Lecture 3 Wet etching

- **Basic of wet etching**
  1. **purpose: transfer the pattern made in resist lithography to the underlying layer.**
  2. **Common used materials or thin film in MEMS: silicon, silicon dioxide, silicon nitride, Al, Cr, Ti, Au, Pt, etc.**
  3. **wet etching: using wet chemical, dry etching: using gas plasma, ion, reactive ion etching.**
  4. **key: precise control of pattern dimensions, safty, and cost efficiency.**

- **Silicon etching**
  Isotropic silicon wet etching

HNA system (*HNO_3+HF*), etching rate can be 50 μm/min:

a. Holes injection

$$HNO_3 + H_2O + HNO_2 \rightarrow 2HNO_2 + 2OH^- + 2h^+$$

b. Oxide formation

$$Si^{4+} + 4OH^- \rightarrow SiO_2 + H_2$$

c. Oxide etched

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

Total reaction:

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

Iso-Etch Curve:

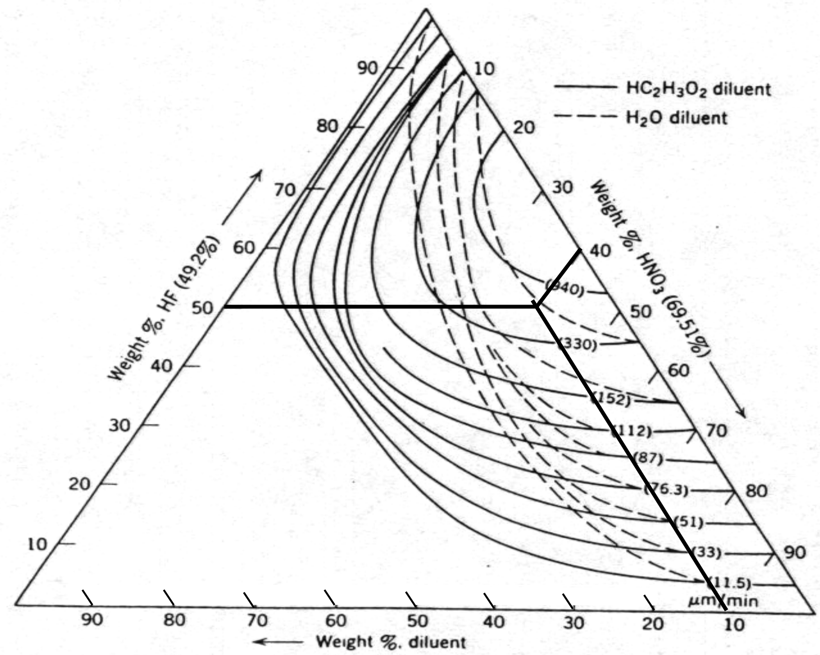


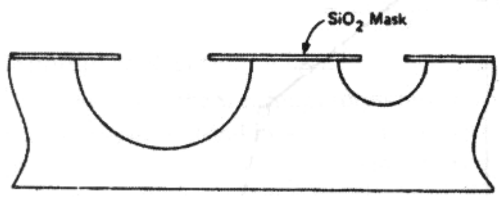
Fig. 9.1 Isoetch curves for silicon ($HF:HNO_3$: diluent system). From Robbins and Schwartz [5]. Reprinted with permission of the publisher, The Electrochemical Society, Inc.

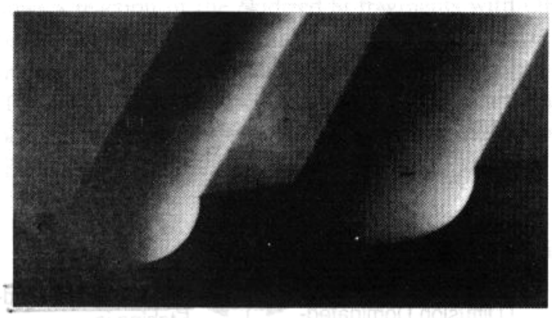
Effects:

High HF Low HNO_3: oxidation limit, rough surface

High HNO_3 Low HF: etching limit, smooth surface

Examples of isotropic etching:





Masking materials:

TABLE 4.6 Masking Materials for Acidic Etchants[a]

Masking	Etchants: Piranha (4:1, H_2O_2:H_2SO_4)	Buffered HF (5:1 NH_4F:conc. HF)	HNA
Thermal SiO_2		0.1 µm/min	300–800 Å/min; limited etch time, thick layers often are used due to ease of patterning
CVD (450°C) SiO_2		0.48 µm/min	0.44 µm/min
Corning 7740 glass		0.063 µ/min	1.9 µ/min
Photoresist	Attacks most organic films	Okay for short while	Resists do not stand up to strong oxidizing agents like HNO_3 and are not used
Undoped Si, polysilicon	Forms 30 Å of SiO_2	0.23 to 0.45 Å/min	Si 0.7 to 40 µm/min at room temperature; at a dopant concentration <10^{17} cm^{-3} (n or p)
Black wax			Usable at room temperature
Au/Cr	Okay	Okay	Okay
LPCVD Si_3N_4		1 Å/min	Etch rate is 10–100 Å/min; preferred masking material

[a] The many variables involved necessarily means that the given numbers are approximate only.

- **Silicon dioxide etching**
  1. **Using HF or BHF(buffered HF or BOE) in different concentration, typically from 10:1 to 4:1.**
  2. **Both HF or BHF have poor wetting characteristics on silicon surface, need surfactants the reduce this problem.**
  3. **Domain etching**

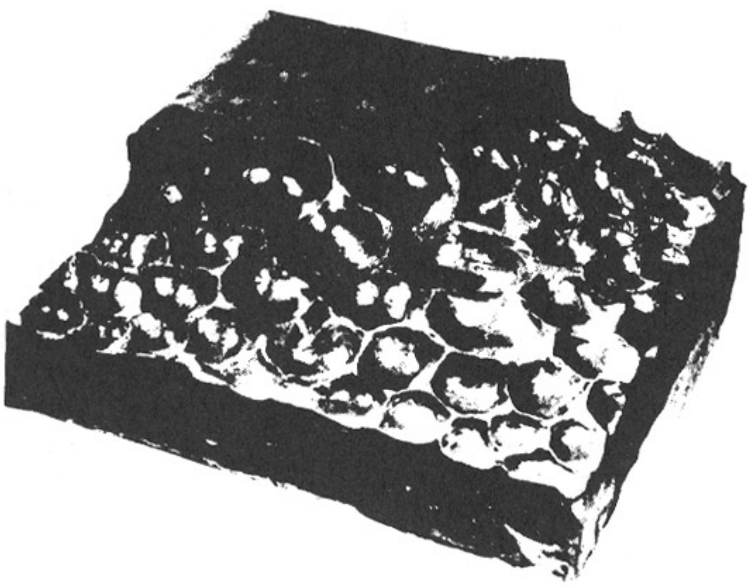


Figure 11.5 Domain nature of SiO_2 etching [2]

4. important two objectives in SiO_2 wet etching:

a. minimize under cut

b. provide sufficient side wall slop

5. Four important parameters

a. Concentration (the third sensitive)

For undoped oxide, etching rate ~0.09-0.15 μm/min for 5:1-7:1. (etching rate: BSG<dry oxide<wet oxide<PECVD oxide<PSG)

Note: reducing concentration reduces ethching rate as well as lateral etching (under cut)

b. Time (the least sensitive one)

The usually controlled parameter for different etching depth.

c. temperature (most sensitive one)

Most sensitive factor in relative to undercutting.

Relationship for etching rate to temperature:

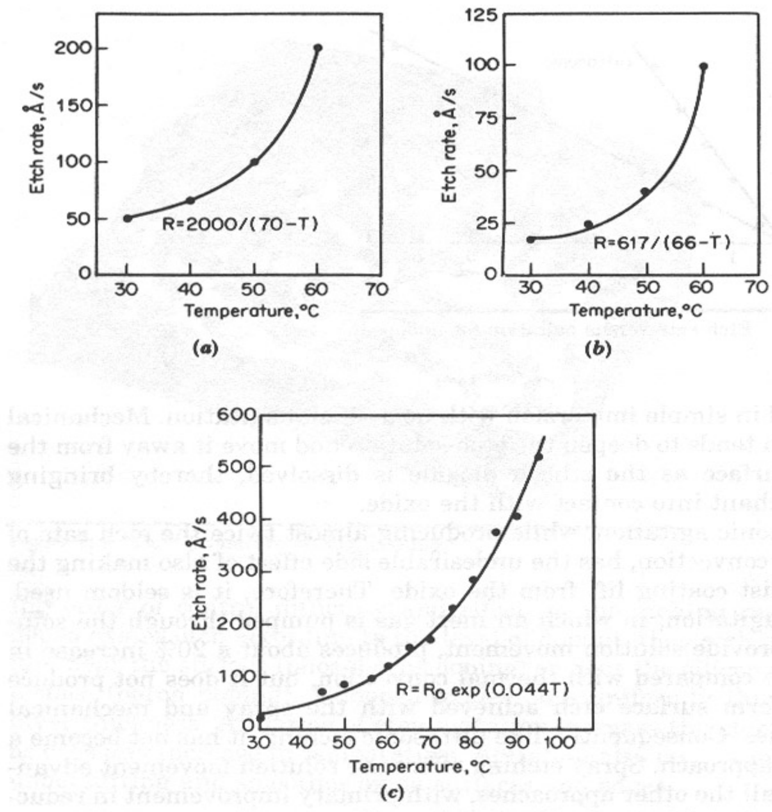


Figure 11.3 Etch rate versus temperature for doped and undoped silicon dioxide: (*a*) phosphorus-doped oxide; (*b*) boron-doped oxide; (*c*) undoped oxide.[2]

d. agitation (the second sensitive)

including thermal convection, spray, mechanical, bubble, and ultrasonic

fastest: ultrasonic, slowest: thermal convection.

Large under cut: ultra sonic, and bubble

Most popular, less under cut and effective ones: mechanical and spray (spry also provide smooth surface)

6. Slop control
By changing the ratio of ammonium fluoride (NH_4F) to hydro fluoric acid (HF) along with temp change:

7:1 NH_4F/HF at 25° C: steep side wall.
30:1 NH_4F/HF at 55° C: near flat, highly undercut side wall.

- **Silicon nitride etching**

1. **Using phosphoric acid (need reflux and above 100° C) or hydrofluoric acid.**
2. **Resist must be highly post bake to withstand resist lift off.**
3. **US patent # 3859222 utilizes the combination of 1-6 parts of fluoroboric acid to 100 parts phosphoric acid (H_3PO_4) at 105° C +-5° C, which is not highly corrosive to resist. This etchant can attack silicon dioxide as well:**

   Increasing fluoroboric acid=>increasing silicon oxide etching rate.
   Increasing temp =>increasing silicon nitride rate.

4. **Hard bake resist, silicon dioxide (not etched in phosphoric acid), polysilicon (not etched in HF, but BHF).**

- **Aluminum etching**

1. **etchants including phosphoric acid, nitric acid, acetic acid, and water (typically: H_3PO_4: HNO_3:CH_3COOH:H_2O=80%:5%:5%:10% immersion or spray at above 45 ° C, etch rate~0.3 μm/min)**
2. **etching happened similar to silicon, nitride acid form aluminum oxide on surface and phosphoric acid and water dissolve the material.**
3. **etching rate depends on etch composition, temperature, agitation, and time.**
4. **Mask materials: positive PR, not negative, because of the reflection from Al surface which cause resist bridging.**
5. **Spray etching overcome isotropy problems in immersion etching by directing the etch at the wafer.**

- **Polysilocon**

  Using diluted HNA system

- **Titanium**

  HF based solution or NH_4OH+H_2O_2+H_2O

- **Gold and silver**

  Au:
  1. **etchant HCL: HNO_3=3:1 (aqua regia, large undercut), KI and iodine in water (KI+I_2+H_2O= 4:1:40, more practical, but opaque), or cyanide –based (toxic)**
  2. **mask materials: resist**

  Ag:
  1. **Can be etched in acidic or basic etchants, like NH_4OH+H_2O_2+CH_3OH**
  2. **mask materials: resist**

- **Chromium**

Need de-passivation (remove oxide layer) before etchant can attack

- **Platinum and Palladium**

  Pt: etchant HCL: HNO_3=3:1 (aqua regia) above 25°C
  Pd: HCl+HNO_3+CH_3COOH=1:10:10, or KI+I_2+H_2O= 4:1:40

- **Tables**

TABLE 9.1 Compositions of Commonly Used Concentrated Aqueous Reagents

Reagent	Weight %
HCl	37
HF	49
H_2SO_4	98
H_3PO_4	85
HNO_3	70
$HClO_4$	70
CH_3COOH	99
H_2O_2	30
NH_4OH	29 (as NH_3)

TABLE 9.3 Some Crystallographic Etches for Silicon

Formulation	Remarks
1 ml HF 3 ml HNO_3 10 ml CH_3COOH	Dash etch, 8 hr
1 ml HF 1 ml CrO_3 (5 M in H_2O)	Sirtl etch, for (111) silicon, 5 min
2 ml HF 1 ml $K_2Cr_2O_7$ (0.15 M in H_2O)	Secco etch, for (100) and (111) silicon, 5 min
60 ml HF 30 ml HNO_3 60 ml CH_3COOH (glacial) 60 ml H_2O 30 ml solution of 1 g CrO_3 in 2 ml H_2O 2 g $(CuNO_3)_2 \cdot 3H_2O$	Wright etch, for (100) and (111) silicon, 5 min. long shelf life
2 ml HF 1 ml HNO_3 2 ml $AgNO_3$ (0.65 M in H_2O)	Silver etch, for faults in epitaxial layers
200 ml HF 1 ml HNO_3	For *p–n* junction delineation, 1 min

TABLE 9.5 Etchants for Noncrystalline Films[a]

Material	Etchant	Remark
SiO_2	28 ml HF 170 ml H_2O 113 g NH_4F	BHF, 1000–2500 Å/min at 25°C
	15 ml HF 10 ml HNO_3 300 ml H_2O	P-etch, 128 Å/min at 25°C
	1 ml BHF 7 ml H_2O	800 Å/min
BSG	1 ml HF 100 ml HNO_3 100 ml H_2O	R-etch, 300 Å/min for 9 mole % B_2O_3, 50 Å/min for SiO_2
	4.4 ml HF 100 ml HNO_3 100 ml H_2O	S-etch, 750 Å/min for 9 mole % B_2O_3, 135 Å/min for SiO_2
PSG	28 ml HF 170 ml H_2O 113 g NH_4F	BHF, 5500 Å/min for 8 mole % P_2O_5
	15 ml HF 10 ml HNO_3 300 ml H_2O	P-etch, 34,000 Å/min for 16 mole % P_2O_5, 110 Å/min for SiO_2
	1 ml BHF 7 ml H_2O	800 Å/min
Si_3N_4	HF	140 Å/min, CVD at 1100°C 750 Å/min, CVD at 900°C 1000 Å/min, CVD at 800°C
	28 ml HF 170 ml H_2O 113 g NH_4F	BHF, 5–10 Å/min
	H_3PO_4	100 Å/min at 180°

[a]Listed in the order in which they are described in Section 9.1.7 [51].

TABLE 9.5 ***(Continued)***

Material	Etchant	Remark
Polysilicon	6 ml HF 100 mol HNO_3 40 ml H_2O	8000 Å/min, smooth edges
	1 ml HF 26 ml HNO_3 33 ml CH_3COOH	1500 Å/min
SIPOS	1 ml HF 6 ml H_2O 10 ml NH_4F (40%)	2000 Å/min for 20% O_2 film
Al	1 ml HCl 2 ml H_2O	80°C, fine line, can be used with gallium arsenide
	4 ml H_3PO_4 1 ml HNO_3 4 ml CH_3COOH 1 ml H_2O	350 Å/min, fine line, will attack gallium arsenide
	16–19 ml H_3PO_4 1 ml HNO_3 0–4 ml H_2O	1500–2500 Å/min, will attack gallium arsenide
	0.1 M $K_2Br_4O_7$ 0.51 M KOH 0.6 M $K_3Fe(CN)_6$	1 μm/min, pH 13.6, no gas evolved during etching
Au	3 ml HCl 1 ml HNO_3	Aqua regia, 25–50 μm/min
	4 g KI 1 g I_2 40 ml H_2O	0.5–1 μm/min, can be used with resist
Ag	1 ml NH_4OH 1 ml H_2O_2 4 ml CH_3OH	3600 Å/min, can be used with resists, must be rinsed rapidly after etching

Material	Etchant	Remark
Cr	1 ml HCl 1 ml glycerine	800 Å/min, needs depassivation
	1 ml HCl 9 ml saturated $CeSO_4$ solution	800 Å/min, needs depassivation
	1 ml, 1 g NaOH in 2 ml H_2O 3 ml, 1 g $K_3Fe(CN)_6$ in 3 ml H_2O	250–1000 Å/min, no depassivation resist mask can be used
Mo	5 ml H_3PO_4 2 ml HNO_3 4 ml CH_3COOH 150 ml H_2O	0.5 μm/min, resist mask can be used
	5 ml H_3PO_4 3 ml HNO_3 2 ml H_2O	Polishing etch
	11 g $K_3Fe(CN)_6$ 10 g KOH 150 ml H_2O	1 μm/min
W	34 g KH_2PO_4 13.4 g KOH 33 g $K_3Fe(CN)_6$ H_2O to make 1 liter	1600 Å/min, high resolution, resist mask can be used
Pt	3 ml HCl 1 ml HNO_3	Aqua regia, 20 μm/min, precede by a 30-s immersion in HF
	7 ml HCl 1 ml HNO_3 8 ml H_2O	400–500 Å/min, 85°
Pd	1 ml HCl 10 ml HNO_3 10 ml CH_3COOH	1000 Å/min
	4 g KI 1 g I_2 40 ml H_2O	1 μm/min, opaque, must be rinsed before visual inspection

Reference:

1. Integrated circuit fabrication technology, David J. Elliott, McGRAW-HILL international editions, 1989.
2. VLSI Fabrication Principles-silicon and gallium arsenide, Sorab K. Ghandhi, second edition, John Wiley & Sons, Inc., 1994.