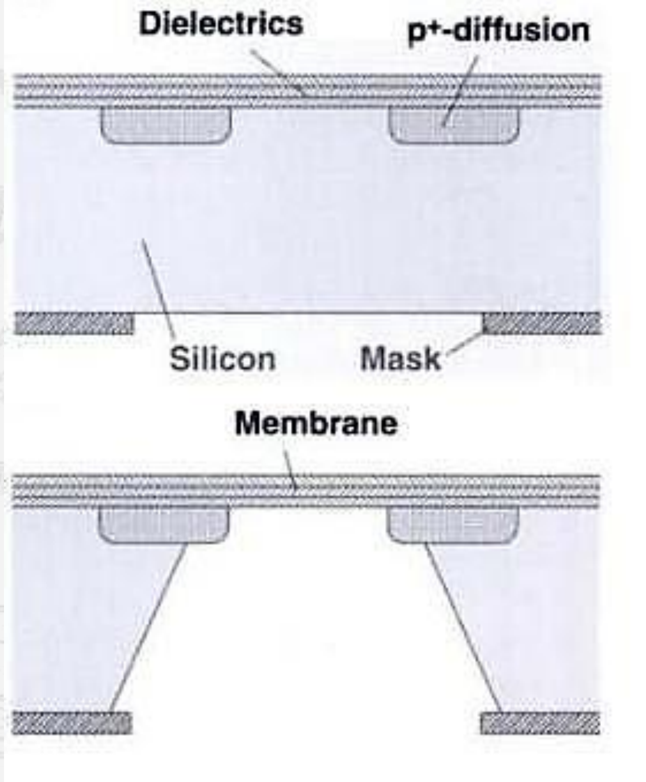
❑ Advantages
- Simplest of all etch-stops
- Cheap

❑ Disadvantages
- Low Accuracy
- Not very reliable

Boron Etch-Stop

- Heavily B doped silicon has a very low etch rate

- Membranes can be created by doping the top of the wafer etching from the back

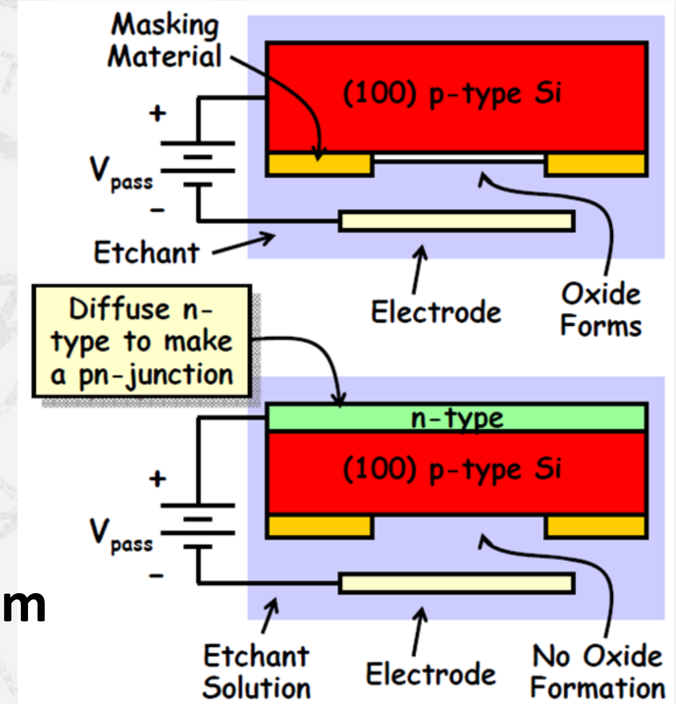


Advantages
- Relatively simple process
- High selectivity and reliability

Disadvantages
- Microstructures subjected to high tensile stress
- Not compatible with CMOS process

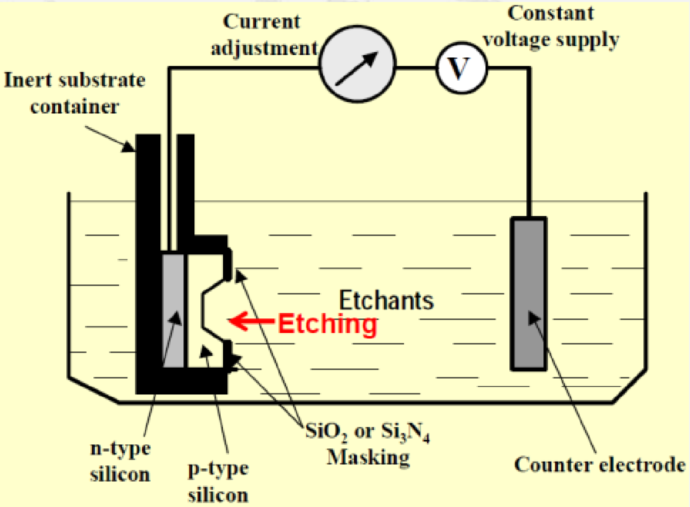
Electrochemical etch

- Reverse biased
- Anisotropic etch
- High selectivity
- Passivation potential
- TMAH/KOH
- Three electrode vs. four electrode system



Etch rate modulation

- Open circuit potential
- Passivation potential
- SiO2 etch stop
- Anodic current flow
- KOH/TMAH



Electrochemical Etch

❑ Advantages

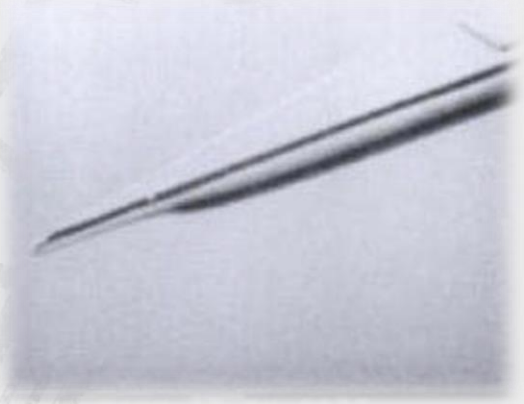
- Doesn't require as high doping level as boron
- Better thickness control
- Less stress on wafer
- Batch fabrication (Electrodless)

❑ Disadvantages

- Requires cumbersome fixtures to insulate electrical wiring
- from etchant

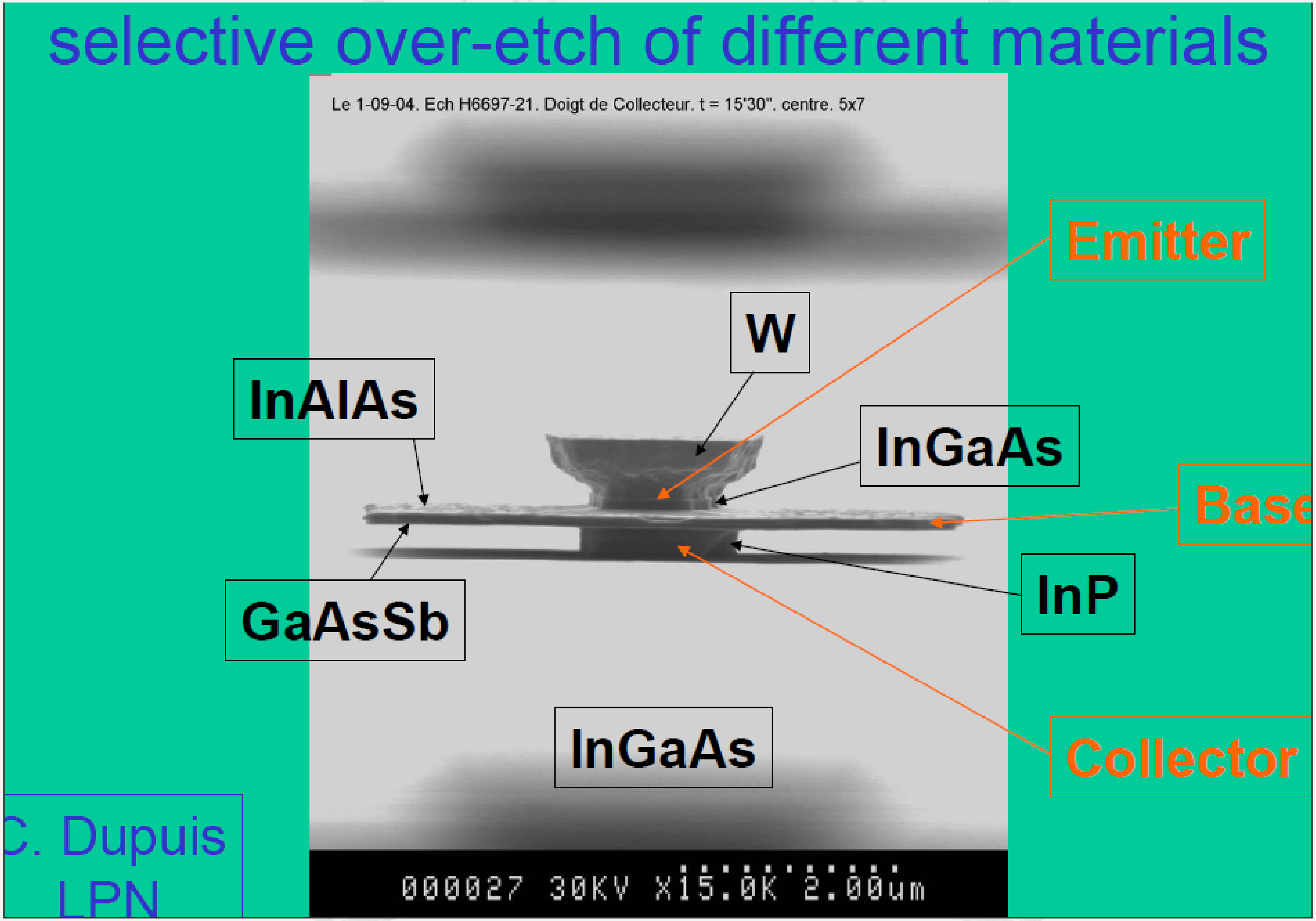
❑ Typical Applications

- Thin membranes
- Pressure Sensors
- Actuators
- Micro-needles used by neurophysiologist as a
- minimally invasive tool to monitor neural signals



Selective over-etch of different materials

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



Dry Etching

Dry etching?

❑ Advantages

- Eliminates handling of dangerous acids and solvents
- Isotropic or anisotropic/vertical etch profiles
- Directional etching without using the crystal orientation of Si
- Reliable pattern transfer into underlying layers
- High resolution and cleanliness
- Less undercutting
- Better process control

❑ Disadvantages:

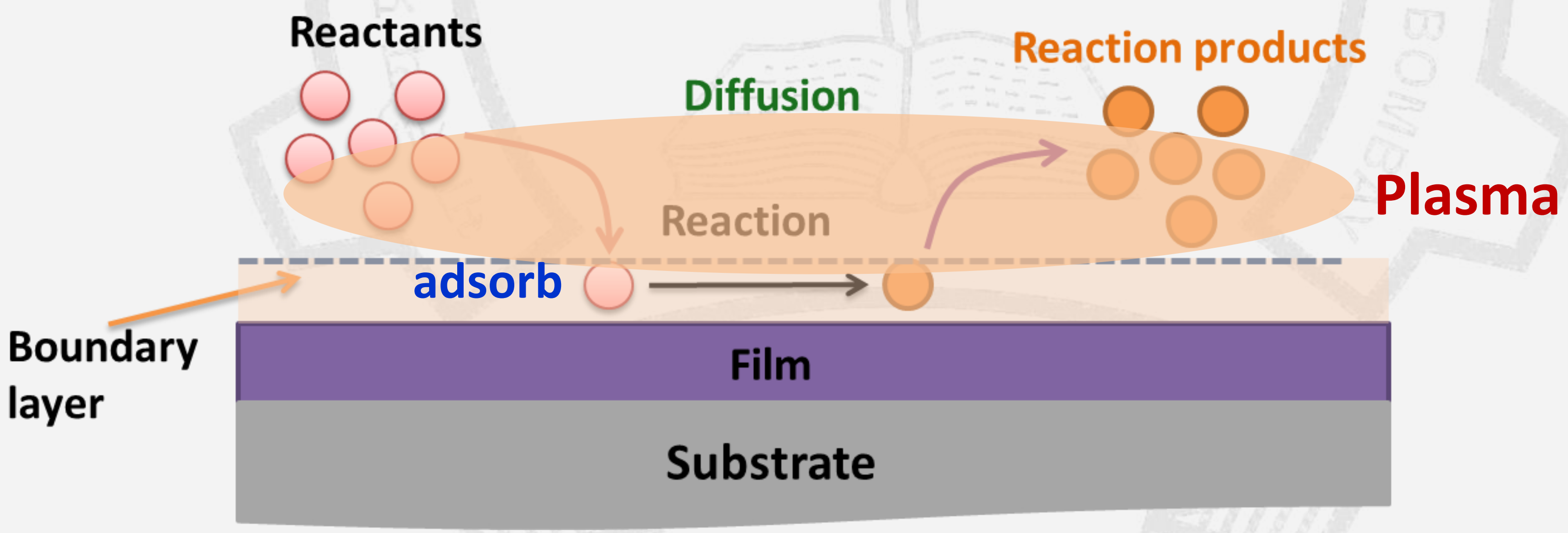
- Some gases are quite toxic and corrosive.
- Re-deposition of non-volatile compound on wafers.
- Expensive equipment ($200-500K for R&D, few million for industrial tools).

❑ Types of dry etching:

- Non-plasma based: Spontaneous reaction of suitable reactive gas mixture.
- Plasma based: Radio frequency (RF) power to drive chemical reaction.

Plasma-based etching

- Directional etching due to presence of ionic species in plasma and (self-) biased electric field. (The self-bias electric field is not applied *externally*, but is created *spontaneously* in RF plasma)
- Two components exist in plasma
  - Ionic species result in directional etching.
  - Chemical reactive species result in high etch selectivity.
- Control of the ratio of ionic/reactive components in plasma can modulate the dry etching rate and etching profile.



$$Si(s) + 4F(g) = SiF_4(g)$$