Chapter 1.10

Miscellaneous Etchants

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Aluminum Etchant Type A (Transene Co., Inc.)

- For VLSI aluminum etching, there is available a pre-mixed phosphoric/acetic acid mixture. Etch rate: ~ 100 Å/sec at 50ºC.
- Corrosive. Avoid contact with eyes, skin and clothing. Avoid inhalation.

Aluminum Etchant for VLSI

- Etch rate ~ 2000 Å/min.
  16 parts phosphoric acid
  2 parts DI water
  1 part acetic acid
  1 part nitric acid

Aluminum Etchants - Others

- These will not etch gold, etc.
- Phosphoric acid at 60ºC
- Sodium hydroxide (10% solution)

- Trisodium phosphate at 190ºC
- These will not etch ZnO. Etch rate ~ 100 Å/sec.
- 10 g $K_3Fe(CN)_6$
- 1 g Potassium hydroxide (KOH) in 100 ml water at room temperature.

Antimony Etchant

- Etch (off of silicon) : HNO_3
  H_2O : HCl : HNO_3 (1:1:1)
  H_2O : HF : HNO_3 (90:1:10)

Aqua Regia

- HCl : HNO_3 (3:1)
- Evaporation - removal:
  50% DI water
  45% HCl
  5% $CuSO_4$
- Dissolves gold.
- Never store in a tightly sealed container!

Bismuth Etchant

- 5 ml Sulfuric acid
  5 ml Hydrogen peroxide
  90 ml DI water

  No heat necessary. Etches quickly.
- H_2O : HCl (10:1)

Brass

- Use brass dip (Turco) for etching and cleaning.
- Ferric chloride (etch)
- Ammonium persulfate: 20 g to 100 ml H_2O

Cadmium Sulfide Etchant (CdS)

- Dislocation pits on the (0001). Distinguishes between A and B faces.
  HNO_3 : CH_3COOH : H_2O (6:6:1)

Cadmium Telluride (CdTe)

- Polishes
  10 ml HNO_3
  20 ml H_2O
  4 g $K_2Cr_2O_7$
- Pits
  5% Br_2 in methanol
  5 mg $AgNO_3$

Chromium Etchant

- HCl : H_2O_2 (3:1) - This will also etch gold film.
- HCl : H_2O (1:1) - Heat to 50ºC, immerse substrate and touch with aluminum wire.

Chromium/Nichrome Etchant

- HCl : H_2O_2 (3:1) - This will also etch gold film.
- HCl and touch with aluminum wire.

Cobalt

- H_2O : HNO_3 (1:1)
- HCl : H_2O_2 (3:1)

Columbium

- HF : HNO_3 (1:1)

Copper

- Brass Dip, RT-2 Resist Stripper, FeCl solutions
- H_2O : HNO_3 (1:5)
- Oxide removal - cold solution of ammonium carbonate (slight etch)

Dislocation Etchants

- **Sirtl Etchant**

  1 part conc. HF or 50 g CrO_3 in 100 ml H_2O
  1 part CrO_3 (5 M) 1:1 = HF : CrO_3 solution
  500 g/L of solution

  Etch rate ~ 3.5 µm/min. Good on {111}, poor on {100}, faceted pits.

- **Secco Etchant**

  2 parts conc. HF
  1 part $K_2Cr_2O_7$ (0.15 M)
  44 g/L of solution

  Etch rate ~ 1.5 µm/min. Best with ultrasonic agitation. Good on all orientations. Non-crystallographic pits.

- **Wright-Jenkins Etchant**

  2 parts conc. HF
  2 parts conc. acetic acid
  1 part conc. nitric acid
  1 part CrO_3 (4M)
  400 g/L of solution
  2 part $Cu(NO_3)_2 + 3\ H_2O$ (0.14 M)
  33 g/L of solution

  Etch rate ~ 1.7 µm/min. Ultrasonic agitation not required. Good on all orientations. Faceted pits, good shelf life.

- **ASTM Dislocation Etchant**

  600 ml HF
  30 ml HNO_3
  0.2 ml Br_2
  28 g $Cu(NO_3)_2 + 3\ H_2O$
  Dilute 1:10 with H_2O

Gallium Arsenide

- 1-2% Br_2 in ethanol
  H_2SO_4 : H_2O_2 : H_2O (5:1:1)

  Good polishing etches
- Fused KOH at 300ºC

Good crystallographic dislocation pits on the (100) surfaces

- 1 ml HF
  2 ml H_2O
  8 mg $AgNO_3$
  1 g CrO_3
  Dislocation lines and striations

Gallium Phosphide

- Behaves similarly to GaAs and the above etches may be used.
- HF : Acetic Acid : Saturated KMn_2O_4 sol'n (1:1:1)

  Good striations, free from pits on (110) surfaces

Germanium Etchant (and Germanium-Silicon)

- H_2O_2 (30%) at 90ºC

  Etch rates:
  100% Ge 4000 Å/min
  80% Ge 1000 Å/min
  60% Ge and less do not etch

- H_2O at 90ºC

  Etch rates:
  100% Ge ~ 200 Å/min
  < 60% Ge does not etch

- RCA SC-1 (NH_4OH : H_2O_2 : H_2O) at 75ºC

  Etch rates:

100% Ge	~ 4 um/min
80% Ge	~ 9000 Å/min
60% Ge	~ 500 Å/min
40% Ge	~ 30 Å/min
20% Ge	~ 10 Å/min
0% Ge	~ 5 Å/min

Gold

- Aqua Regia: HCl : HNO_3 (3:1)
- Saturated solution of KI in H_2O, 1 iodine crystal

Indium

- Reacts with acids (HCl)
- Slow etch (1000 Å/min.)
  HNO_3 : H_2O (1:1)
  Hot HCl : HNO_3 (3:1)

Indium Antimonide

- HNO_3 : HF : Acetic Acid (5:3:3)
  Polishes rapidly as it does most semiconductors, but bubble formation can ruin the polish.
- 0.2N solution of $FeCl_3$ in HCl
  Develops pits.
- HF : Acetic Acid : 2N $HMnO_4$ (1:1:1)
  Good pit-free striations of (211) surfaces

Indium Phosphide

- Cut on diamond saw using slow feed. Lap using 5u powder. Degrease in acetone, then methanol. Chemical etch using 5% bromine by weight for about 2 minutes using a swirling motion. Rinse in methanol, DI water, N_2 dry.

Indium Tin Oxide (ITO)

In order to etch ITO it is needed to reduce it to a metallic state. The reactions are:

$Zn + HCl = H_2 + ZnCl2$

H_2 reduces ITO
$SnO_2 + H_2 = Sn$ or SnOx with x smaller than 1
$Sn + HCl = H_2 + SnCl_4$ which is soluble

- The procedure:
  conc. HCl: H_2O=1:1 at 50ºC.

  Add a small amount of Zn powder (on edge of a spatula). Put the wafer in the solution for about 1 min. Watch for turbidity of the ITO. Transfer the wafer to another beaker containing conc. HCl (no dilution), for about 1 min.

  Take the wafer out and check if all the film was etched. Return to first solution if needed, at 50 degrees.

- $HCl:HNO_3$ (3:1)

Iron Etchant

- $H_2SO_4 : H_2O$ (1:1)
  $HCl : H_2O$ (1:1)
  $HNO_3 : H_2O$ (1:1)
- To remove rust: saturated oxalic acid solution.

Kovar

- Cleaner:

Ferric ammonium sulfate	50 g
H_2SO_4	125 ml
HCl	150 ml

  Heat to 60-80ºC

- Electrolysis:
  HCl and salt, alternating voltage. Kovar or carbon electrode
  10% solution of HCl and a handful of salt

Lead

- Acetic acid : H_2O (1:1)
- Lead deposited on glass can be removed with dilute HNO_3.

Lucite

- Softens with acetone
- Acetone : formaldehyde

Magnesium

- Hot H_2O : NaOH (10:1 by weight)
  Follow with $H_2O : CrO_3$ (5:1 by weight)

Magnesium Fluoride

- Dissolves (sometimes) in hot commercial ferric chloride.

Mercury

- Dissolves and reacts in HNO_3.
- To clean (purify), bubble air through mercury, filter and vacuum distill.

Molybdenum (Moly)

- Hot concentrated H_2SO_4
- Aqua Regia
- $HCl : H_2O_2$ (1:1) (etches stainless steel)

- ► Electrolysis 15 V ac moly or carbon electrode in pure H_2SO_4
- ► Dissolves in H_2O : HNO_3 : H_2SO_4 (1:1:1) cold
- ► 45% formic acid : 45% H_2O_2 : 10% H_2

Heat 2 min at 80ºC.

Monel

- ► Clean with 50% HNO_3 : salt. Wash with water, then dip in 50% solution HNO_3, then rinse in water, then dip in ammonium hydroxide and dry.

Nichrome

- ► HCl : copper chloride (1:1)
- ► $Ce(SO_4)_2$ 7.9 g
  Water 130 ml
  Add:
  35 ml HNO_3

Nichrome Etchant (Transene Co., Inc.)

- ► Contains nitric acid. Slightly irritating to skin. Wash area thoroughly if contacted.

Nickel

- ► HF : HNO_3 (1:1)
- ► Electrolysis:
  dc nickel electrode. H_2SO_4 or H_3PO_4. Reverse polarity several times, finish with nickel part as electrode.

Nickel Etchant (Transene Co., Inc.)

- ► Contains nitric acid. Highly irritating to eyes, skin and mucous membranes, avoid inhalation of vapors.
- ► Avoid contact with reducing agents.

Nickel Oxides

- ► HCl

Niobium

- ► HF: HNO_3 (1:1)

P-Etchant (Phospho-Silicate Glass [PSG] Etchant)

- ► 3 parts HF
  2 parts HNO_3
  60 parts DI water

Palladium

- ► HC l : HNO_3 (3:1) Hot

Picein Wax

- ► Withstands all acids (including HF)
- ► Thin/dissolve in trichloroethylene (TCE)

Piranha

- ► Excellent oxidant; removes most organic residues.
  5 parts H_2SO_4
  1 part H_2O_2
- ► **Note:** Always add peroxide to sulfuric acid, never vice versa! This is a self-heating solution.

Platinum

- Dissolves in Aqua Regia

  $HCl : HNO_3$ (3:1) 85°C

Polish - Fairchild's "Magic Polish"

- A - 2.5 g I_2 in 1100 ml acetic acid
  B - HNO_3 : HF (3:1)
  Add A to B (1:1) just prior to use.

Polysilicon Etchant (See also Silicon Etchant)

- 64% HNO_3 / 33% H_20 / 3% NH4F
- 189 ml HNO_3 / 96 ml H_20 / 7.5 ml NH_4F

Preferential Etch (See Dislocation Etchant Wright-Jenkins Etchant)

Rhodium

- $HCl : HNO_3$ (3:1) Hot

Ruthenium

- $HCl : HNO_3$ (3:1) Hot

Silicon Etchant - Polycrystalline Silicon (Bell Labs)

This solution is mixed and bottled by Microlab staff. Bottles are stored in the tall white acid cabinet next to sink 432C (old lab).

- Etch rate ~ 100 Å/sec
  33% DI water / 3% NH_4F / 64% HNO_3
  Bottle content:
  960 ml DI water
  75 ml NH_4F (ammonium fluoride)
  1890 ml HNO_3 (nitric acid)

Big Batch Silicon Etch (staff only)

Big batch slicon etch is used by staff to rework Tylan dummies in the heated bath, left side of sink7.
48% DI water / 48% HNO_3 / 2% HF at 50ºC

Silicon Etchants - Single-Crystal (Sensors)

- **EDP Etchant for Single Crystal Silicon**

  EDP etchant can be used on p-type wafers with <100> orientation, masked with either silicon dioxide or silicon nitride. It leaves a cleaner, smoother silicon surface with partial etch than KOH (see below). Heavy boron doping acts as an etch stop for EDP. Since EDP does not etch oxide, it is important to remember to dip off any native oxide from the silicon surfaces to be etched in HF solution. Etch rates and temperatures are given below. Complete instructions on the use of EDP are given in Chapter 1.3 of the lab manual.

- Ethylenediamine $N H_2O(C H_2)_2N H_2$ 1 mole = 50.10 g
  Pyrocatechol $C_6H_4(O H_2)$ 1 mole = 109.1 g
  Water H_2O 1 mole = 18.02g

- **F&K Etchant** - Finne & Klein, Bell Labs at Murray Hill. J. Electrochem. Soc., Vol. 114, No. 9, September 1967, pp. 965-970

Ethylenediamine	500 ml	35.1 mole%
Pyrocatechol	88 g	3.7 mole%

Water	234 ml	61.2 mole%
Etch temp:	110ºC	
Etch Rate ratio:	<100>:<110>:<111>	50:30:3
Initial Etch Rate:	28 µm/hr	
Oxygen Exposure:	up to > 50 µm/hr	
Mask Resistance:	SiO_2	200 Å/hr

This is the earliest reported EDP (or EPW) composition. It is generally used in the temperature range 100-118ºC. At lower temperatures it develops insoluble residues. This composition, as well as other uncatalyzed EDP compositions, tends to 'age' rapidly with exposure to oxygen. The etch rate *increases* with time to 50 µm/hr and higher.

The addition of pyrazine increases the <100> etch rate while making it less sensitive to oxygen expose. Pyrazine has a very small effect on the <111> etch rate so the <100>/<111> ratio increases with pyrazine content. The selectivity to boron content is reported by Reisman et al. to be similar for the F & K, B, and S etches. Also, the smoothness of the etching surface is improved by the addition of 0-6 g/L pyrazine. 8 g/> has shown some unevenness, <111> pyramids form, possibly due to the very high <100>/<111> etching ratio. IBM recommends 4 g of pyrazine to every liter of ethylene diamine for a smooth surface.

► **"B" Etchant** - E. Bassous, IBM Research Center, Yorktown Heights, N.Y., U.S. Patent 3,921,916 (1975).

Ethylenediamine		500 ml
Pyrocatechol	80 g	
Water	160 ml	
Temperature Range:		100-118ºC
Boiling Point:	18ºC	

<100> Etch Rate (with pyrazine added):

	Pyrazine per 500 ml Ethylenediamine		
	0 g	**1.0 g**	**3.6 g**
at 100ºC	14 µm/hr	42 µm/hr	50 µm/hr
at 115ºC	26 µm/hr	65 µm/hr	75 µm/hr

► Mask Resistance:
SiO_2 150 Å/hr
Si_3N_4 80 Å/hr

This composition with or without pyrazine provides residue-free etching above 100ºC.

► **"F" (Fast) Etchant** - A. Reisman et al., IBM Research Center, Yorktown Heights, N.Y., J. Electrochemical Soc., Vol. 126, No. 8, August 1979, pp. 1406-1415.

Ethylenediamine		500 ml
Pyrocatechol	160 g	
Water	160 ml	
Temperature Range:		100-118ºC

<100> Etch Rate (with pyrazine added):

	Pyrazine per 500 ml Ethylenediamine		
	0 g	**1.0 g**	**3.0 g**
at 115ºC	27 µm/hr	68 µm/hr	81 µm/hr

► **"S" (Slow) Etchant** - A. Reisman et al., IBM Research Center, Yorktown Heights, N.Y., J. Electrochemical Soc., Vol 126, No. 8, August 1979, pp. 1406-1415.

Ethylenediamine	500 ml
Pyrocatechol	80 g
Water	66 ml
Temperature Range:	50-115ºC

<100> Etch Rate (with pyrazine added):

	Pyrazine per 500 ml Ethylenediamine
	3.6 g
at 50ºC	4.5 µm/hr
at 75ºC	13 µm/hr
at 95ºC	26 µm/hr
at 105ºC	34 µm/hr
at 115ºC	45 µm/hr

► **"M" (Medium) Etchant** - Based on A. Reisman et al., as above.

This etch is useful for etching below the boiling point in order to minimize agitation of the wafer. It etches at a rate between the "F" and "S" etches (hence "M" for medium). This etch prevents the formation of residues by the "F" etch by slowing oxidation of the surface through the reduction of the water content.

Ethylenediamine	500 ml
Pyrocatechol	160 g
Water	125 ml
Temperature Range:	105ºC

<100> Etch Rate (with pyrazine added):

	Pyrazine per 500 ml Ethylenediamine
	3.0 g
at 115ºC	63 µm/hr

Other references:

K.E. Petersen, Proc. IEEE, vol. 70, No. 5, May 1982, pp. 420-457.
K.E. Bean, IEEE Trans. ED-25, No. 10, October 1978, pp.1185-1193.
N.F. Raley etal., J. Electrochemical Soc., vol. 131, No.1, January 1984, pp.161-171.

► **KOH Etchant for Single Crystal Silicon**

KOH is a strongly anisotropic etch, preferring the <100> crystal plane. (The differential etch rate at 80ºC is on the order of 400:1.) Lines of rectangular areas to be etched must be parallel or perpendicular to the wafer flat. It is possible to etch around rectangular geometries, i.e., leave islands of silicon, if the proper convex corner compensation is used to prevent rounding off of the corner due to undercutting along the <411> plane.

750 g KOH :	1500 ml H_2O
Temperature:	80ºC
Etch Rate:	1 µm/minute

► **TMAH Etchant for Single Crystal Silicon**

TMAH solution is commonly stocked in a 25 % concentration. Calculate the amount of 25% solution and DI water to make the desired etchant concentration (often 3%-15%). Under the hood, open TMAH container, add the desired amounts of solution to a DI water to bath, and heat to 80°C. Silicon nitride and silicon dioxide are both good masks for TMAH.

Silicon Dioxide Etchant (Buffered HF)

- NH : HF_4 (6:1)
  Etch rate: ~1000 Å/min.

Silicon and Germanium Etchant

- CP-8 (fast) HNO_3 : HF (5:3)
  CP-6 HNO_3 : HF (5:1)
  CP-4 HNO_3:HF : acetic acid (540 ml : 200 ml : 200 ml)

Silicon-Germanium (polycrystalline)

- H_2O_2 (30%) at 90ºC
  Etch rates:
  100% Ge 4000 Å/min
  80% Ge 1000 Å/min
  60% Ge and less do not etch
- H_2O at 90ºC
  Etch rates:
  100% Ge ~200 Å/min
  < 60% Ge doesn't etch
- RCA SC-1 (NH4OH: H_2O_2: H_2O) at 75ºC
  Etch rates:

100% Ge	~ 4 um/min
80% Ge	~ 9000 Å/min
60% Ge	~ 500 Å/min
40% Ge	~ 30 Å/min
20% Ge	~ 10 Å/min

0% Ge ~ 5 Å/min

Silicon Monoxide Etchant

- Saturated solution of NaOH
- THIN FILMS OF SiO REACT EXPLOSIVELY WITH HF!

Silicon Nitride Etchant

- Hot phosphoric acid ~ 150ºC

Silver

- NH4OH: H_2O_2 (1:1)
- Remove with HNO_3
- Clean with dilute HNO_3 : NH4 (1:1)

Stainless Steel

- HF: HNO_3
- Aqua Regia (depends upon grade of stainless steel)
- HCl
- Electrolytic in diluted HCl

Tantalum

- HF: HNO_3 : H_2O (1:1:1)
  10 parts 30% KOH solution at 90ºC
  1 part 30% H_2O_2

This mixture etches Ta_2O_5 and tantalum nitride at rates of 1000-2000 Å/min. Attacks photoresists and must therefore be used with a metal mask (e.g. gold).

Tin

- HF : HNO_3 (1:1)
- HF : HCl (1:1)
- Clean with ammonium chloride
- Remove with HCl

Titanium

- H_2O : HF : HNO_3 (50:1:1)
- H_2O : HF : H_2O_2 (20:1:1)
- HF : H_2O : ethylene glycol (20:10:220)

No heating necessary. Rate ~ 1600 Å/min.

- For evaporation, deposit Al before Ti to facilitate cleaning of glass cylinder.
- Titanium dioxide is soluble in hot H_2SO_4.

Titanium/Tungsten

- Hydrogen peroxide

Tungsten

- 45% formic acid : 45% H_2O_2 : 10% H_2O
  Heat 2 minutes at 80ºC.
  Bleach
  HNO_3 : HF (1:10-15). This will not etch gold.
  Boiling hydrogen peroxide
  Fused NaOH (pellets, melted, 318ºC)
- Electrolytic $NaNO_2$
  HF: HNO_3 (1:1)
  15 V ac with iron electrode ($NaNO_2$ for polished finish)
- Cleaning
  Boil in 20% solution NaOH for 15 minutes of HNO_3 : HF (1:1) for a few seconds.
- Potassium ferricyanide-based etch

K H_2PO_4	34.0 grams
KOH	13.4 grams
$K_3Fe(CN)_6$	33.0 grams
H_2O	~1.0 liter

Etches tungsten without significantly attacking resist.

Turpentine

- Insoluble in water. Soluble in alcohol, chloroform, ether, acetic acid.

Vanadium

- H_2 : HNO_3 (1:1)
- HF: HNO_3 (1:1)

Westinghouse Etchant (Si Polish Etch)

- HF : acetic acid : HNO_3 (3:5:15)

Zinc

- Reacts with HCl.

ZnO

- acetic acid : phosphoric acid : H_2O (1:1:30)

  The etch rate is approximately 5000 Å/min.

Zirconium

- H_2O:HF : HNO_3 (50:1:1)
- H_2O:HF : H_2O_2 (20:1:1)

See also:
Dislocation Etches Secco Etch
Silicon and Germanium Etchant, CP-4, 6 and 8

- Ref.: J. Electrochem. Soc. 119. #7, 1972.