

Etching

Etch Definitions

- Isotropic Etching: same in all direction
- Anisotropic Etching: direction sensitive
- Selectivity: etch rate difference between 2 materials
Other layers below one being etch
Masking material (photoresist)
- Undercutting: material removed under the mask

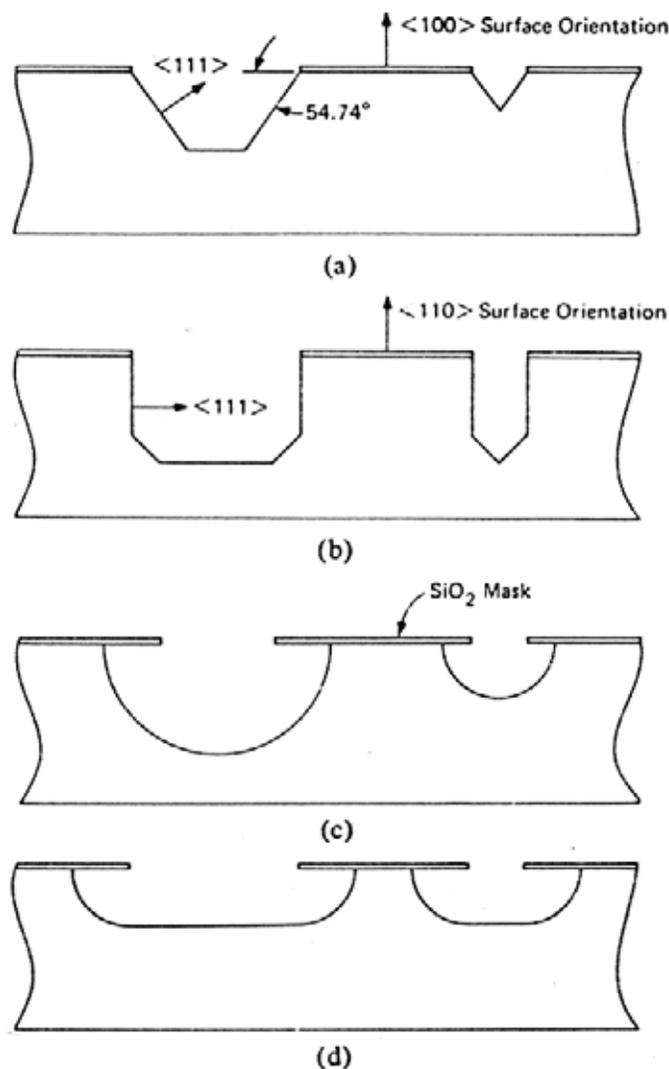
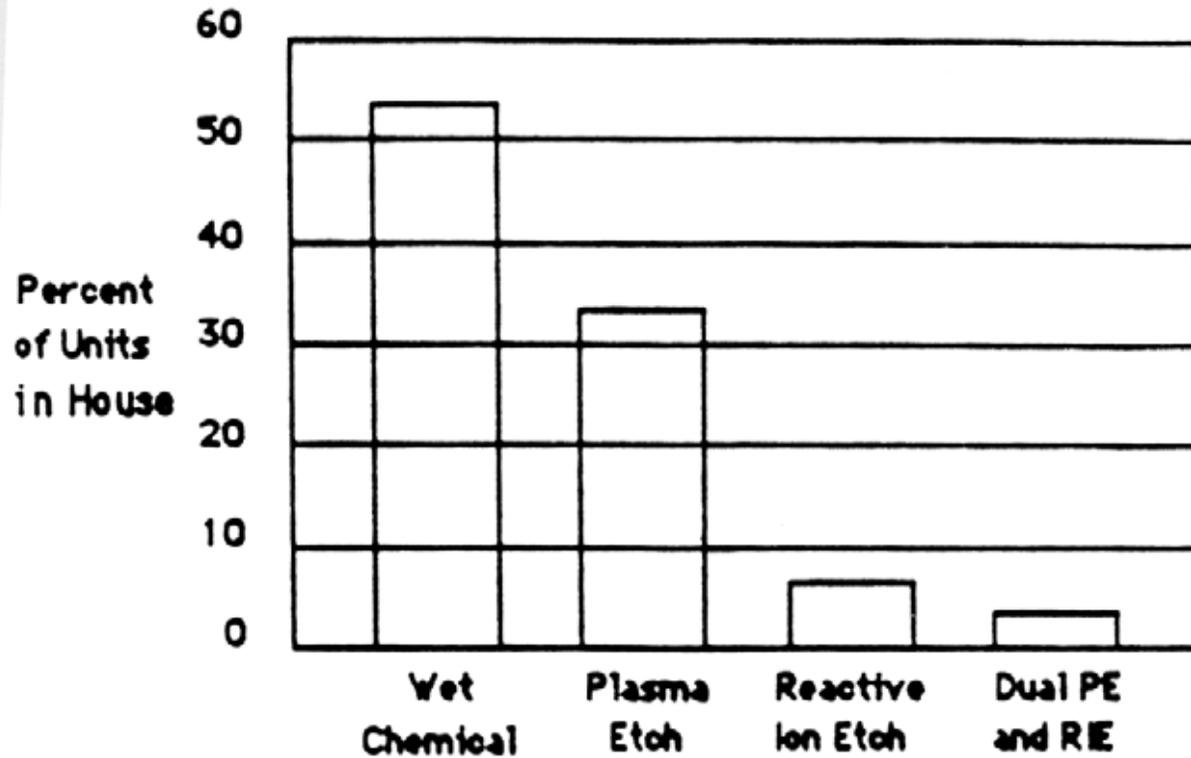


Fig. 4. A summary of wet chemically etched hole geometries which are commonly used in micromechanical devices. (a) Anisotropic etching on $\langle 100 \rangle$ surfaces. (b) Anisotropic etching on $\langle 110 \rangle$ surfaces. (c) Isotropic etching with agitation. (d) Isotropic etching without agitation. Adapted from S. Terry [29].

Two Major types of etching

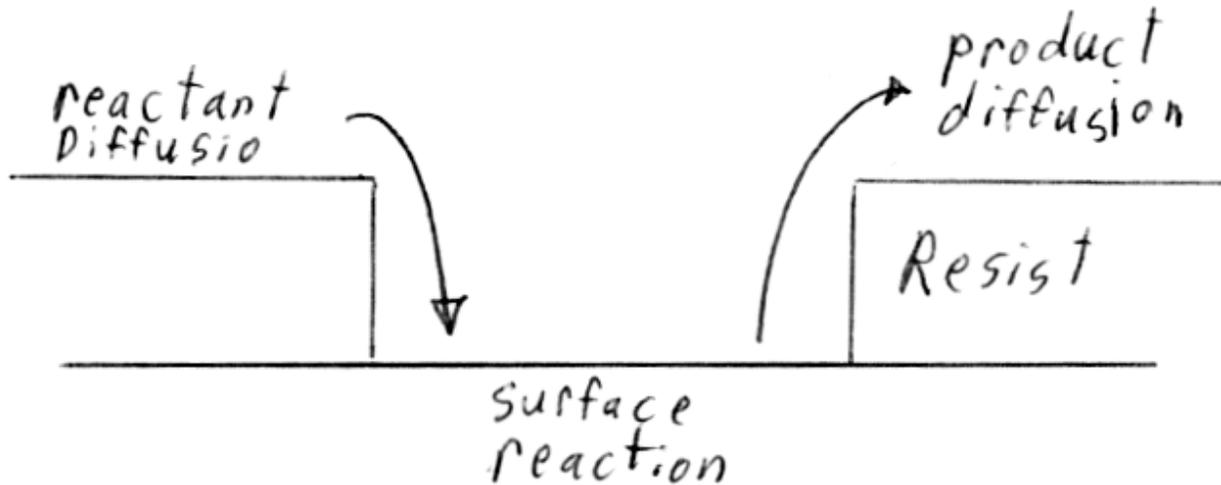
- Wet Etching: Liquid acids/bases
- Dry Etching:
 - Plasma etching (PE)
 - Reactive Ion Etching (RIE)



Percent of Different Types of Etching Equipment in House
Fig 1

Basic Wet Etch Process

- Diffusion of reactant to surface
- Surface Reaction (absorption, reaction, desorption)
- Diffusion of products from surface



Rate Limiting Step

- Rate limiting: slowest step
- Diffusion limited: reactant/product controlled
Thus very agitation sensitive
- activation limited: surface reaction controlled
Temperature sensitive

$$rate = R_0 \exp\left[-\frac{E_A}{KT}\right]$$

R_0 = rate constant (depends on reactant density)

E_A = activation energy (in eV)

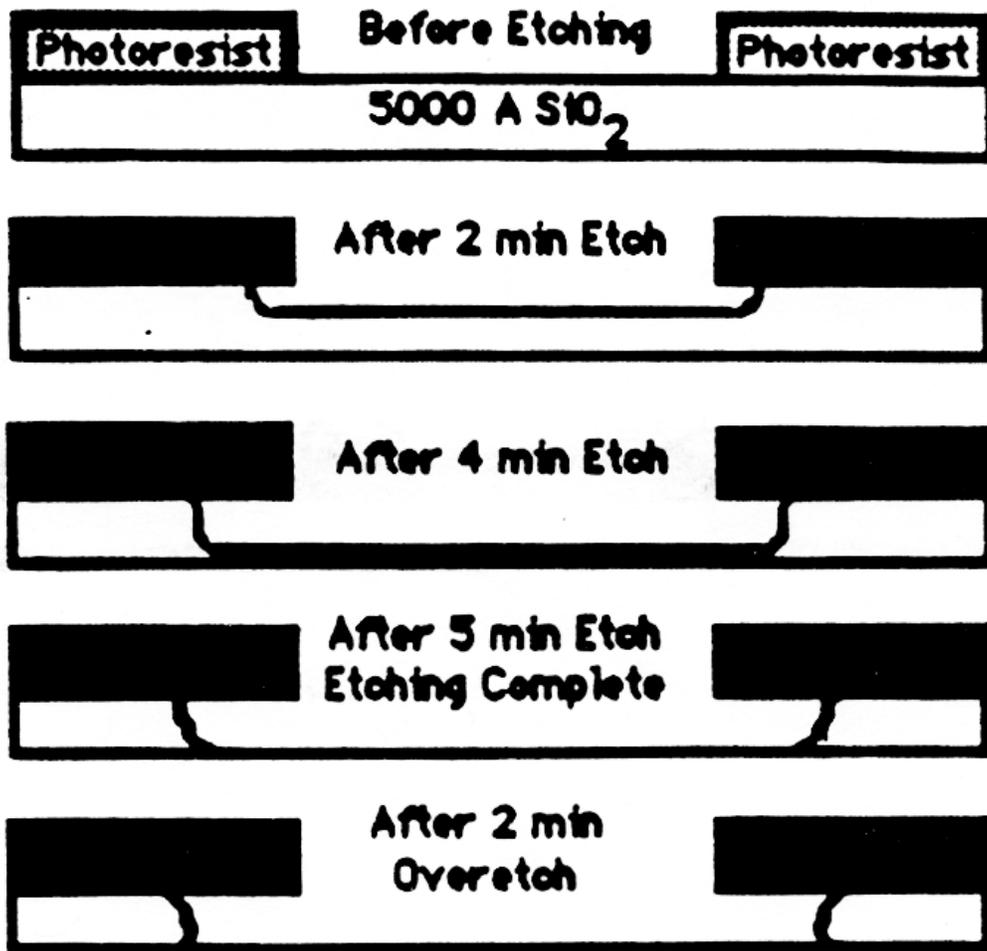
T = Temperature (Kelvin)

K = Boltzman's constant

- Called Arrhenius behavior

Typical Wet Etching Process

- Etch proceeds both vertically and horizontally
- At etch end has undercut edges
- Etch proceeds at slower rate for etch stop material
- Long overetch creates significant undercut

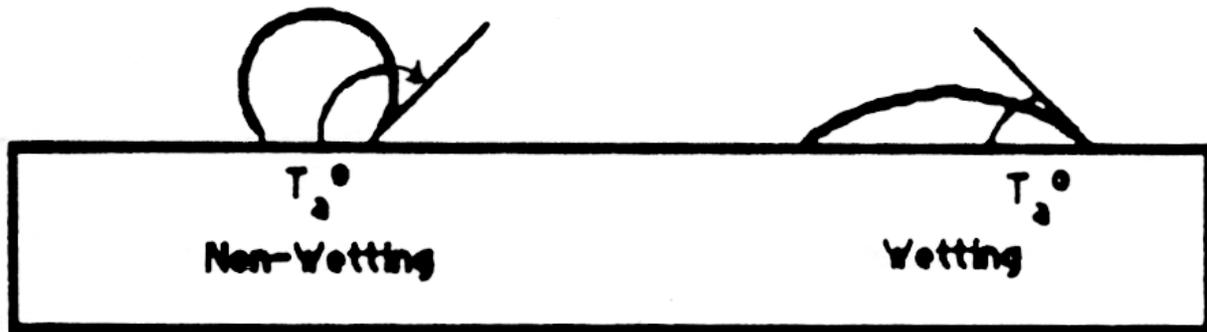


Oxide Etching Sequence in 1000 A/min BOE

Fig 10

Wetting of surface

- Hyrdophilic: water loving
Wetting of surface, angle $< 90^\circ$
- Hyrdophobic: water hating
Non-wetting of surface, angle $> 90^\circ$



Wetting Contact Angles

Non-Wetting $T_c > 90^\circ$, Wetting $T_c < 90^\circ$, Spreading $T_c = 0^\circ$

Common Chemicals used in Wet Etches

- HF used for glass/silicon etch
- Nitric Acid used in silicon etch
- Phosphoric for Aluminum etch
- Ammonium Fluoride in glass Buffered Oxide Etch
- Ammonium Hydroxide in RCA Clean
- Acetic Acid as buffer agent

Table 6-1 Properties of common chemical reagents

Name	Formula	Molecular weight	Concentration†	Dissociation constant‡
Hydrofluoric acid	HF	20.0	49%	3.53×10^{-4}
Nitric acid	HNO ₃	63.0	69.5%	(Strong acid)
Acetic acid, "Glacial"	H ₄ C ₂ O ₂ CH ₃ COOH	60.0	99%	1.76×10^{-5}
Sulfuric acid	H ₂ SO ₄	98.1	98%	1.20×10^{-2}
Phosphoric acid	H ₃ PO ₄	98.0	85%	7.52×10^{-3}
Ammonium fluoride	NH ₄ F	37.0	40%	Salt, dissolves in water
Ammonium hydroxide	NH ₄ OH	35.05	29%	1.79×10^{-5}

† Concentration by weight, in water, as commonly supplied.

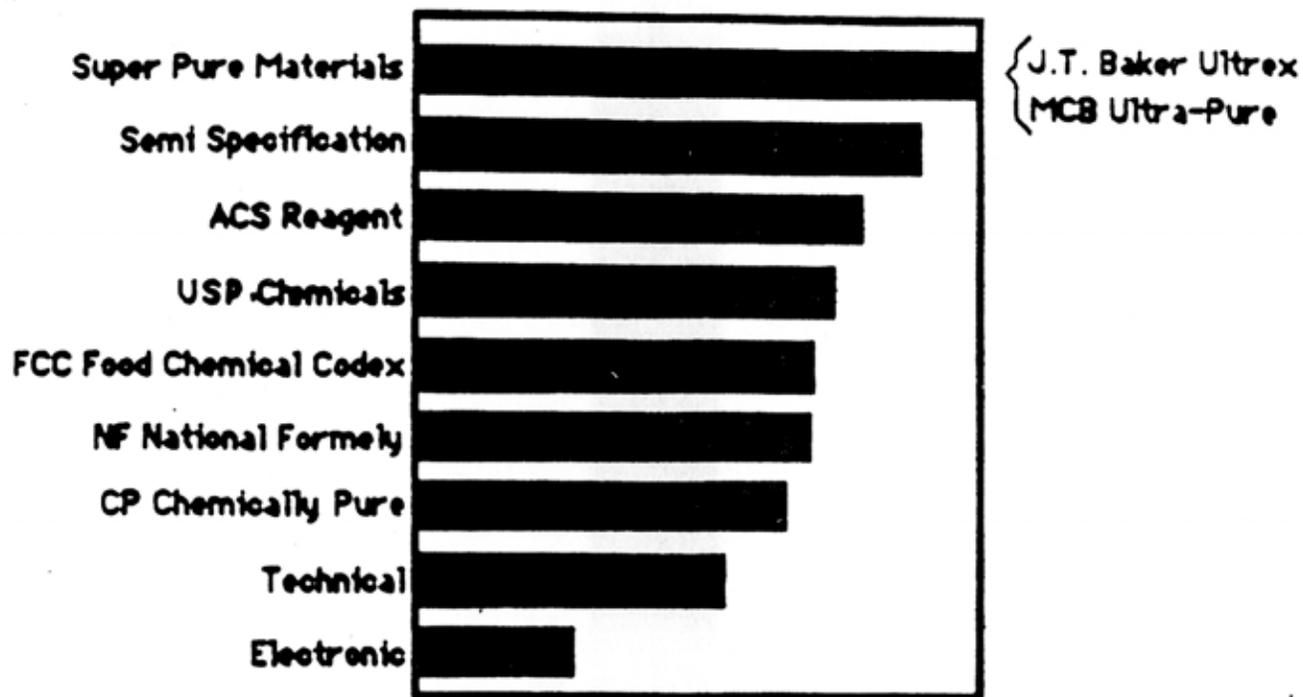
‡ At 25°C. For multibasic acids, the first dissociation constant is given.

Typical Wet Etchants

	COMMON ETCHANT	ETCH TEMP	RATE Å /MIN	METHOD
SiO ₂	HF & NH ₄ F (1 : 8)	Room	700	Dip & wetting agent predip
SiO ₂	HF & NH ₄ F (1 : 8)	Room	700	Dip & wetting agent predip
SiO ₂ (Vapox)	Acetic Acid & NH ₄ F(2 : 1)	Room	1000	Dip
Aluminum	H ₃ PO ₄ : 16 HNO ₃ : 1 Acetic : 1 H ₂ O : 2 Wetting Agent	40 - 50°C	2000	a) Dip & agitation b) Spray
Si ₃ N ₄	H ₃ PO ₄	150 - 180°C	80	Dip
POLYSi	HNO ₃ : 50 H ₂ O : 20 HF : 3	Room	1000	Dip

Figure 9.20 Summary of wet etching process.

Relative Chemical Purities



Relative Chemical Purity

Fig 23

Typical Impurity Levels in MOS Grade Chemicals

Table 27

J.T. Baker Chemicals

<u>Chemical</u>	<u>CH₃COOH</u>	<u>NH₃OH</u>	<u>HCL</u>	<u>HF</u>	<u>H₂O₂</u>	<u>H₂SO₄</u>
<u>Impurity</u>	<u>Level in Parts Per Million</u>					
Aluminum	0.1	0.1	1.0	0.05	1.0	0.1
Ammonium					5.0	
Arsenic	0.005	0.05	0.005	0.03	0.01	0.005
Barium	1.0	1.0	1.0	0.5	1.0	1.0
Boron	0.05	0.02	0.05	0.05	0.1	0.01
Cadmium	1.0	0.5	1.0	1.0	1.0	0.5
Calcium	1.0	1.0	1.0	1.0	1.0	1.0
Chloride		0.5		5.0	2.0	1.0
Chromium	0.5	0.5	0.5	0.01	0.02	0.5
Cobalt	0.1	0.5	0.1	0.5	0.5	0.5
Copper	0.01	0.01	0.01	0.05	0.01	0.01
Gallium	0.05	0.05	0.05	0.05	0.05	0.05
Germanium	0.05	0.5	1.0	1.0	1.0	0.5
Gold	0.5	0.5	0.5	0.05	0.5	0.5
Heavy Metals (As Pb)	0.3	0.2	0.1	0.1	0.5	0.4
Iron	0.1	0.05	0.1	0.5	0.5	0.2
Lithium	1.0	1.0	1.0	1.0	1.0	1.0
Magnesium	1.0	1.0	1.0	0.5	0.1	1.0
Manganese	1.0	0.5	1.0	0.5	1.0	0.5
Nickel	0.1	0.1	0.05	0.1	0.02	0.1
Phosphate	1.0	0.4	0.05	1.0	2.0	0.5
Potassium	1.0	1.0	1.0	1.0	2.0	1.0
Silicon	1.0	1.0	1.0		1.0	0.5
Silver	0.5	0.5	0.1	0.1	0.5	0.5
Sodium	1.0	1.0	1.0	1.0	1.0	1.0
Strontium	1.0	1.0	1.0	1.0	1.0	0.5
Sulfate	0.5	1.0	0.5	5.0	5.0	
Sulfite			0.8			
Tin	1.0	1.0	1.0	1.0	0.5	0.5
Zinc	1.0	1.0	1.0	1.0	1.0	0.5

Proper Wet Etching Station

- Fume hood to remove gases
- Moveable shield to protect workers

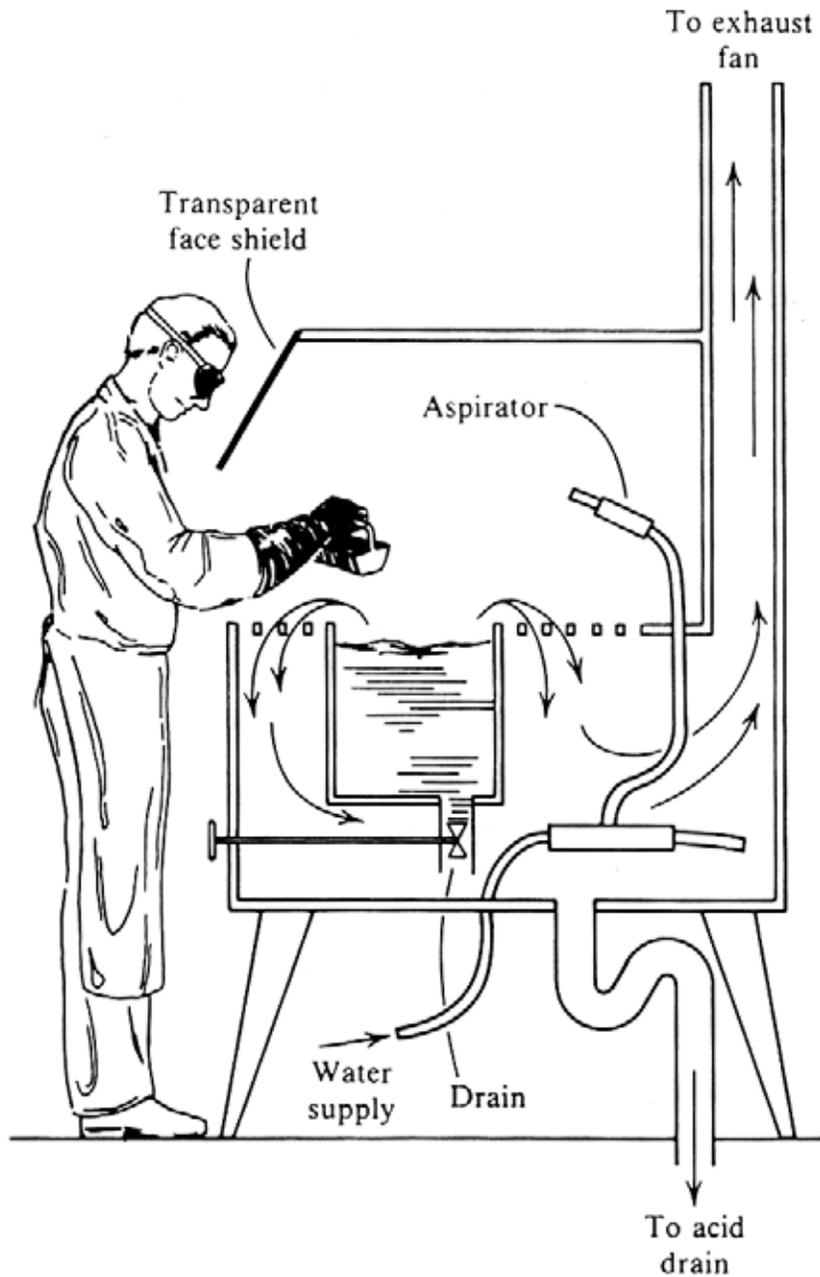
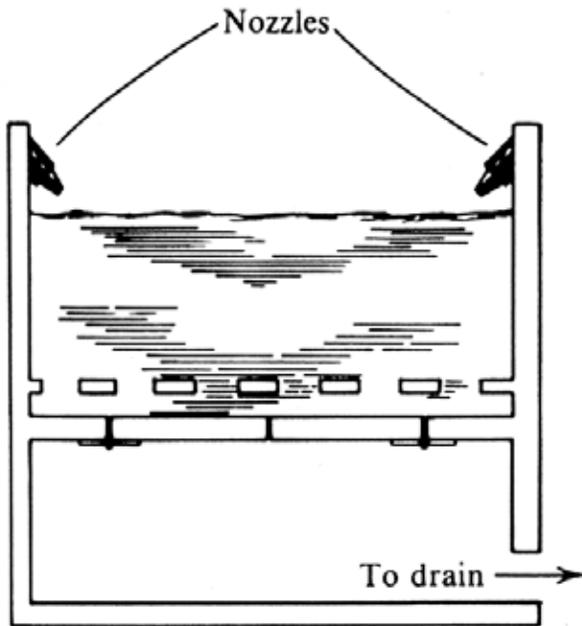


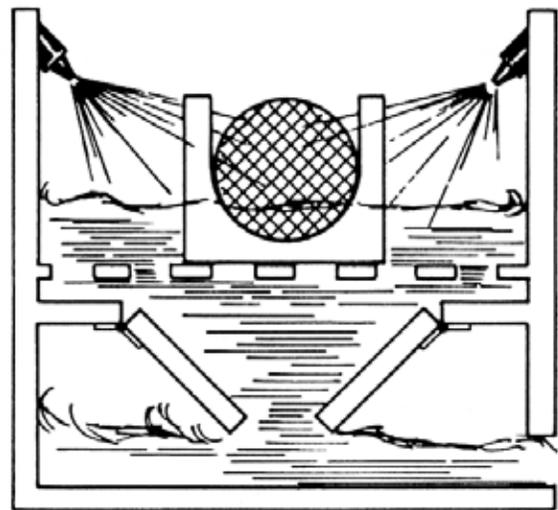
Figure 6-5 A workstation for acid etching. Note the face shield to prevent splattering, the perforated top for fume control, the remote-controlled drain and aspirator for acid removal, and the arrangement of drain and exhaust systems.

Professional Wet Etch Tub

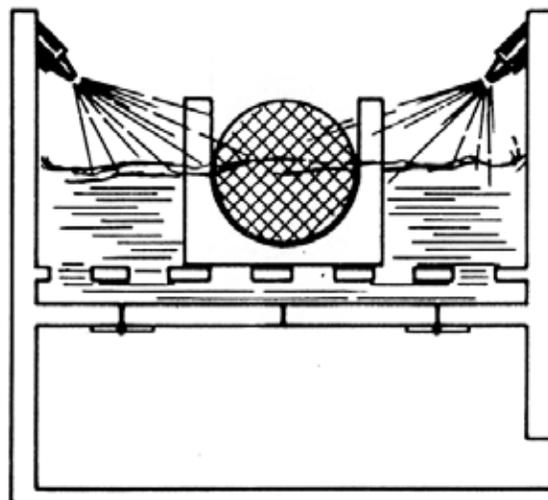
- Tub is full before wafers inserted (a)
- Quick dump after etching for massive change (b)
- Refilled with etchant (c)



(a)



(b)



Recirculating Wet Etch Tub

- Tubs made of Teflon
- Temperature controlled

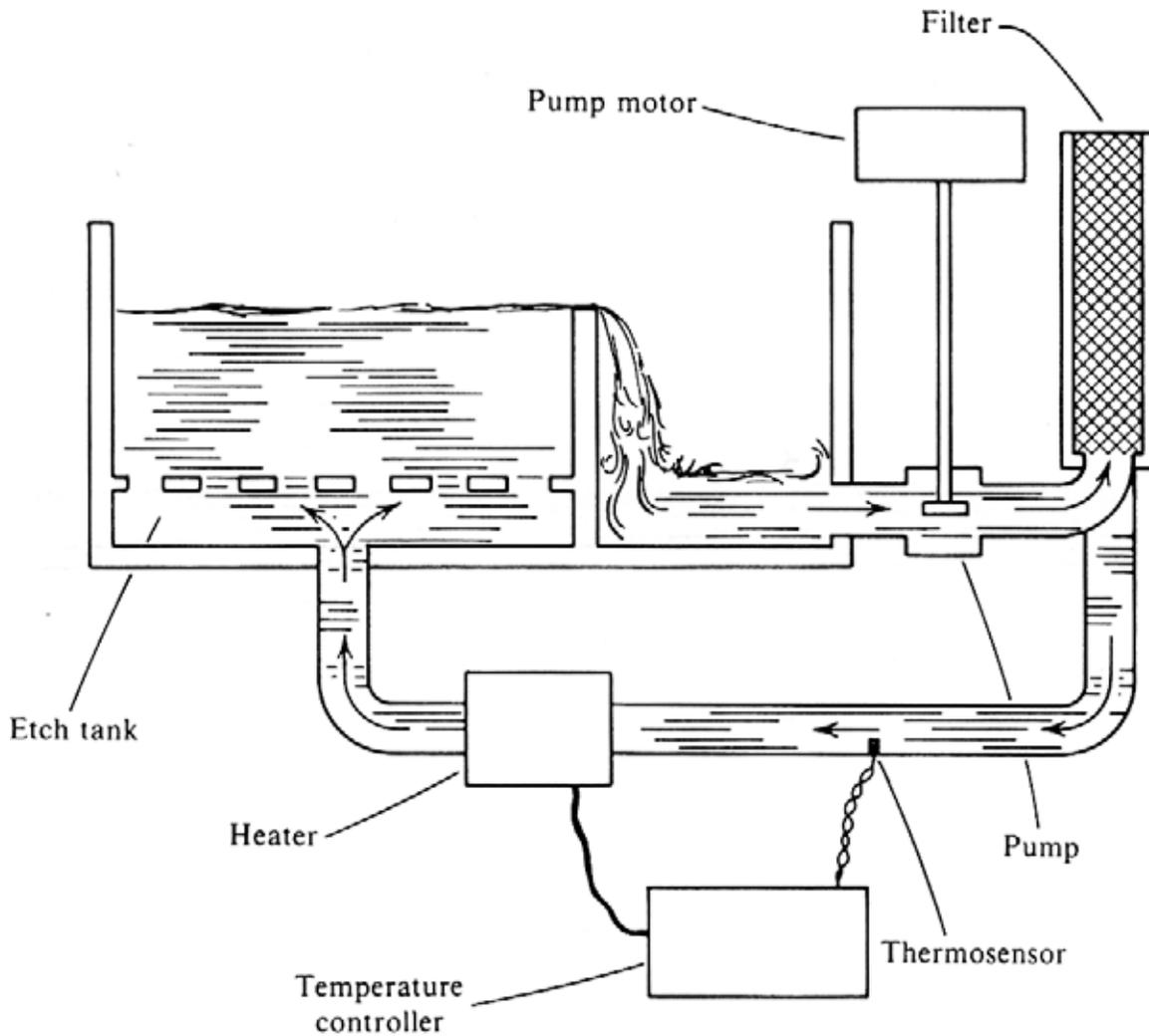
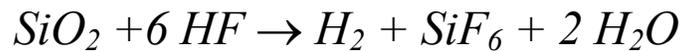


Figure 6-4 Recirculating, filtered, temperature-controlled bath for the etching of microelectronic substrates.

Silicon Dioxide (Glass)

- Glass - silicon dioxide: SiO_2
- Used as a dielectric insulator between conductors
- Also gate dielectric in Mosfets
- Grown by Furnace oxidation (Wet/Dry)
- Also by Chemical Vapour Deposition
- Etched with HF containing solutions in reaction



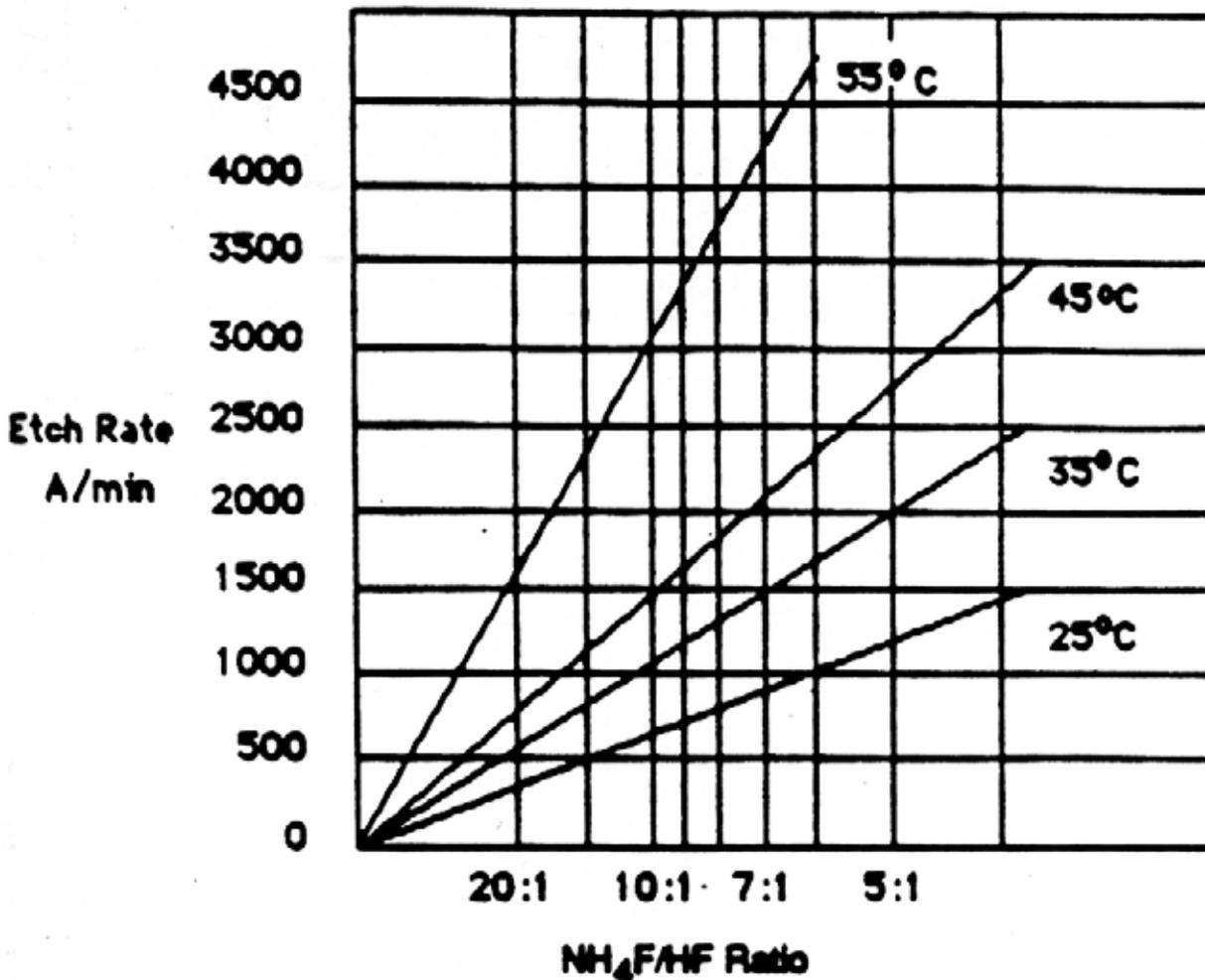
- Depends on free fluorine



- Note the free hydrogen produced

Buffered Oxide Etch of Glass

- Straight HF undercuts resist
- Straight HF also diffuses through resist
- Causes Adhesion loss on resist in long etches.
- Since etch rate depends on free F^- ions
- Can stabilize F level with adding Ammonium Fluoride NH_4F
- Enhance etch rate and stabilize PH level
- creates Buffered Oxide Etch (BOE) or Buffered HF (BHF)
- Note increase in etch rate with temperature



Oxide Etch Rates in Buffered Hydrofluoric Acid
Fig 4

Agitation Enhancement of Etching

- Diffusion limited process controlled by reactant/product
- Increased agitation adds reactant, removes products
- Also removes hydrogen bubbles
- Ultrasonic sound generates controllable agitation

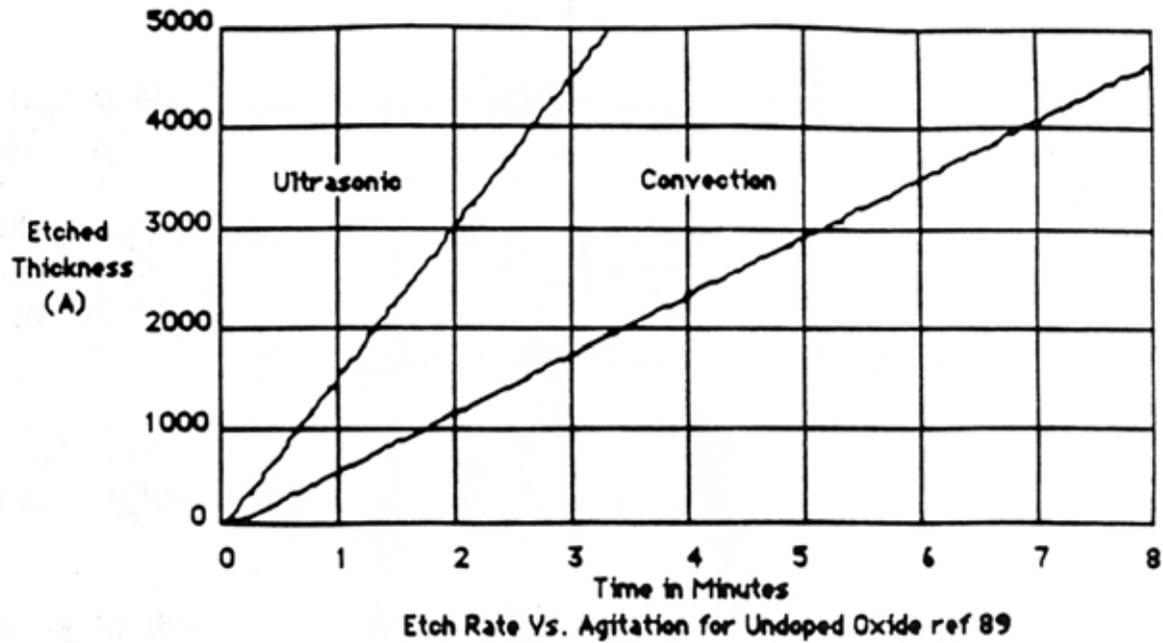


Fig 8

Agitation and Bubbles

- Agitation necessary to remove Hydrogen bubbles
- Bubbles become trapped in between lines/holes:
blocks them: creates a bridge
- Bubbles on surface leave layer behind
sometimes called snowball

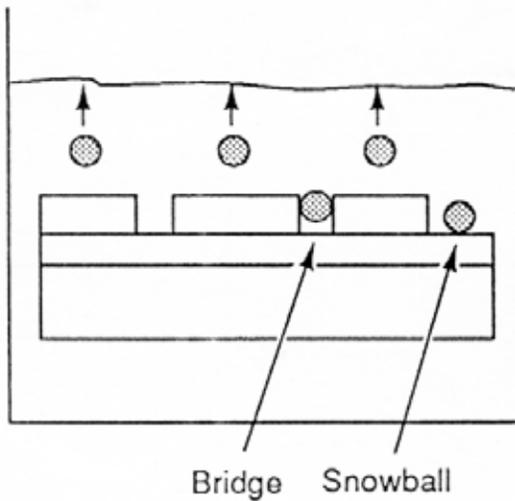


Figure 9.19 Hydrogen bubble blockage of etchant.

Deposited Doped Oxides

- Deposited oxides: high Boron, Phosphorous, Arsenic
- Makes glass "soft" for other operations
- Dopant can significantly affect etch rate
- Boron lowers etch rate initially, then raises when enough B

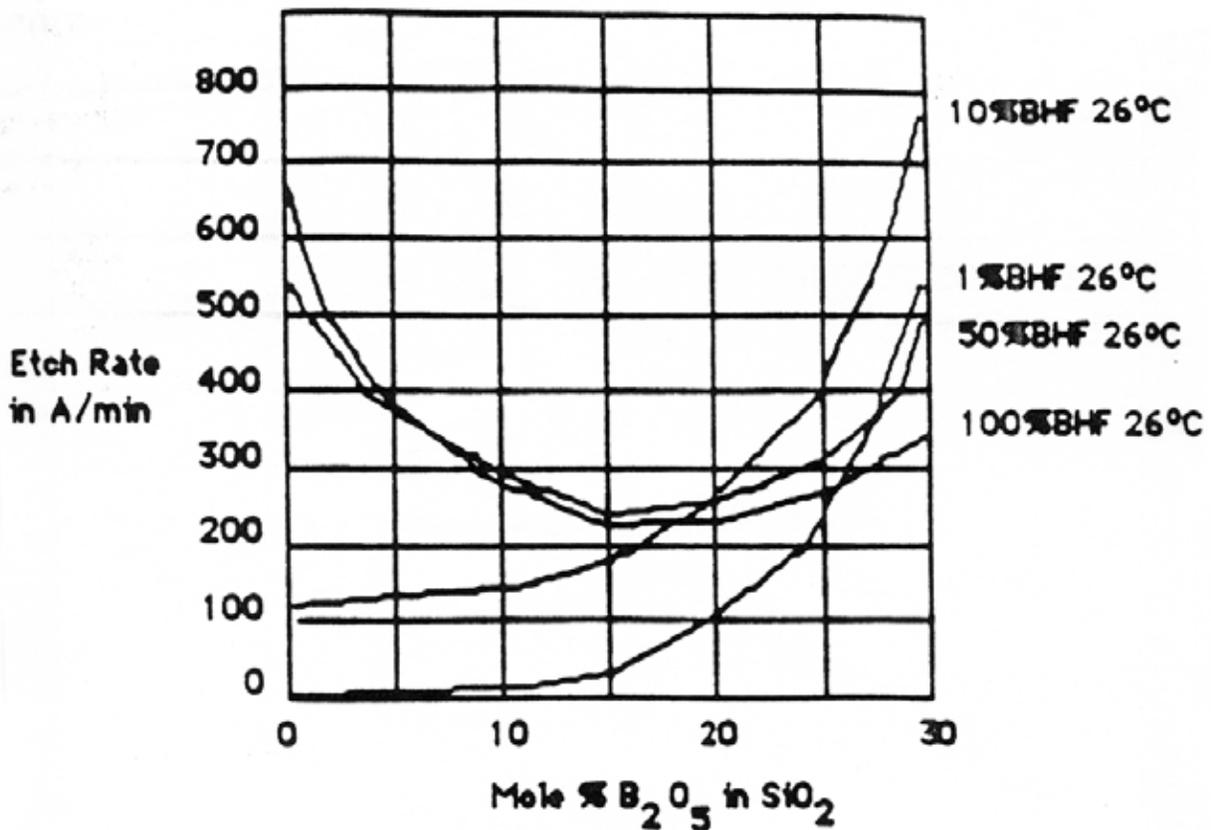
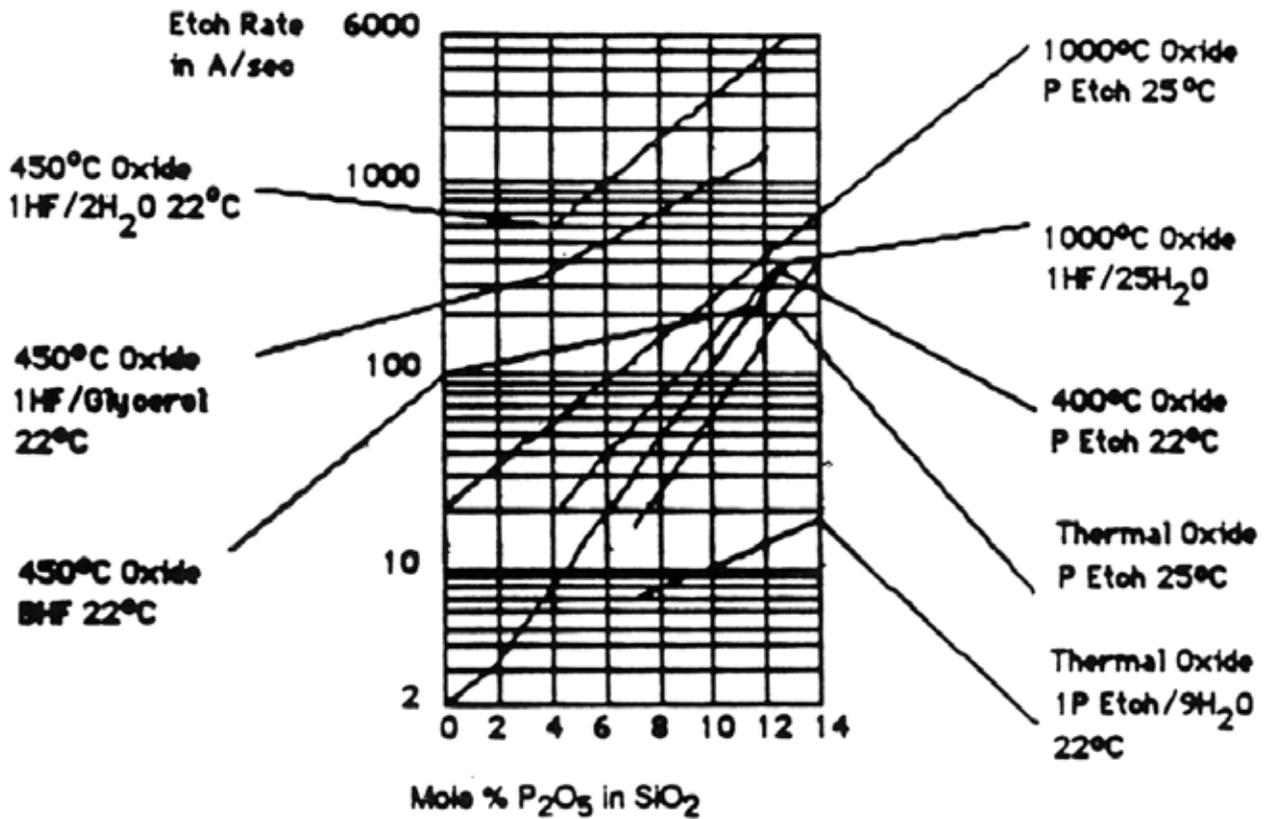


Fig 7
ref 91

Wet Etch Phosphosilicate Glass (PSG)

- Glass with high phosphorus
- used for layers between conductors
- BOE etch rate increases with P content



Arsenic Doped Glass

- Arsenic doping enhances etch rate
- Lower density of Glass, faster etch rate

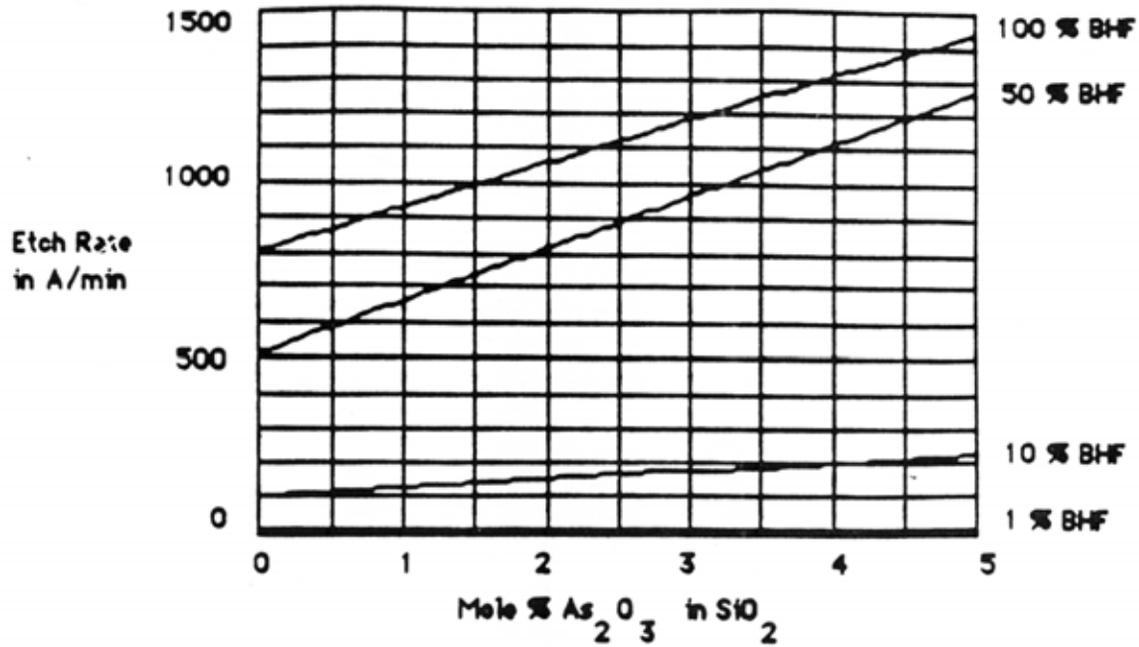


Fig 5
ref 91

Etching and Undercutting

- Perfect etching would be anisotropic
- Would generate Vertical sidewalls (c)
- Isotropic etch gets undercutting of resists
removal of material under resist edge
- Because etch rate differs across wafer
Undercutting different across wafer

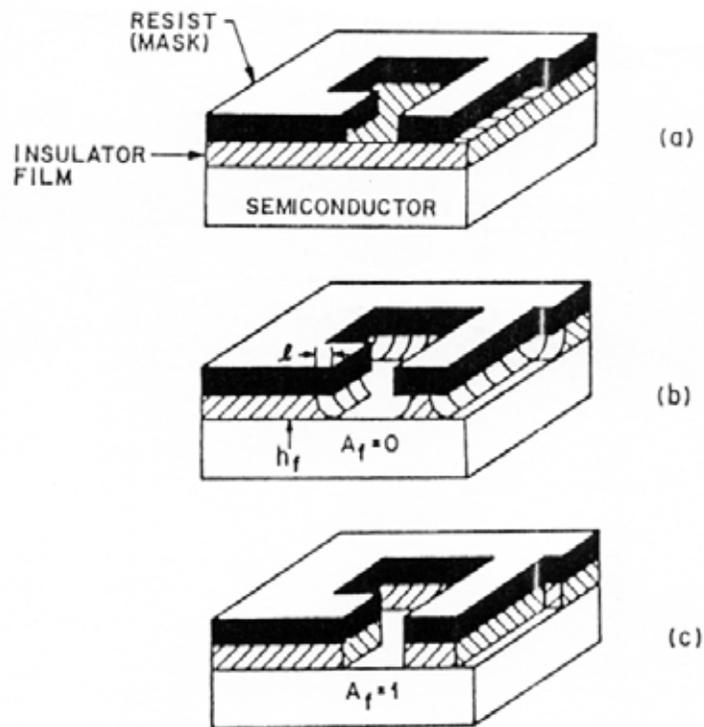


Fig. 5 Comparison of (b) isotropic, and (c) completely anisotropic etching.

Isotropic Wet Etching and Feature Size

- Isotropic etch proceeds at same rate "r" in all directions
- Removes more at top edge than bottom
- Thus create circular profile of etch with radius

$$R = rt$$

where t = time of etch (sec)

r = etch rate (microns/sec)

- Bottom of hole is flat, but edges curved
- Incomplete etch: film layer not fully removed

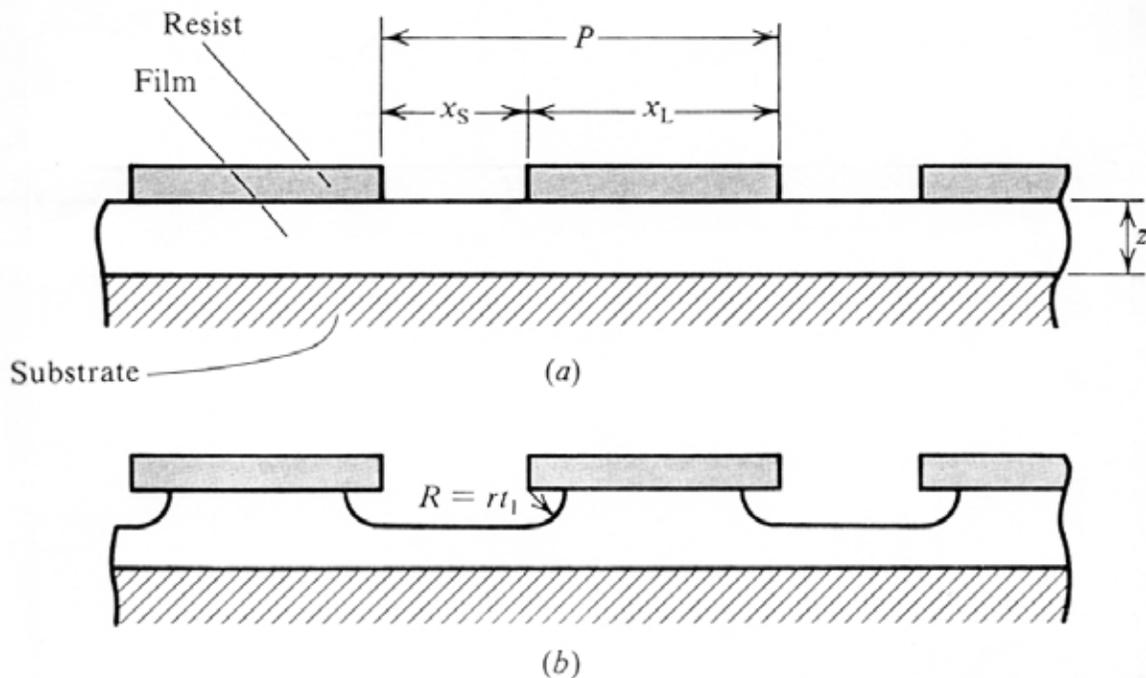


Figure 6-1 Isotropic etching in a wet chemical bath. (a) Unetched, masked film, showing parameters to be used. (b) Partially etched film, etch time t_1 .

Isotropic Wet Etching and Feature Size

- Perfect etch then just clear bottom
- Time of perfect etch is

$$\tau = \frac{z}{r}$$

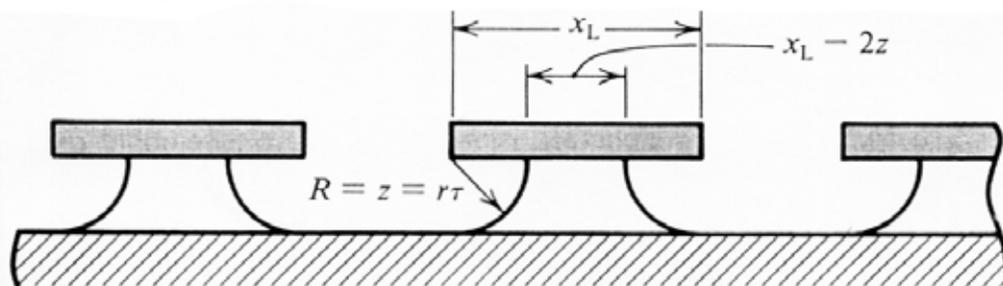
where z = film thickness

- This generates minimum undercut
- Side of lines measured at top/bottom
- For perfect etch get line size at top

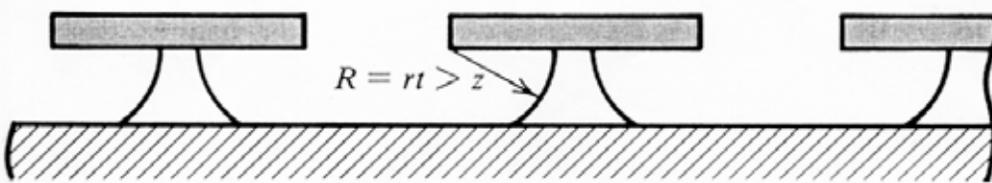
$$x = x_L - 2rt$$

- But unevenness of etch over wafer means must have some overetch (eg 5-10%) at points
- Overetch generates undercut at top: same formula
- Significant undercut at bottom

$$x = x_L - 2\sqrt{rt^2 - z^2}$$



(c)



(d)

(c) Ideally etched film, etch time $\tau = z/r$. (d) Film after overetch, etch time $t > \tau$.

Compensation for Undercut

- Even with ideal isotropic etch get undercut
- Bloat (expand) feature to compensate for undercut
- Set bloat to compensate for difference across wafer
- Resist is also etched,
changing resist profile after etching
- Ideally want perfect "etch stop":
layer below that does not etch

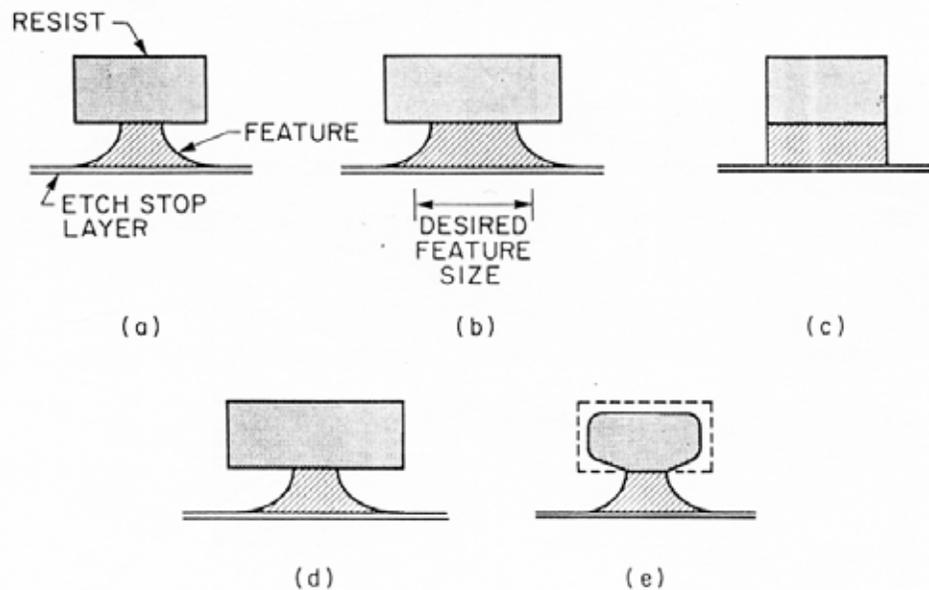


FIGURE 10

A schematic representation of some commonly observed etched profiles: (a) purely isotropic etch, (b) isotropic etch with a compensated mask, (c) anisotropic etch with no horizontal component, (d) isotropic etch with overetch, and (e) isotropic etch with isotropic etching of the mask.

Etch Stops and Hole Undercut

- Layer below generally does etch small amount
- Use an etch which slowly attacks "etch stop layer"
- Etch stop much better than timed etch
- Still get some etching into stop layer
- Holes open more at top than at bottom
- May bloat holes to make certain open

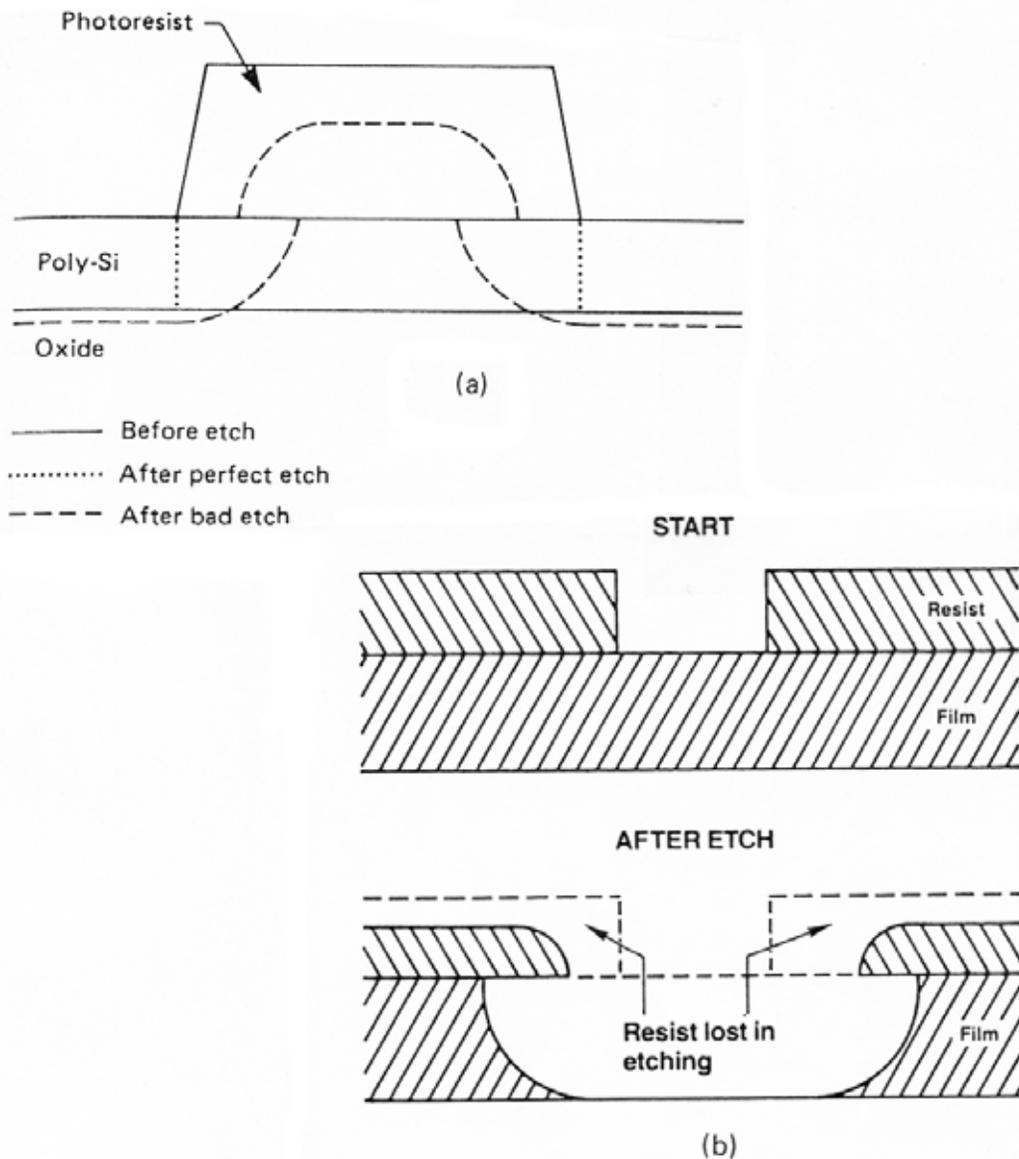


Figure 11.6 Wet-etch undercut profiles: dimensional control problem in (a) door etching¹⁰ and (b) window etching.¹¹

Overetch Profile

- Initial undercut nearly circular
- As proceeds undercut get more vertical
- Difference between top and bottom reduced

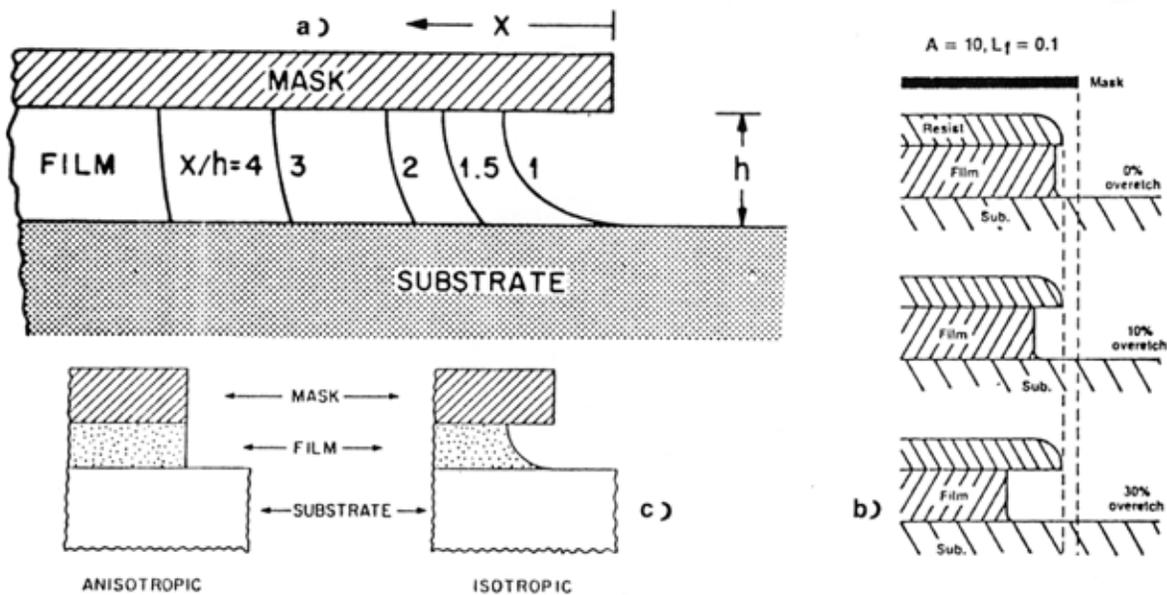


Fig. 6 (a) Isotropic etching of a film vs time ($L_R = 1$). Overetching results in profiles are more vertical. (b) Etching of film versus time when $L_R = 0.1$. (c) Etch bias is a measure of the amount by which the etched film undercuts the mask at the mask film interface. Fig. (c) Copyright, 1983, Bell Telephone Laboratories, Incorporated, reprinted by permission.

Sloped Sidewalls

- Sometimes want sloped sidewalls: sloped edges
- Easier for layers stepping over edge
- As wet etch undercuts resist begins to lift off.
- May deposit thin fast etch layer under mask
- Generates shallow slope in undercut

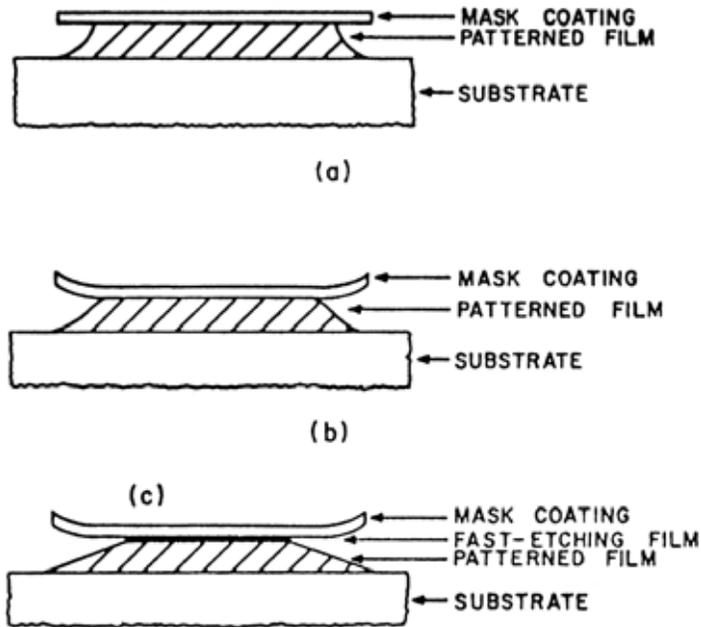


Fig. 12 Different etch profiles produced from various degrees of undercutting during wet etch. (a) Good mask-to-film adhesion. (b) Undercutting has occurred at mask-film interface. (c) Use of fast-etching film to achieve controlled undercutting¹⁴. Reprinted with permission of Academic Press.

Etching Bilayer Film

- Sometimes put down two layers: fast and slow etch
- Fast top layer undercuts with radius R

$$R_f = r_f t$$

- Slow lower layer matches upper at top
- at bottom has its own etch radius

$$R_s = r_s t$$

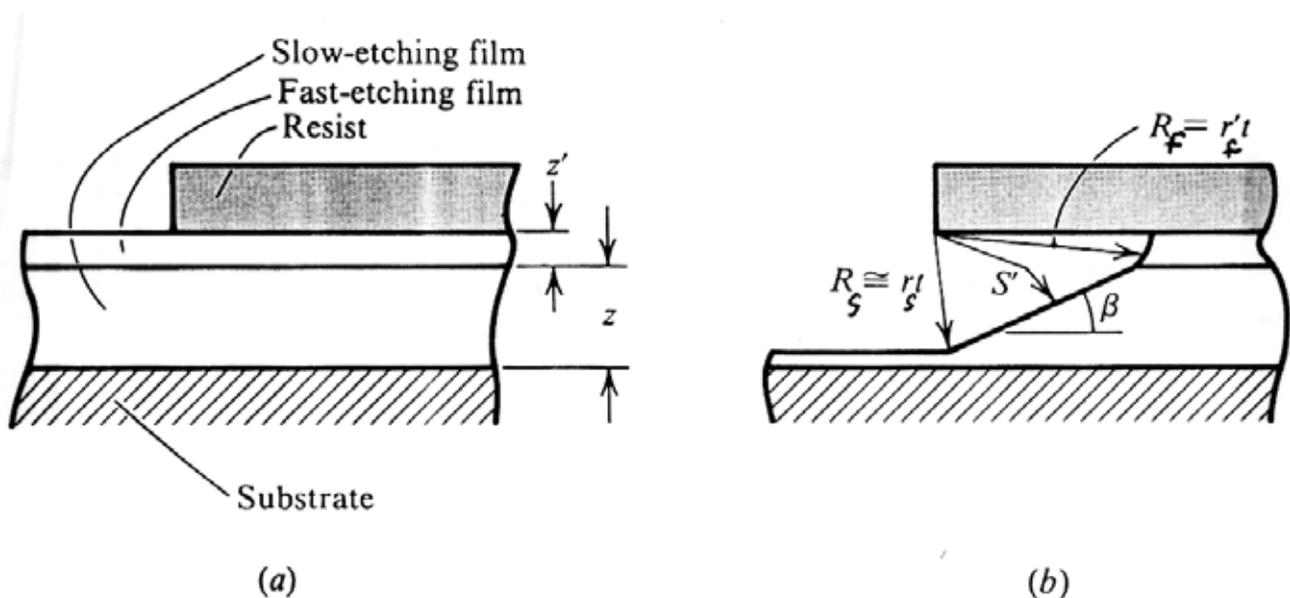


Figure 6-2 Etching of a bilayer film. (a) Unetched, masked film. (b) Generation of a sloped profile as the fast-etching surface layer recedes. β defines the slope of the edge; S' is a typical path by which etchant reaches the sloped area.

Edge Residue and Etching

- When film II steps over film I edge
film II thicker at edge
- More difficult to etch because thicker
- Result often leave residue at edge
- Isotropic wet etch does less of this.

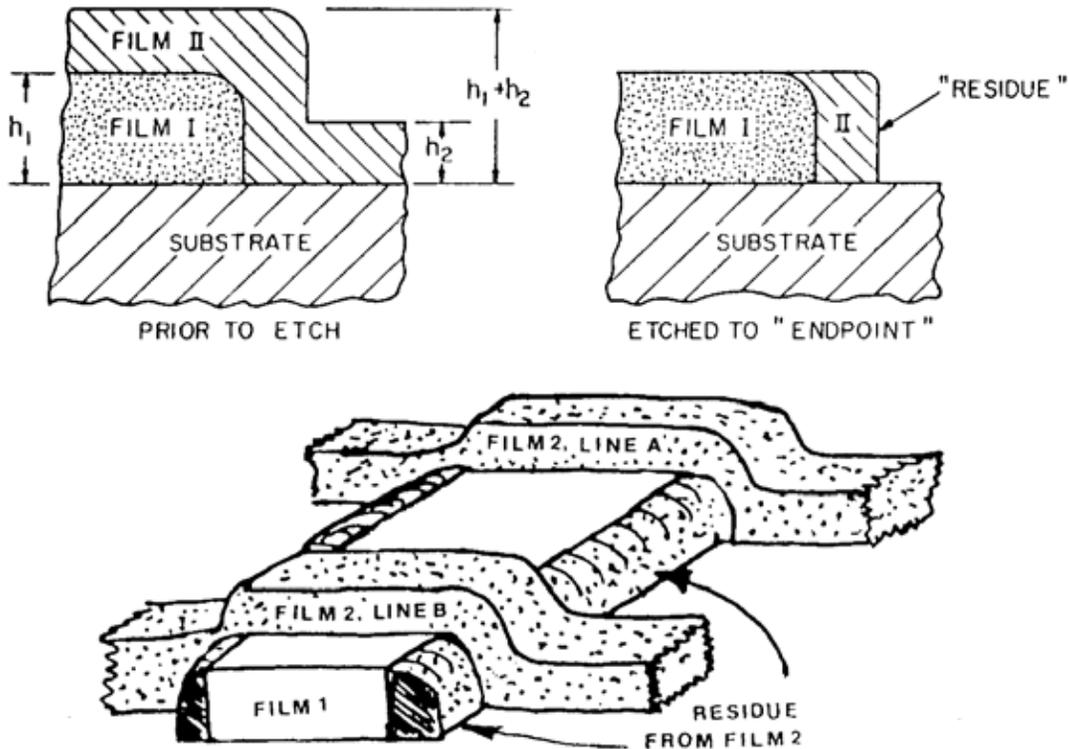


Fig. 9 If etching is anisotropic, overetching is needed to remove residual materials at steps. The degree of anisotropy, $A = 1$ in the example shown. Copyright, 1983, Bell Telephone Laboratories, Incorporated, reprinted by permission.

Silicon Nitride

- Nitride of silicon: Si_3N_4
- Used as a dielectric insulator between conductors
- Also gate dielectric in Mosfets
- Grown by Chemical Vapour Deposition
- Usually non-stoichiometric (not proper composition ratio)
 Si_xN or $\text{Si}_x\text{N}_y\text{H}_z$
- Also grow Silicon Oxynitrides
 $\text{Si}_x\text{O}_y\text{N}_z$
- Very slow etching relative to oxide

Silicon Nitride Etches

- HF poor for Nitride, fast for oxide
 Bad: generally have oxide near nitride
- Means can use nitride as a mask for oxide in BOE etch
- Phosphoric Acid solutions H_3PO_4 best

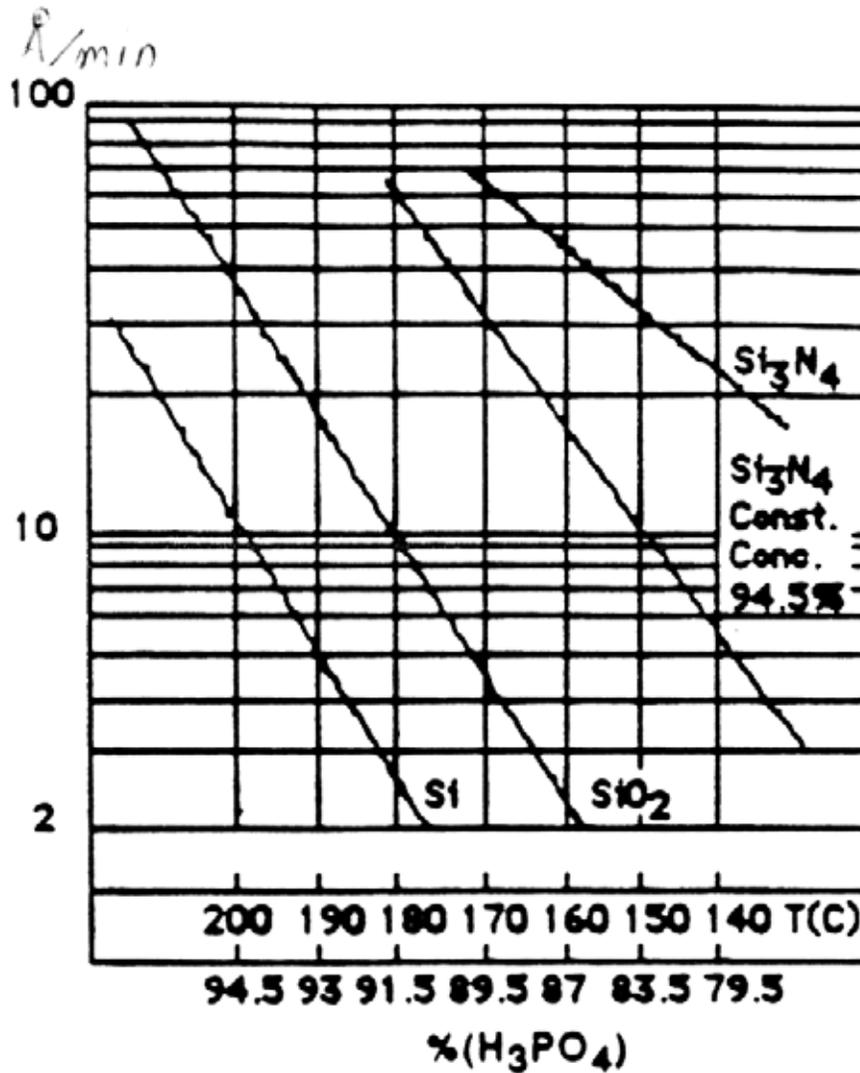
SILICON NITRIDE ETCHES

Table 6

Formula	Comments
1 HF	22°C 140-1000A/min depending on the nitride deposition method
2 28 ml HF, 170 ml H ₂ O, 113 g NH ₄ F	22°C BHF 5-10A/min
3 49% HF, 70% HNO ₃	70°C
4 Molten NaOH	450°C
5 1-6 ml HBF ₄ , 100 ml H ₃ PO ₄	105°C 1 ml to 100 ml has a 1:1 etch rate vs SiO ₂ , at 110°C etches 100 ^o A/min, resist compatible if post baked 140 to 160°C
6 H ₃ PO ₄	140-200 C, Reflux Boiling SiO ₂ etch masks. See Fig. 8

Nitride Etch with Boiling Phosphoric Acid H_3PO_4

- Etches nitride mostly fast
- Resist does lift during etch
- Poor etch of oxide:
- thus often use oxide as a mask for nitride



Silicon Nitride Etch Rate in Boiling Phosphoric Acid

Fig 11

ref 3