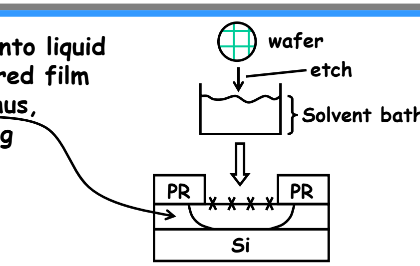
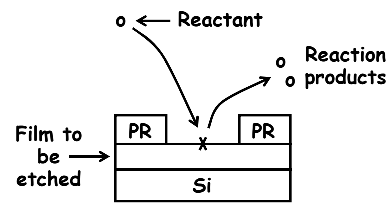
Wet Etching

Wet Etching

- Wet etching: dip wafer into liquid solution to etch the desired film
  - Generally isotropic, thus, inadequate for defining features < 3μm-wide



- General Mechanism -



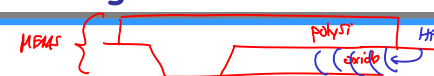
1. Diffusion of the reactant to the film surface
2. Reaction: adsorption, reaction, desorption
3. Diffusion of reaction products from the surface

Wet Etching (cont.)

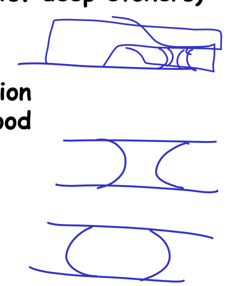
- There are many processes by which wet etching can occur
  - Could be as simple as dissolution of the film into the solvent solution
  - Usually, it involves one or more chemical reactions
    - Oxidation-reduction (redox) is very common:
      (a) Form layer of oxide
      (b) Dissolve/react away the oxide

- Advantages:
  1. High throughput process → can etch many wafers in a single bath
  2. Usually fast etch rates (compared to many dry etch processes)
  3. Usually excellent selectivity to the film of interest

Wet Etching Limitations

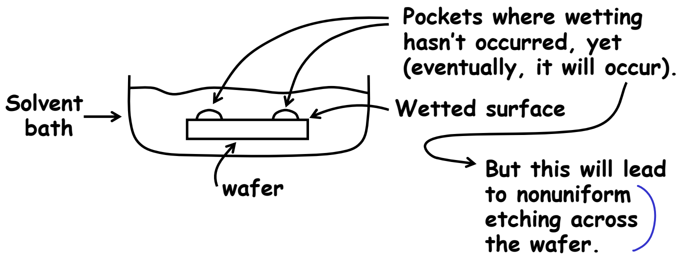


1. Isotropic
   - Limited to <3μm features
   - But this is also an advantage of wet etching, e.g., if used for undercutting for MEMS
2. Higher cost of etchants & DI water compared w/ dry etch gas expenses (in general, but not true vs. deep etchers)
3. Safety
   - Chemical handling is a hazard
4. Exhaust fumes and potential for explosion
   - Need to perform wet etches under hood
5. Resist adhesion problems
   - Need HMDS (but this isn't so bad)



Wet Etch Limitations (cont.)

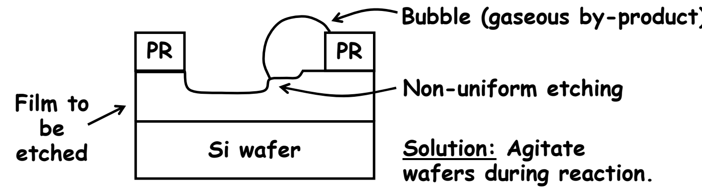
6. Incomplete wetting of the surface:



↳ For some etches (e.g., oxide etch using HF), the solution is to dip in DI water first, then into HF solution → the DI water wets the surface better

Wet Etch Limitations (cont.)

7. Bubble formation (as a reaction by-product)
↳ If bubbles cling to the surface → get nonuniform etching



Some Common Wet Etch Chemistries

Wet Etching Silicon:

Common: $Si + HNO_3 + 6HF \longrightarrow H_2SiF_6 + HNO_2 + H_2 + H_2O$ (NH_4F)

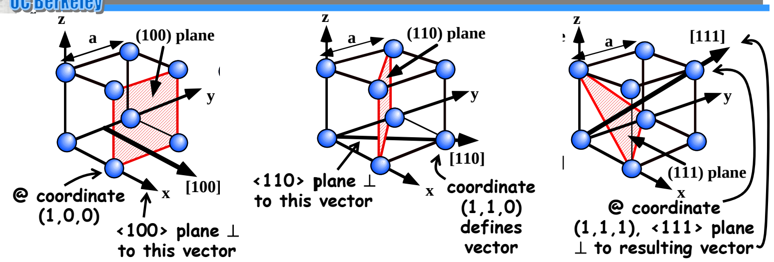
(isotropic)

HNO_3 (nitric acid) → (1) forms a layer of SiO_2

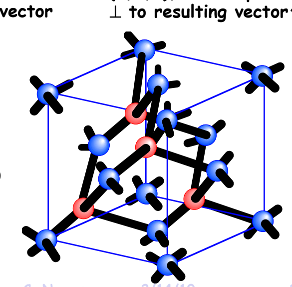
6HF (hydrofluoric acid) → (2) etches away the SiO_2

Different mixture combinations yield different etch rates.

Silicon Crystal Orientation



- Silicon has the basic diamond structure
  - ↳ Two merged FCC cells offset by (a/4) in x, y, and z axes
  - ↳ From right:
    - # available bonds/cm^2 <111>
    - # available bonds/cm^2 <110>
    - # available bonds/cm^2 <100>
    - (Increasing ↑)



Anisotropic Wet Etching

Anisotropic etches also available for single crystal Si:

- Orientation-dependent etching: <111>-plane more densely packed than <100>-plane
  - <100>: Faster E.R.; <111>: Slower E.R.
  - …in some solvents

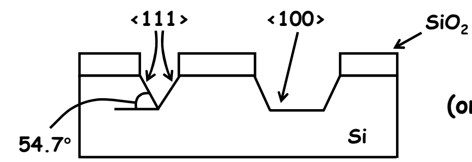
One such solvent: KOH + isopropyl alcohol

(e.g., 23.4 wt% KOH, 13.3 wt% isopropyl alcohol, 63 wt% H_2O)

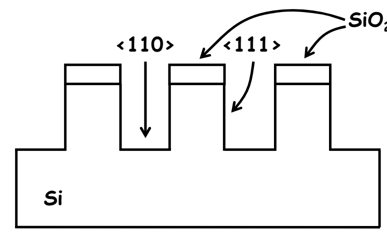
$\Rightarrow$ $E.R._{<100>} = 100 \times E.R._{<111>}$

Anisotropic Wet Etching (cont.)

Can get the following:



(on a <100> - wafer)



(on a <110> - wafer)

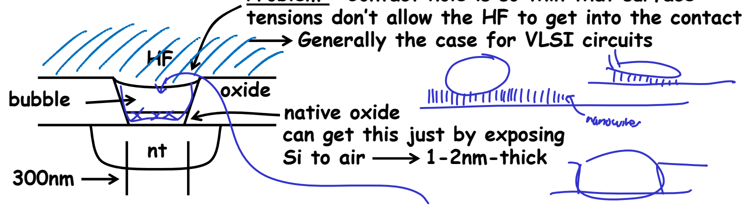
$\Rightarrow$ Quite anisotropic!

Wet Etching SiO_2

$$SiO_2 + 6HF \longrightarrow H_2 + SiF_6 + 2H_2O$$

Generally used to clear out residual oxides from contacts

Problem: Contact hole is so thin that surface tensions don't allow the HF to get into the contact
$\longrightarrow$ Generally the case for VLSI circuits



Solution: add a surfactant (e.g., Triton X) to the BHF before the contact clear etch

1. Improves the ability of HF to wet the surface (hence, get into the contact)
2. Suppresses the formation of etch by-products, which otherwise can block further reaction if by-products get caught in the contact

More Wet Etch Chemistries

- Wet etching silicon nitride
  - Use hot phosphoric acid: 85% phosphoric acid @ 180°C
  - Etch rate ~ 10 nm/min (quite slow)
  - Problem: PR lifted during such etching
  - Solution: use SiO_2 as an etch mask (E.R. ~2.5 nm/min)
    - A hassle → dry etch processes more common than wet
- Wet etchining aluminum
  - Typical etch solution composition:

80% phosphporic acid, 5% nitric acid, 5% acetic acid, 10% water
(H_2PO_4) (HNO_3) (CH_3COOH) (H_2O)

(1) Forms Al_2O_3 (aluminum oxide)
(2) Dissolves the Al_2O_3

- Problem: H_2 gas bubbles adhere firmlly to the surface → delay the etch → need a 10-50% overetch time
- Solution: mechanical agitation, periodic removal of wafers from etching solution

Wet Etch Rates (f/ K. Williams)

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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.

ETCHANT / EQUIPMENT / CONDITIONS	TARGET MATERIAL	MATERIAL: SC Si <100>	Poly n+	Poly undop	Wet Ox	Dry Ox	LTO undop	PSG unanl	PSG annld	Stoic Nitrid	Low-σ Nitrid	Al/2% Si	Sput Tung	Sput Ti	Sput Ti/W	OCG 820PR	Olin HntPR
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 0	P 0
10:1 HF Wet Sink Room Temperature	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 Temperature	Silicon oxides	-	0	0	97	95	150	W	1500	6	1	W	0	-	-	0	0
5:1 BHF Wet Sink Room Temperature	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_2O : 5 NH_4F) Wet Sink Room Temperature	Silicon	1500	3100 1200 6000	1000	87	W	110	4000	1700	2	3	4000	130	3000	-	0	0
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 : 2 H_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 : 1 H_2O_2 : 1 HF) Wet Sink Room Temperature	Titanium	-	12	-	120	W	W	W	2100	8	4	W	0 0 <10	8800	-	0	0
H_2O_2 (30%) Wet Sink Room Temperature	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 Temperature	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 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 Attacked 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.*

Film Etch Chemistries

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- For some popular films:

Material	Wet etchant	Etch rate [nm/min]	Dry etchant	Etch rate [nm/min]
Polysilicon	HNO_3:H_2O:NH_4F	120-600	SF_6 + He	170-920
Silicon nitride	H_3PO_4	5	SF_6	150-250
Silicon dioxide	HF	20-2000	CHF_3 + O_2	50-150
Aluminum	H_3PO_4:HNO_3:CH_3COOH	660	Cl_2 + $SiCl_4$	100-150
Photoresist	Acetone	>4000	O_2	35-3500
Gold	KI	40	n/a	n/a