

Silicon Dioxide Etch using Buffered Hydrofluoric Acid

Standard Operating Procedure

Faculty Supervisor: Prof. Robert White, Mechanical Engineering (x72210)

Safety Office: Peter Nowak x73246 (Just dial this directly on any campus phone.)
(617)627-3246 (From off-campus or from a cell phone)

Tufts Emergency Medical Services are at x66911.

For more information on glass etching with Hydrofluoric Acid (HF) see:

G. Spierings. "Wet Chemical Etching of Silicate Glasses in Hydrofluoric Acid Based Solutions", Journal of Materials Science, **28** (1993), pp. 6261-6273.

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Warning: Buffered Hydrofluoric Acid (BHF) contains Hydrofluoric Acid (HF), an extremely dangerous material. Because of the ability of BHF to produce severe *delayed* tissue damage without necessarily producing pain, any contact with BHF should receive immediate first aid and medical evaluation, even if the injury appears minor or no pain is felt. Work carefully in the hood with full personal protective equipment.

If BHF does get on your skin, rinse the affected area with water for 5 minutes, and then apply calcium gluconate gel. The calcium gluconate is stored in clearly marked boxes near both hoods. Have someone in the lab call Tufts EMS.

1. Material Requirements:

1.1 Equipment: Three polyethylene beakers or polymethylpentene screw cap jars, PTFE tweezers or stainless steel 4" wafer tweezers, PTFE wafer handling tools

Warning: BHF attacks glass! You cannot put it in a glass container. Polymethylpentene and polyethylene are fine to use. Polystyrene (plastic Petri dishes are polystyrene!) is not considered compatible with long-term HF exposure.

1.2 Chemicals: Ultratech NP 13:2. Also called BHF (buffered hydrofluoric acid) or BOE (buffered oxide etch) – contains 30-50% Ammonium Fluoride and 5-10% Hydrofluoric acid.

1.2.1 Hazards associated with chemicals:

1.2.1.1 Ultraetch NP: liquid or vapors are extreme health hazards; cause severe burns and bone loss, which may not be immediately painful or visible. Significant exposure (100 mL) to HF can kill directly. Please use extreme caution; BHF is very hazardous, both acutely and long term.

1.3 Engineering Controls: Conduct procedure in ventilated fume hood. Store bottles of chemicals (sealed tightly) in the acid cabinet with secondary containment. Work area should contain an eye wash and safety shower.

1.4 Personal Protective Equipment: Trionic gloves on top of nitrile gloves, apron, goggles, and face-shield. Never work with BHF without all this equipment.

2.0 Procedure:

This etch will remove silicon dioxide. It will only attack silicon and silicon nitride at a very slow rate. Some metals etch in BHF (Titanium, Aluminum) some do not (Chromium, Gold, Platinum). You can mask a BHF etch with photoresist for a short etch (20 mins or so). If you etch longer, the photoresist will start to peel off. You can also mask BHF etches with silicon nitride or Cr/Au.

Complete all processes in the fume hood.

2.1 Buffered Hydrofluoric Acid (BHF) etch: variable time

Warning: BHF etches glass! Therefore, you must do BHF processing in polyethylene(PE) or polymethylpentene(PMP) containers only!

- 2.1.1 Get a polyethylene (PE) beaker or polymethylpentene (PMP) jar that will fit your samples for processing (you should find one labeled “HF” on the shelves). Put it on fab wipes in the hood. Try to use the smallest container that will work for your sample size to reduce waste.
- 2.1.2 Fill two more PMP or PE containers with DI water.
- 2.1.3 In the polyethylene beaker or polymethylpentene jar, pour in enough BHF to cover the samples.
- 2.1.4 Cap the BHF bottle and put it away.
- 2.1.5 Transfer the sample into the BHF carefully with tweezers or PTFE wafer tools.
- 2.1.6 Let the sample etch for the required length of time. Etch rate will vary with oxide composition and depositions method. You should verify etch rate with your own experiments on your own samples. Etch rate can vary.

Ultraetch NP 13:2

Material	Etch Rate	Source
BK7 glass wafer	650 nm/min	Measured at Tufts by C. Gray 2007
Pyrex glass wafer	20 nm/min	Measured at Tufts by C. Gray 2007
Thermal SiO ₂ thin film	70 nm/min	Measured at Tufts by R. White 2007
Glass slide (Pearl catalog No. 7101)	400 nm/min	
Sputtered Titanium	20 nm/min	

Hydrofluoric Acid 49% (undiluted – straight from the bottle)

Material	Etch Rate	Source
Pyrex glass 7740	8.2 um/min	Measured at Tufts by R. White 2007 Sensors & Actuators A 116 pp. 150-160 (2005)
Pyrex glass 7740	7.2 um/min	
Thermal SiO ₂ thin film	1.4 um/min	
Borofloat glass	6.7 um/min	
Soda lime glass	27 um/min	

2.2 DI Water rinse: 2x 5 min:

- 2.2.1 When the BHF etch is complete, transfer the sample carefully to the rinse container with tweezers or PTFE wafer tools.
- 2.2.2 Leave the tweezers/tools (which have BHF on them now) to soak in the DI water container with the sample.
- 2.2.3 Let the sample and tweezers soak for 5 mins.
- 2.2.4 Transfer to the second rinse container for 5 more minutes.

2.3 Sample dry:

- 2.3.1 Remove your samples and blow them dry with the air gun.
- 2.3.2 After removing the majority of the water with the air gun, you can further dry your wafers on a hotplate or in the convection oven if needed.

Note: Bare silicon is hydrophobic; silicon dioxide is hydrophilic. So, if you have removed all of the oxide, the silicon surface should be hydrophobic and the water will bead up. After your wafer is dry, you can also check to see if the oxide has been removed from the exposed areas by checking its color under a microscope using white light. You can find color vs. film thickness charts on the web. The Nanocalc can also be used to measure film thickness.

3.0 Cleanup

- 3.1 If you are planning to do another etch in the near future, save the BHF by screwing the cap onto the polymethylpentene jar, labeling the lid with your name, "BHF", and the date, and leaving the jar in the hood. Do not save BHF in a jar for more than 2 weeks.
- 3.2 If you do not plan to do another BHF etch in the near future, dump the used BHF into the HF waste bottle. There is a polyethylene funnel you should use. The HF waste bottle must also be made of polyethylene. It should be labeled as containing HF and ammonium fluoride. Check of "corrosive" and "toxic" on the hazardous waste tag.
- 3.3 Pour the first rinse container into the processing container, and then into the waste bottle.
- 3.4 Now pour the 2nd rinse container into the first, then into the process container and finally into the waste bottle.
- 3.5 Refill the 2nd rinse container with water, repeat the rinse above once more, but now dump the rinse water into the "dilute acid/base waste" 55 gallon HDPE drum.
- 3.6 Return all labware to its proper location.
- 3.7 Wipe up any drips in the area with chemical wipes and dispose in either acid trash.

4.0 Storage:

- 4.1 Buffered Hydrofluoric acid should be stored in the acid cabinet in a tightly capped polyethylene bottle.

5.0 Waste Disposal:

5.1 Acid waste:

- 5.1.1 BHF wipes are disposed of in the acid trash can.
- 5.1.2 BHF waste is collected in the HF waste container and stored in the satellite storage area with secondary containment.

- 5.1.3 Dilute water waste from second and third rinses goes into the dilute water waste 55 gallon HDPE drum.

6.0 Accident Procedures:

6.1 Contact: Read MSDS prior to working with any chemical to familiarize yourself with the symptoms of exposure and recommendations for treatment.

6.1.1 HF Acid:

- 6.1.1.1 Skin contact: Rinse affected area with water for 5 minutes, removing contaminated clothing during the rinse. Apply generous amounts of calcium gluconate gel to the area. **Get immediate medical attention. Don't be shy. Call the medical center if you got BHF on your skin. Tufts Emergency Medical Services are at x66911.**
- 6.1.1.2 Eye contact: Immediately flush with water for 20 minutes while holding the lids open. Do not apply calcium gluconate. **Get immediate medical attention. Call Tufts Emergency Medical Services are at x66911.**
- 6.1.1.3 Ingestion: Do not induce vomiting. **Get immediate medical attention. Call Tufts Emergency Medical Services are at x66911.**
- 6.1.1.4 Inhalation: Remove to fresh air. Resuscitate if necessary. Take care not to inhale any BHF released from the victim's lungs. **Get immediate medical attention. Call Tufts Emergency Medical Services are at x66911.**

6.2 Spill:

- 6.2.1 If a small, contained spill occurs, such as inside the hood, wipe it up with chemical wipes and dispose of in the appropriate trash container (acid trash).
- 6.2.2 If a large spill occurs that you are not comfortable cleaning up, evacuate the lab and notify the Tufts emergency services (x66911) immediately. Clean up should only be performed by authorized personnel according to MSDS guidelines. Notify the faculty advisor.
- 6.2.3

If at any time you feel a situation is dangerous, do not hesitate to call the safety office (x73246, Peter Nowak), the lab manager (Jim Vlahakis, james.vlahakis@tufts.edu), or the faculty supervisor (x72210, Robert White).

Report all accidents (injuries, major spills, fires) to the safety office at x73246 (Peter Nowak), the lab manager (Jim Vlahakis, james.vlahakis@tufts.edu), and the faculty supervisor (x72210, Robert White).

For emergencies, call Tufts Emergency Services at 617-627-6911 (cell) or x66911 from a campus phone.