Lecture 17:

Non Silicon Wet Etching

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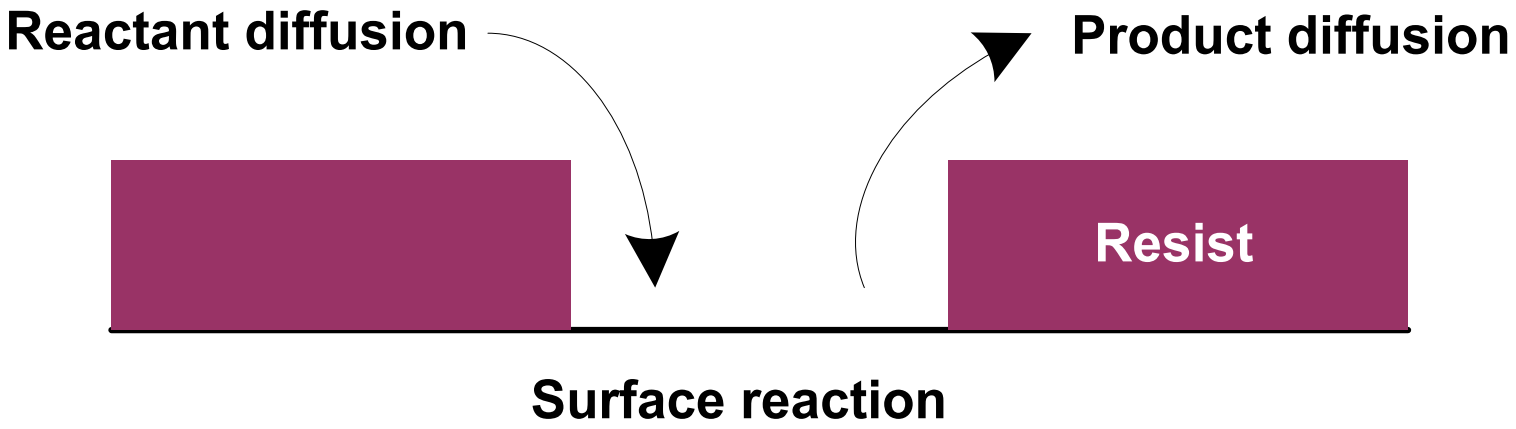
Basic Wet Etch Process

- Diffusion of reactants to the surface
- Reaction on the surface
  (absorption, reaction, desorption)
- Diffusion of products from the surface



Oxide etching sequence in BOE

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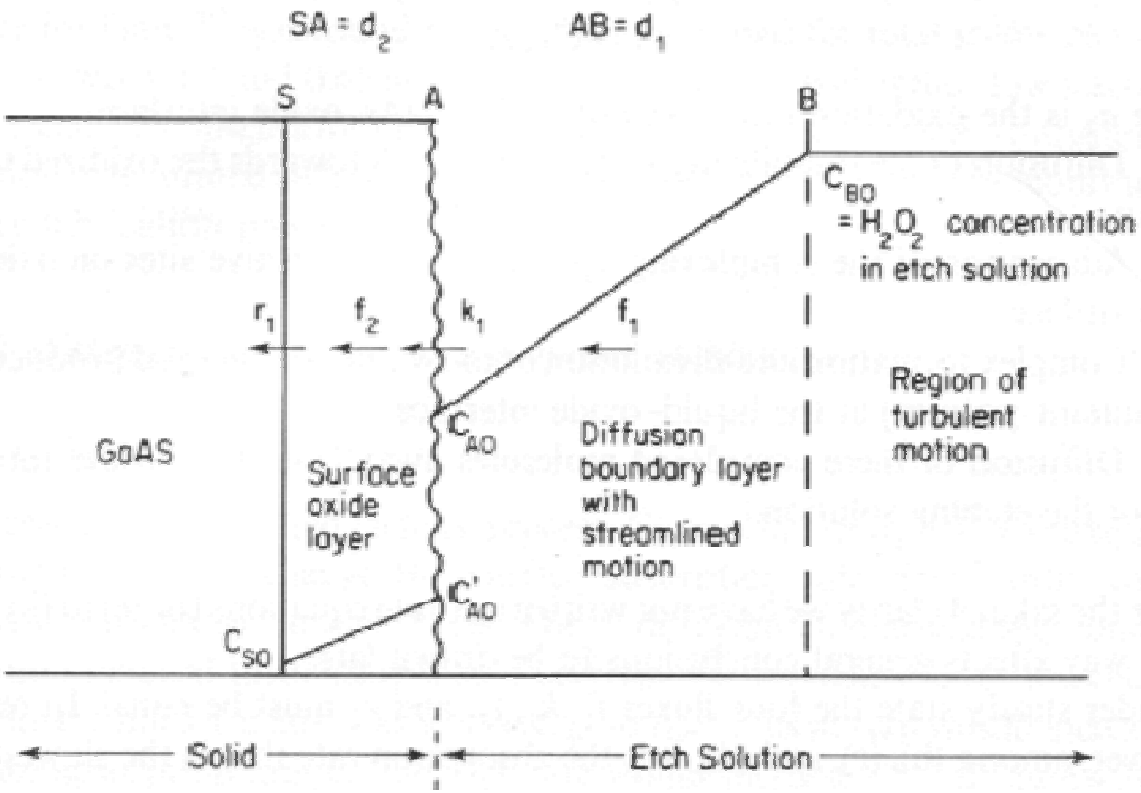
A Schematic View of the Etch Process

- Concentration gradient of the oxidizing component, H_2O_2 in the etch solution close to the surface and inside the thin surface oxide, during a wet chemical etching process



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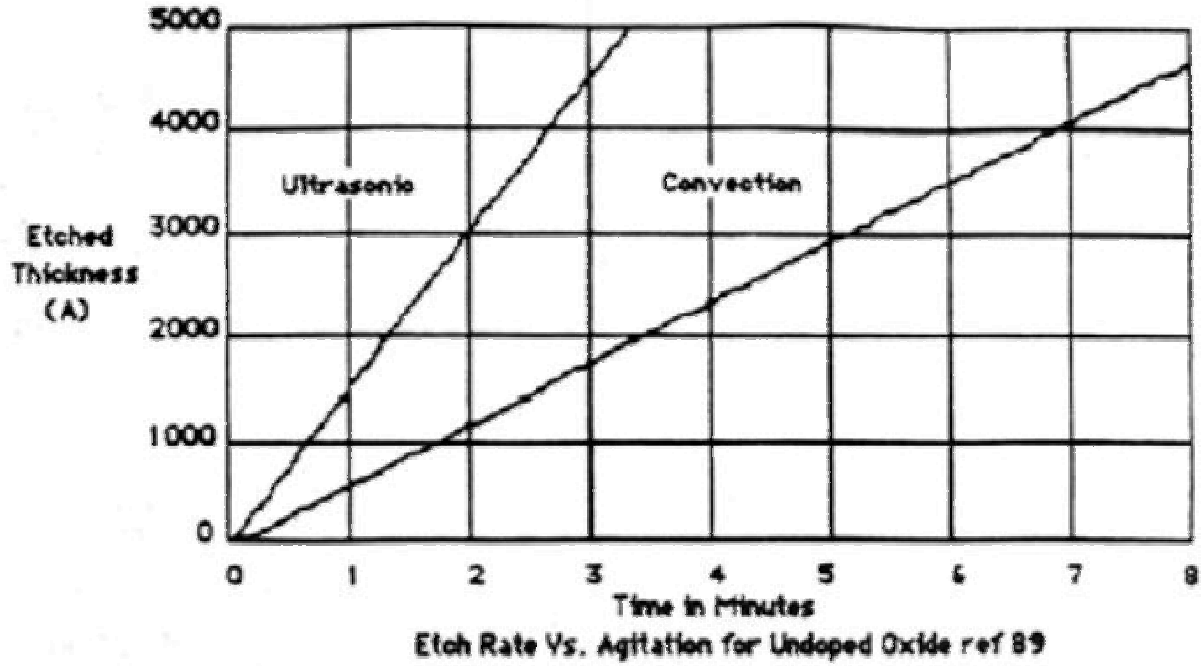
Agitation in Etching Process

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



Etch Rate Vs. Agitation for Undoped Oxide ref 89

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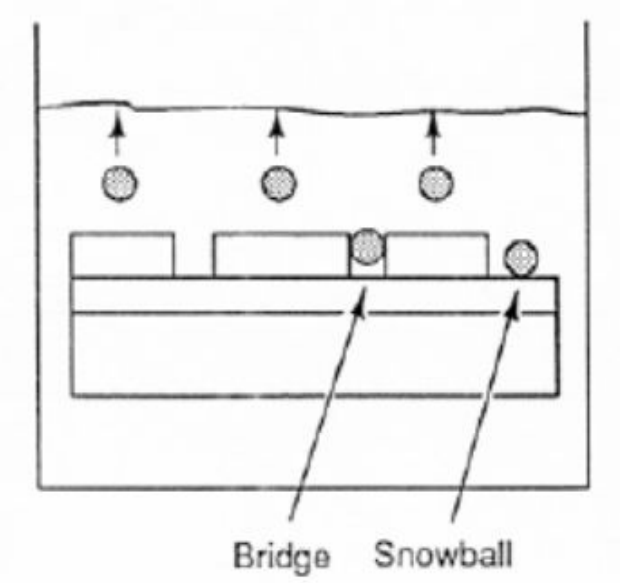
Agitation and Bubbles

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



Hydrogen bubble blockage of etchant

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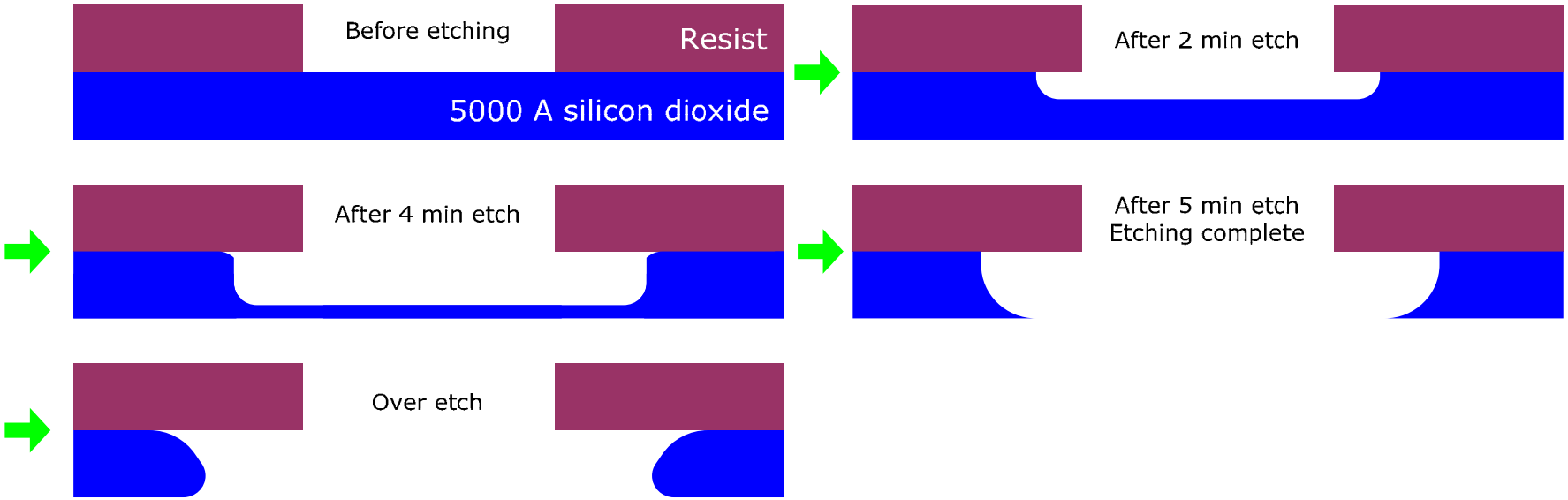
Typical Wet Etch profile

- The etch process goes on both vertical and horizontal directions
- Undercut effect at the edge of the resist
- Etch process is slower than before at the etch stop
- Over etch process creates significant undercut



Oxide etching sequence in BOE

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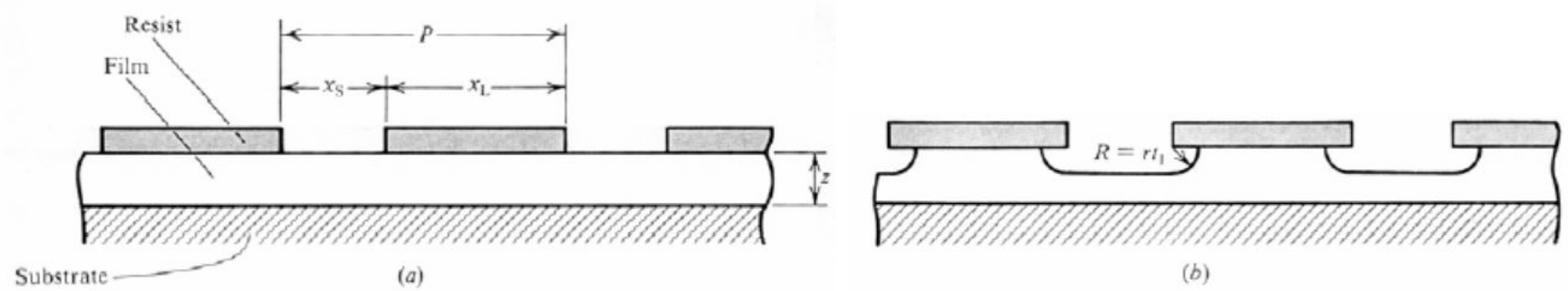
Isotropic Wet Etching and Feature Size (1)

- 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 (um/sec)
- Bottom of hole is flat, but edges curved
- Incomplete etch: film layer not fully removed



Isotropic etching in a wet bath. (a) unetched, mask film, showing parameters to be used
(b) Partially etched film

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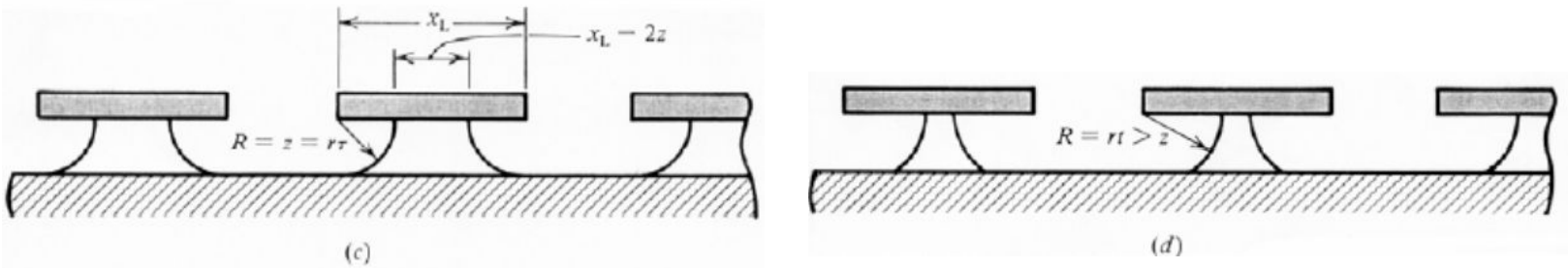
Isotropic Wet Etching and Feature Size (2)

- Perfect etch then just clear bottom
- Time of perfect etch is z/r (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 over etch at points
- Over etch generate undercut at top



(c) Ideally etch film (d) film after over etch

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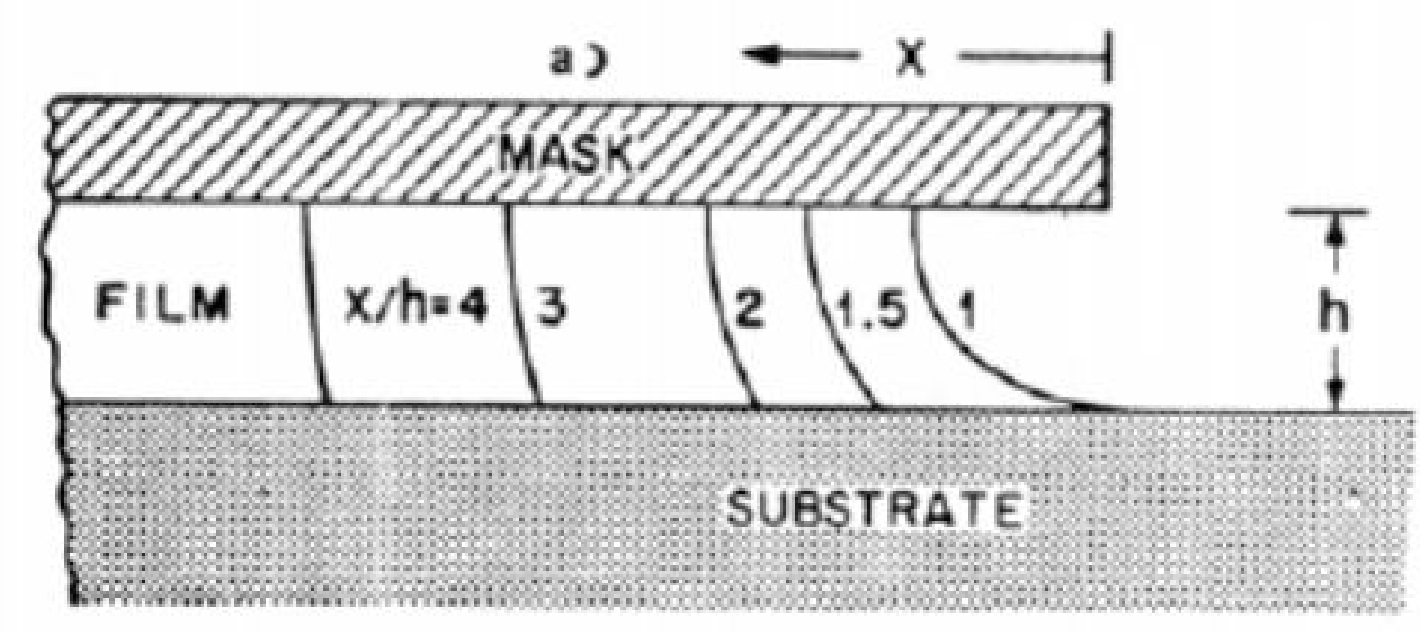
Overetch Profile

- Initial undercut nearly circular
- As proceeds undercut get more vertical



Wet ecth profile

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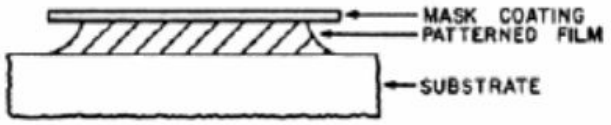
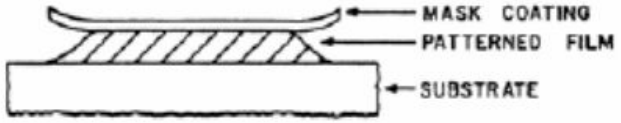
Sloped Sidewalls

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



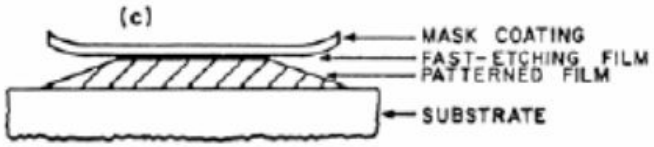
(a)

a) Good mask to film adhesion



(b)

b) Undercutting has occurred at mask film interface



c) Used of fast etching film to achieve controlled undercutting

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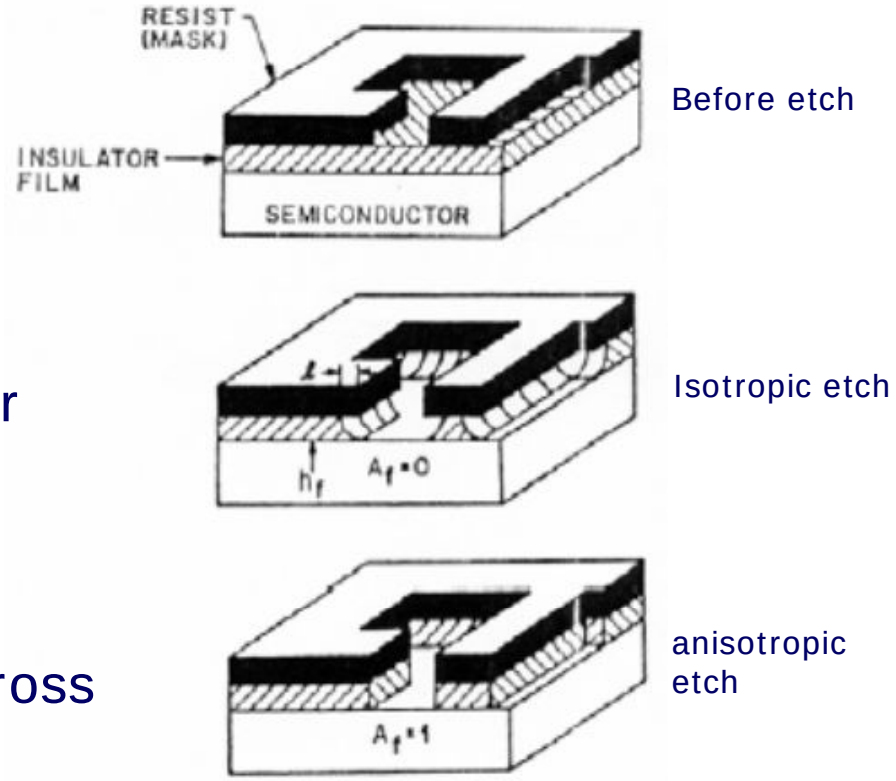
Etching and Undercutting

- Perfect etching would be anisotropic
- Would generate vertical sidewalls
- Isotropic etch gets undercutting of resists removal of material under resist edge
- Because etch rate differs across wafer

  undercutting different across wafer



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Wet Etch Chemicals

- Concentration of various acids for wet etching

Acid	Concentration	Property
Acetic acid	Pure	-
Sulfuric acid	96%	-
Phosphoric acid	85%	Deliquescent* solid at room temperature
hydrofluoric acid	49%	boiling point : 19.5 ° C
Nitric acid	70%	liquid in the range near room temperature

* Deliquescent : tending to melt or dissolve; *especially* **:** tending to undergo gradual dissolution and liquefaction by the attraction and absorption of moisture from the air

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Silicon Dioxide Wet Etchants (1)

- HF-based etchants are used mainly for etching silicon dioxide, although they can also be used to remove silicon nitride
- HF-based solutions should be handled with Teflon containers →not glass containers, which will be attacked

- Reaction
  - Pure HF etching

$$SiO_2 + 6HF \rightarrow H_2SiF_{6(aq)} + 2H_2O$$

  - The reaction in BHF solution

$$SiO_2 + 4HF + 2NH_4F \rightarrow (NH_4)_2SiF_6 + 2H_2O$$

  - The reaction involving the HF^{-}_{2} ion

$$SiO_2 + 3HF^{-}_{2} + H+ \rightarrow SiF^{2-}_{6} + 2H_2O$$

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Silicon Dioxide Wet Etchants (2)

- Concentrated HF (49%)
  - Concentrated hydrofluoric acid (49% by weight, remainder water)
  - Etches oxides very rapidly → often used to remove sacrificial oxide when micromachining
  - Concentrated HF tends to peel off photoresist, while lower concentrations (less then 3:1) do not
- 10:1 HF
  - 10:1 HF:H_20: concentrated HF (49% HF)
  - Typically used for stripping oxide and for HF dips, diluted HF is cheaper than buffered HF
- 25:1 HF
  - 25:1 HF:H_20: concentrated HF (49% HF)
  - This slow etch is used for HF dips to strip native oxide without removing much of the other oxides that may be on a wafer

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Silicon Dioxide Wet Etchants (3)

- 5:1 BHF
  - 5:1 buffered hydrofluoric acid (also know as buffered oxide etch, or BOE)
  - "5:1" refers to five parts by weight of 40-weight-percent ammonium fluoride (the buffer) to one part by weight 49 – weight-percent hydrofluoric acid

    → which results in a total of about 33% NH_4F and 8.3% HF by weight.
  - This etchant can be masked with photoresist
  - It is the often best choice for controlled etching of oxide
  - Note increase in the etch rate with temperature

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Silicon Nitride Wet Etchant

- Phosphoric acid (85%)
  - Phosphoric acid (85% by weight, remainder water) at 160 ° C
  - The nitride is typically masked with densified PSG
    → If the PSG mask is not densified, it is removed faster and may also have pores through which the acid can seep
  - The nitride can also be patterned with poly-Si

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Metal Wet Etchants (1)

- Aluminum Etchant Type A
- 80% H_3PO_4 + 5% HNO_3 + 5% CH_3COOH + 10% H_2O
- This etchant is designed to etch Al at 6000 A/min at 50 ° C
- It can be masked with PR
- Reaction
  - Al is first oxidized by the nitric acid
  - The phosphoric acid and water simultaneously etch the resulting oxide
  - With the concentrations gives, these two processes occur at roughly the same rate
  - The phosphoric acid also removes the native Al oxide

    → no additional component is needed

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Metal Wet Etchants (2)

- Titanium etchant
  - Mixed from 20:1:1 → H_2O:HF (49%): H_2O_2 (30%)
  - HF is the active ingredient is this etchant, so it also etches oxides

    → raising the fraction of HF in the solution increases the etch rate
  - It can be masked with PR

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Metal Wet Etchants (3)

- CR-7 (Chromium etchant)
  - 9% $(NH_4)_2Ce(NO_3)_6$ + 6% $HClO_4$ + H_2O
  - This etchant is formulated to selectively etch chromium, and was also found to etch copper and silver at useful rates
  - It can be masked with PR
  - The chemical reaction

$$3Ce(IV)(NH_4)_2(NO_3)_{6(aq)} + Cr\ (s) \rightarrow Cr(III)(NO_3)_{3(aq)} + 3Ce(III)(NH_4)_2(NO_3)_{5(aq)}$$

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Metal Wet Etchants (4)

- CR-14 (Chromium etchant)
  - 22% $(NH_4)_2Ce(NO_3)_6$ + 8% CH_3COOH + H_2O
  - This etchant is formulated to selectively etch chromium
  - It was also found to slowly etch vanadium and copper
  - It etches chromium a little slower than CR-7, but have more a consistent etch rate, as well as much less undercut of PR
  - The etch reaction is the same as for CR-7

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Metal Wet Etchants (5)

- Moly etch
  - 180:11:11:150 → H_3PO_4:CH_3COOH:HNO_3 (70%):H_2O
  - It can be masked with PR, which is etched at a moderate rate

- H_2O_2 at 50 °C (Hydrogen peroxide 30% by weight)
  - Etch target is tungsten, but etches it slowly
  - Heating increases the etch rate
  - Ultrasonic agitation aids in etch uniformity by helping to remove bubbles

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Metal Wet Etchants (6)

- Cu $FeCl_3$ 200
  - Copper etchant: 30% $FeCl_3$ + 3~4% HCl + H_2O
  - CE-200 can be patterned with PR
  - Reaction
    - $FeCl_3$ dissociates in water to generate Fe^{3+} and Cl^- ions

      $Cu_{(s)} + 2Fe_3+ + 3Cl^- \rightarrow CuCl^-_3 + 2Fe^{2+}$
    - The Fe^{3+} ions are reduced to Fe^{2+}, which remain in solution, while the copper metal is oxidized to Cu^{2+}
    - HCl assists in the dissolution of the ferric chloride, and also etches copper itself

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Metal Wet Etchants (7)

- Cu APS 100
  - Copper etchant: 15~20% $(NH_4)_2S_2O_8$ + H_2O at 30 ° C
  - PR can be used as an etch mask
  - The overall reaction

$$Cu_{(s)} + (NH_4)_2S_2O_8 \rightarrow CuSO_{4(aq)} + (NH_4)_2SO_{4(aq)}$$

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Metal Wet Etchants (8)

- Dil. Aqua Regia
  - 3:1:2 → HCl (37%):HNO_3 (70%):H_2O
  - This solution is self heating to about 30 ° C for tens of minutes
  - The water was added to the standard aqua regia solution to reduce the attack of PR
  - Aqua regia targets noble metals

  - The overall reaction (Au)

$$Au_{(s)} + 4H^{+} + NO^{-}_{3} + 4Cl^{-} \rightarrow AuCl^{-}_{4} + NO_{(g)} + 2H2O_{(l)}$$

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Metal Wet Etchants (9)

- AU-5
  - Gold etchant: 5% I_2 + 10% KI + 85% H_2O
  - Such iodine solutions are the color of dark coffee, making it impossible to observe a submerged sample
  - Rinsing with running water must be done to remove the solution from the surface → isopropanol or methanol can be used for a faster rinse
  - PR can be used as an etch mask
  - The overall reaction

$$2Au_{(s)} + I_{2(aq)} \rightarrow 2AuI_{(aq)}$$

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Metal Wet Etchants (1)

- NiCr TFN
  - Nichrome etchant: 10~20% $(NH_4)_2Ce(NO_3)_6$ + 5~6% HNO_3 + H_2O
  - It is formulated to etch nickel-chromium alloy
  - It etched pure nickel slowly, but etched chromium, copper, and molybdenum faster than the NiCr alloy
  - PR can be used as an etch mask

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GaAs Wet Etch (1)

- Unique Advantages of GaAs over Si
  - High resistivity
  - High electron mobility
  - High saturated drift velocity
  - Wide direct bandgap
  - Operability over a wide temperature range

- Etch conditions
  - Etchants: 30%wt NH_4OH + 30%wt H_2O_2 + H_2O
  - Wafer: (001) GaAs substrate
  - Mask material: PECVD oxide, PECVD low stress nitride
  - Temperature: 18 ℃

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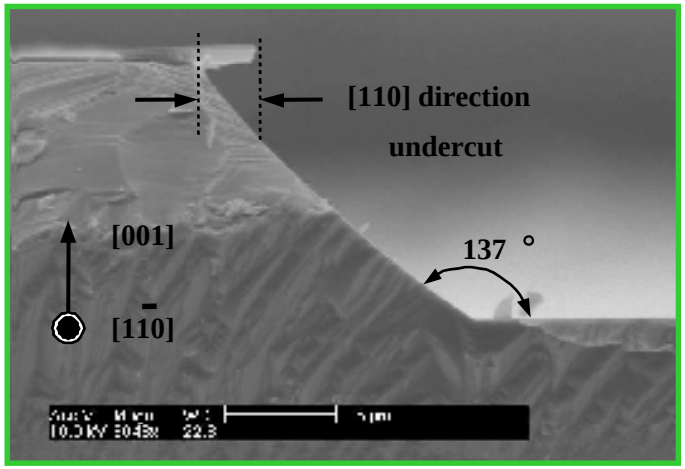
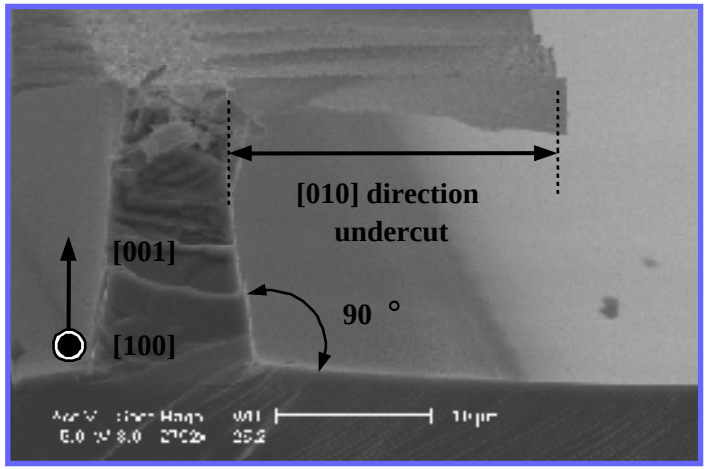
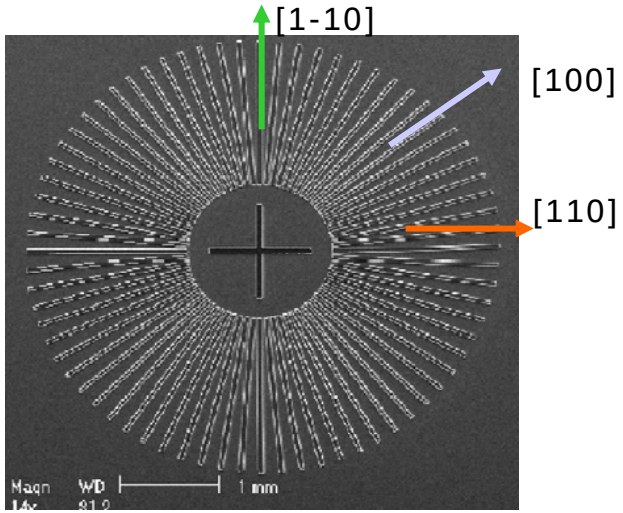
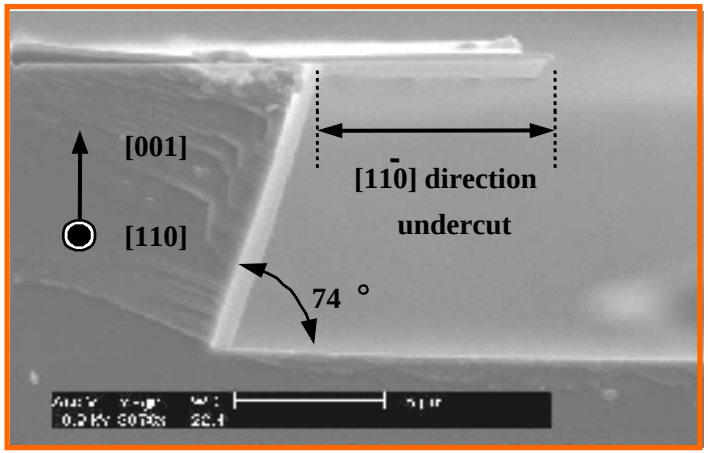
GaAs Wet Etch (2)

- (001) GaAs wet etch results









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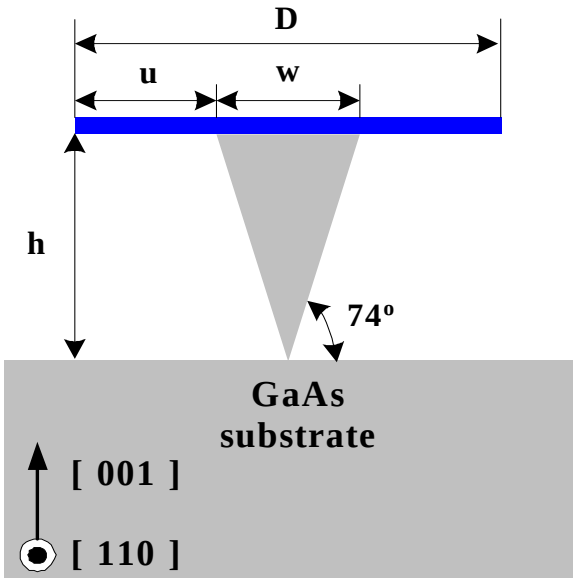
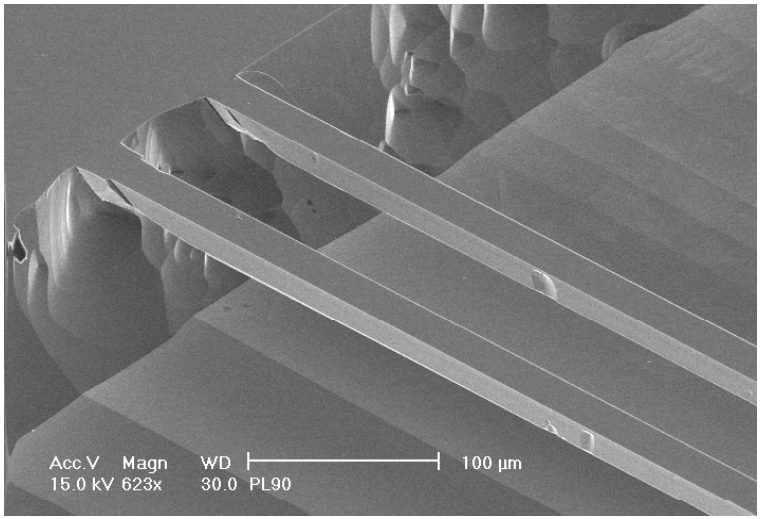
GaAs Wet Etch (3)

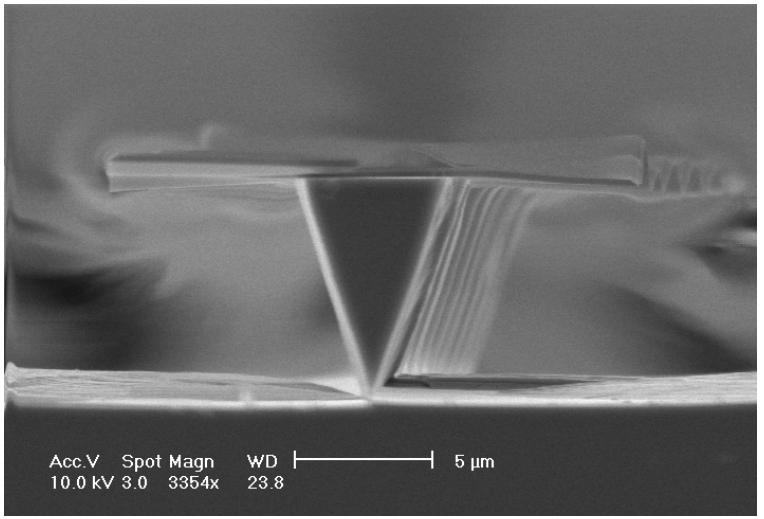
- <110> beam release



$$w = \frac{\tan 16^o}{S \tan 16^o} D \qquad S = \frac{u}{h}$$

$$h = \frac{D}{2(S + \tan 16^o)}$$





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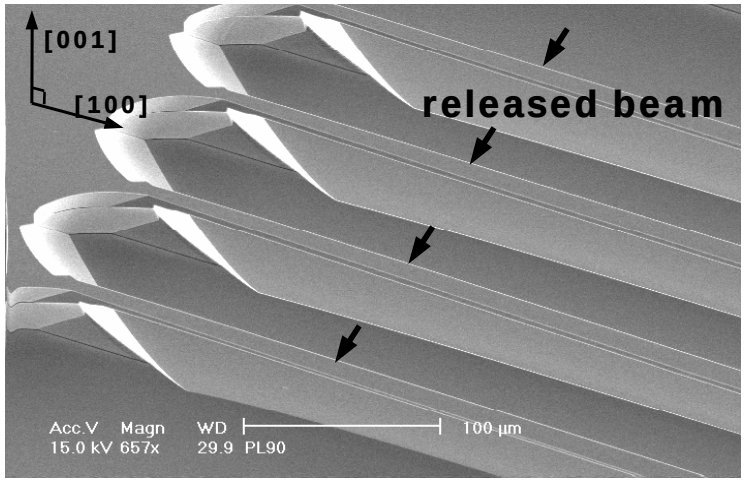
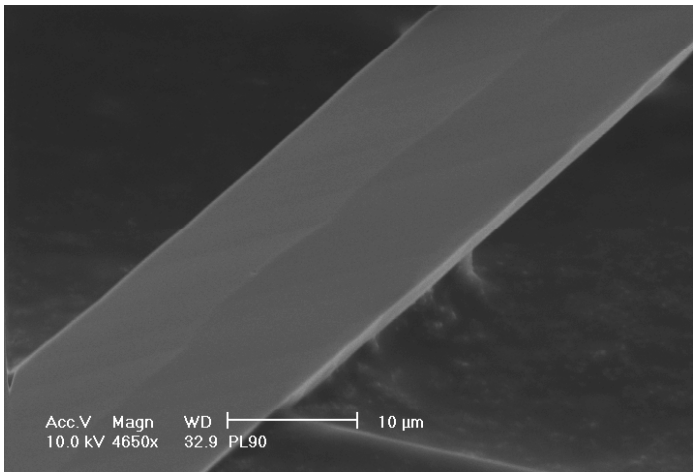
GaAs Wet Etch (4)

- <100> beam release



(a) released [100] direction beams



(b) backside of the released beam

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Other Wet Etchants (1)

- Piranha
  - The piranha (also known as sulfuric-peroxide) is a mix of H_2SO_4 (96%):H_2O_2 (30%) → 4:1
  - It is heated 120 °C
  - It is used as a cleaning solution that strips organics and some metals

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Other Wet Etchants (2)

- Acetone
  - Pure acetone, also known as dimethyl ketone.
  - It is used to strip photoresist and for cleaning off organics.
  - It removed photoresists rapidly, as expected, but did not etch polyimide.
- Methanol
  - Pure methanol
  - It is used for cleaning and in supercritical drying.
  - Methanol removed photoresist, but did not etch polyimide.
- Isopropanol
  - Pure isopropanol, also known as isopropyl alcohol (IPA) and 2-propanol.
  - It is used for cleaning off organics.
  - In contrast to methanol, isopropanol was found to remove photoresist at a moderate rate.

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Etch Rate Table (1)

Wet Etch Rates for Micromachining and IC Processing (Å/min)

The top etch rate was measured by the authors with fresh solutions, etc. The center and bottom values are the low and high etch rates observed by the authors and others in our lab under less carefully controlled conditions.

		MATERIAL															
ETCHANT EQUIPMENT CONDITIONS	TARGET MATERIAL	SC Si <100>	Poly n+	Poly not doped	Wet Ox	Dry Ox	LTO not doped	PSG not annealed	PSG annealed	Stoic Nitride	Low Stress Nitride	Alum 2% SI	Sput Tung	Sput Ti	Sput Ti/W	OCG 820 PR	Olin Hunt PR
Concentrated HF (49%) *Wet Sink* *Room Temperature*	Silicon oxides	- 	0 	- 	23k 18k 23k	F 	>14k 	F 	36k 	140 	52 30 52	42 0 42	<50 	F 	- 	P O	P O
10:1 HF Wet Sink Room Temp	Silicon oxides	-	7	0	230	230	340	15k	4700	11	3	2500 2500 12k	0	11k	<70	0	0
25:1 HF Wet Sink Room Temp	Silicon oxides	-	0	0	97	95	150	W	1500	6	1	W	0	-	-	0	0
5:1 BHF Wet Sink Room Temp	Silicon oxides	-	9	2	1000 900 1080	1000	1200	6800	4400 3500 4400	9	4 3 4	1400	<20 0.25 20	F	1000	0	0
Phosphoric Acid (85%) Heated Bath with Reflux 160°C	Silicon nitrides	-	7	-	0.7	0.8	<1	37	24 9 24	28 28 42	19 19 42	9800	-	-	-	550	390
Silicon Etchant (126 HNO_3 :60 H_2 :5 NH_4F) Wet Sink Room Temp	Silicon	1500	3100 1200 6000	1000	87	W	110	4000	1700	2	3	4000	130	3000	-	0	0

Notation: - = test not performed; W = Not performed, but known to Work (100 Å/min); F = not performed, but known to be Fast (10 kÅ/min); P = some of film Peeled during etch or when rinsed; A = film was visibly Attached and roughened. Etch areas are all of a 4-inch wafer for the transparent films and half of the wafer for single-crystal silicon and the metals. Etch rates will vary with temperature and prior use of solution, area of exposure of film, other materials present (e.g., photoresist), film impurities and microstructure, etc. Some variation should be expected.

Ref.) K. R. Williams, and R. S. Muller, JMEMS, Vol. 5, No. 4, pp. 256-269, 1996

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Etch Rate Table (2)

ETCHANT EQUIPMENT CONDITIONS	TARGET MATERIAL	SC Si <100>	Poly n+	Poly not doped	Wet Ox	Dry Ox	LTO not doped	PSG not annealed	PSG annealed	Stoic Nitride	Low Stress Nitride	Alum 2% SI	Sput Tung	Sput Ti	Sput Ti/W	OCG 820 PR	Olin Hunt PR
KOH (1 KOH: 2 H_2O by weight) Heated Stirred Bath 80°C	<100>Silicon	14k	>10k	F	77 41 77	-	94	W	380	0	0	F	0	-	-	F	F
Aluminum Etchant Type A (16 H_3PO_4:1 HNO_3:1 HAc:2H_2O) Heated Bath 50°C	Aluminum	-	<10	<9	0	0	0	-	<10	0	2	6600 2600 6600	-	0	-	0	0
Titanium Etchant (20 H_2O:1H_2O_2O:1 HF) Wet Sink Room Temp	Titanium	-	12	-	120	W	W	W	2100	8	4	W	0 0 <10	8800	-	0	0
H_2O_2 (30%) Wet Sink Room Temp	Tungsten	-	0	0	0	0	0	0	0	0	0	<20	190 190 1000	0	60 60 150	<2	0
Piranha (-50 H_2SO_4:1 H_2O_2) Heated Bath 120°C	Cleaning off metals and organics	-	0	0	0	0	0	-	0	0	0	1800	-	2400	-	F	F
Acetone Wet Sink Room Temp	Photoresist	-	0	0	0	0	0	-	0	0	0	0	-	0	-	>44k	>39k

Notation: - = test not performed; W = Not performed, but known to Work (100 A/min); F = not performed, but known to be Fast (10 kA/min); P = some of film Peeled during etch or when rinsed; A = film was visibly Attached and roughened. Etch areas are all of a 4-inch wafer for the transparent films and half of the wafer for single-crystal silicon and the metals. Etch rates will vary with temperature and prior use of solution, area of exposure of film, other materials present (e.g., photoresist), film impurities and microstructure, etc. Some variation should be expected.

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Etch Rate Table (3)

substrate	etch solution	temperature(℃)	end point
SiO_2	7 NH_4F : 1 HF	22	Sheet-off
Pyrolyc oxide	7 NH_4 : 1 HF	22	Sheet-off
PSG • Insulator • Passivation	 7 NH_4F : 1 HF $6H_2O$: $5HC_2H_3O_2$: $1NH_4F$	 22 22	 Sheet-off none
Si_3N_4	H_3PO_4	155	none
Poly-silicon •Doped •Undoped	 $200HNO_3$: $80HC_2H_3O_2$: 1 HF $20HNO_3$: $20HC_2H_2O_2$: 1 HF	 22 22	 Color change
Al	$80H_3PO_4$: $5HNO_3$: $5HC_2H_3O$: 10 H_2O	40 - 50	Color change

Ref: J. D. Lee, "Silicon Integrated Circuit microfabrication technology," 2nd edition

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Reference

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