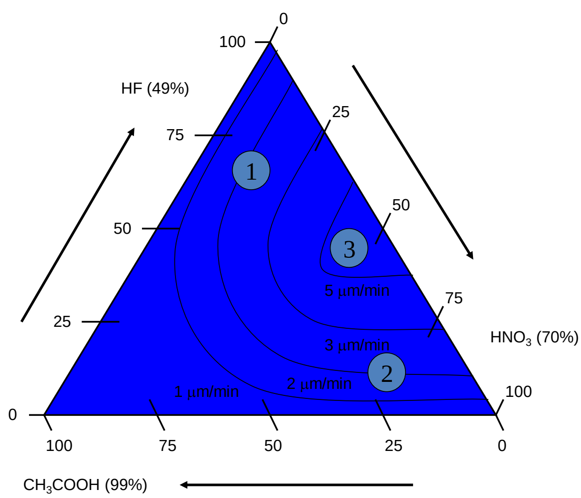
EE 527 MICROFABRICATION

Lecture 21

Tai-Chang Chen
University of Washington

UNIVERSITY OF WASHINGTON

HNA ETCHING OF SILICON - 6

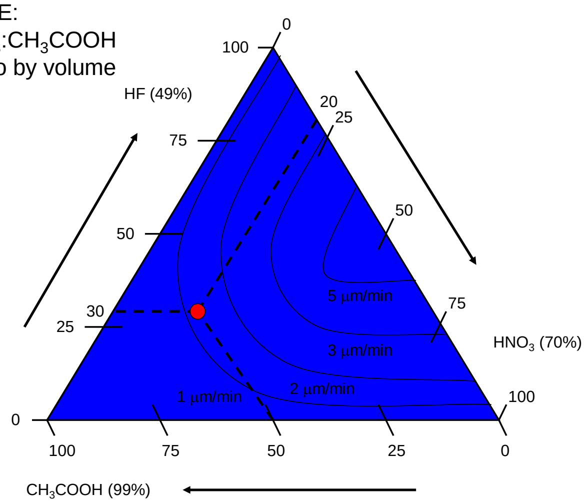


HNA ETCHING OF SILICON - 7

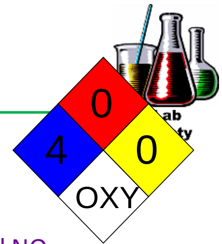
- Region 1
  - For high HF concentrations, contours are parallel to the lines of constant HNO_3; therefore the etch rate is controlled by HNO_3 in this region.
  - Leaves little residual oxide; limited by oxidation process.
- Region 2
  - For high HNO_3 concentrations, contours are parallel to the lines of constant HF; therefore the etch rate is controlled by HF in this region.
  - Leaves a residual 30-50 Angstroms of SiO_2; self-passivating; limited by oxide dissolution; area for polishing.
- Region 3
  - Initially not very sensitive to the amount of H_2O, then etch rate falls of sharply for 1:1 $HF:HNO_3$ ratios.

ISOETCH CONTOURS

EXAMPLE:
$HF:HNO_3:CH_3COOH$
3:2:5 ratio by volume



NITRIC ACID (HNO_3) - 1

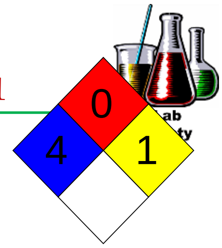


- second most commonly used industrial chemical
- NFPA704M code = 4-0-0-OXY; CAS # [7697-37-2]
- colorless liquid, often reddish-brown from dissolved NO_2
- light exposure produces: $4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2$
- standard reagent concentration is 68-70%, red bottle cap
- while fundamentally a strong mineral acid, it is also considered to be a strong oxidizer

NITRIC ACID (HNO_3) - 2

- primary hazards:
  - reacts with metals and nonmetals, releases NO (3-0-3-XY) and/or NO_2 (3-0-0-XY)
  - concentrated HNO_3 will spontaneously ignite wood, cellulose products
  - concentrated HNO_3 oxidizes proteins
  - concentrated HNO_3 acts as both an acid and an oxidizer!!

HYDROFLUORIC ACID (HF) - 1



- pure HF is a colorless gas above 20C, TLV = 2.5 ppm
- NFPA704M code = 4-0-1; CAS # [7664-39-3]
- a strong dehydrating agent
- has a high affinity for water (hygroscopic)
- dissolved in H_2O it becomes a weak acid (it partially dissociates)
  - BUT IT IS STILL EXTREMELY DANGEROUS!!
- standard reagent concentration is 49%, white bottle cap
- HF dissolves glasses:
  - $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$
- concentrated HF must be stored in polypropylene containers!!
- commercially used for etching glass

HYDROFLUORIC ACID (HF) - 2

- primary hazards:
  - HF vapor produces edema of the lungs and can permanently damage the cornea.
  - HF is extremely dangerous to skin contact, the worst of all acids in terms of damage to tissue, can produce very severe, painful burns.
  - HF has a slight anesthetizing effect, pain is often not noticed until the acid has penetrated a large distance into tissue, often down into bone material where it reacts with Ca and Mg to form fluorides.
  - Because of small size of molecule, HF dissolves easily though pores of skin and cell membranes, and also through many plastics.
  - Use Trionic or heavy neoprene gloves when dealing with HF!!
  - At present there exists no effective remedy for HF burns
    - Some suggest an ointment of 3 oz. magnesium oxide, 4 oz. heavy mineral oil, and 11 oz. white vaseline is helpful.
    - Commercially available calcium gluconate cream is commonly suggested to treat HF burns or exposures.

WET ETCHING OF SiO_2

- Almost always requires HF in some form:
  - HF : H_2O
  - HF : NH_4F (Buffered Oxide Etch = BOE)
- Etch rate is highly dependent upon how the SiO_2 was created:
  - Thermal oxidation creates the most dense and electronically suitable oxide for MOSFETs with generally the slowest etch rate.
  - LPCVD deposited oxides are generally less dense, have more electronic defects, and etch quicker than thermal oxides.
  - Sputtered oxides are generally less dense still, have even more electronic defects, and etch still faster than the LPCVD oxides.
  - Special glass insulating layers have different etch rates still:
    - Low Temperature Oxide (LTO)
    - Phospho-Silicate Glass (PSG)

BUFFERED OXIDE ETCH (BOE)

- Normal etching of SiO_2 will deplete the F^- ion concentration, leading to an etch rate which changes over time.
- This can be fixed by buffering the HF with another source of the F^- ion: NH_4F.
- Buffering with NH_4F also slows the etch rate and results in more polishing of the Si surface (atomically flatter).
- Reactions:
  - Etching: $SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$
  - Buffering: $NH_4F \leftrightarrow NH_3 + HF$
- Many commercial compositions exist:
  - 5:1, 6:1, 7:1, 10:1, 20:1, 30:1, 50:1, and 100:1.
  - Ratios are NH_4F (40% in H_2O) to HF (49% in H_2O)

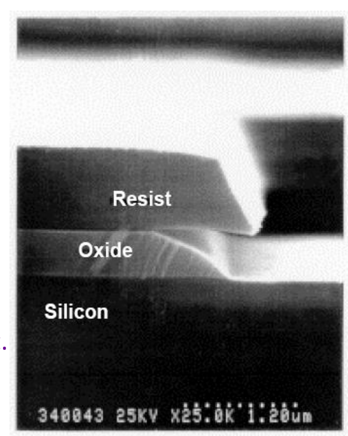
BOE ETCHING OF THERMAL (NATIVE GROWN) SIO_2

- Note that in the literature, 10:1 BOE is not the same as 10:1 HF!
  - 10:1 BOE means 10 NH_4F (40%) to 1 HF (49%)
  - 10:1 HF means 10 H_2O to 1 HF (49%)
- Some typical etch rates at 20°C:

Etch Solution	Etch Rate – thermal SiO_2
6:1 BOE	90 nm/min = 1.50 nm/sec
10:1 BOE	53 nm/min = 0.88 nm/sec
20:1 BOE	30 nm/min = 0.50 nm/sec
10:1 HF	28 nm/min = 0.47 nm/sec
50:1 HF	5.0 nm/min = 0.08 nm/sec

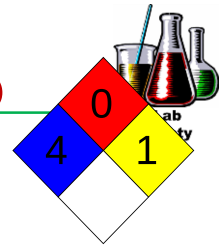
PHOTORESIST UNDERCUTTING BY BOE

- BOE aggressively etches along the photoresist interface.
- Photoresist needs to be hard baked prior to BOE etching.
- Photoresist adhesion also needs to be superb. Primers such as HMDS are useful in achieving this.
- Photoresist puckering along feature edges usually indicates significant undercutting is present.



Photomicrograph from Honeywell "improved BOE" study

BUFFERED OXIDE ETCH (BOE)

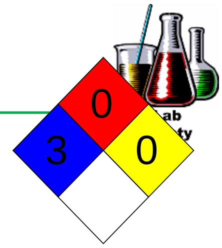


- a solution of (40%) NH_4F and (49%) HF
- 6:1 is the fastest etching (~2 nm/sec grown SiO_2 at 25°C)
- 10:1 is common
- 25:1 is also used for slower etches
- NFPA704M code = 4-0-1
- industry standard solution for etching SiO_2
- NH_4F is a solid crystal, but dissolved in H_2O, it produces some HF and fluorine ion; NH_4F is normally used at 40% concentration.
- NH_4F provides buffering of the fluoride ion. As SiO_2 etching proceeds, the NH_4F replenishes the fluoride ion that is consumed in the creation of SiF_4. This keeps the etch rate more constant.
- primary hazards:
  - the same as for hydrofluoric acid, HF
  - Use Trionic or heavy neoprene gloves when dealing with BOE!!

WET ETCHING OF CHROMIUM (CR)

- HCl (standard 37% concentration, undiluted)
- HNO_3 (standard 70% concentration, undiluted)
- Commercial chromium etchants are usually best to achieve a uniform rate and reproducibility:
  - Cyantek CR-9 chromium etchant is commonly used.

HYDROCHLORIC ACID (HCL)



- pure HCl is a strong-smelling, colorless gas
- TLV = 5 ppm, exposure to > 1500 ppm is usually fatal
- extremely soluble in H_2O
- NFPA704M code = 3-0-0; CAS # [7647-01-0]
- technical grade HCl is slightly yellow due to Fe^{++} impurities
- standard reagent concentration is 37%, blue bottle cap
- primary hazards:
  - corrosive effect on metals
  - vapor toxicity:
    - 1-5 ppm = limit of odor
    - 35 ppm = irritation of throat
    - 50 ppm = barely tolerable
    - 1000 ppm = fatal via lung edema

8