

# Isotropic Silicon Etching using HF/Nitric/Acetic Acid (HNA)

## 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 silicon etching with HF/Nitric Acid (HNA) see:

Schwartz, B., and Robbins, H. "Chemical Etching of Silicon" Journal of the Electrochemical Society, 123 (12), pp. 1903-1909.

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### Notes:

This etch is intended as an isotropic wet etch for silicon and polysilicon. Etch rates are on the order of 3-5  $\mu\text{m}/\text{min}$ . Silicon nitride is the preferred etch mask for an HNA etch.  $\text{SiO}_2$  will be attacked very rapidly by the HF so cannot be used as a mask. DQN photoresist can only be used (with mediocre results) for a short etch. Using a long hardbake (40 minute, 120 °C, oven) after resist develop significantly improves the durability of the resist. Still, it is not possible to etch more than a few microns without the resist being removed, and significant widening and roughening of the pattern should be expected.

### Warning:

*Hydrofluoric Acid (HF) is an extremely dangerous material.* Because of the ability of HF to produce severe *delayed* tissue damage without necessarily producing pain, any contact with HF should receive immediate first aid and medical evaluation, even if the injury appears minor or no pain is felt. Nitric Acid and Glacial Acetic Acid are also strong, corrosive acids and will cause severe burns. Work carefully in the hood with full personal protective equipment.

If HF or a mixture containing HF does get on your skin, rinse the affected area with water for 5 minutes, and then apply calcium gluconate gel. The calcium gluconate is on the metal shelves next to the phone. Have someone in the lab call Tufts EMS.

In addition, *HF attacks glass*, so not glass containers should be used for this process.

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

## 1.2 Chemicals:

**1.2.1 Hydrofluoric Acid (HF) (49%):** HF: 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; HF is very hazardous, both acutely and long term. Compatible with polymethylpentene (PMP), polyethylene (PE), and Teflon (PTFE).

**1.2.2** Nitric Acid (70%): Acute burns to skin and eyes. Severe respiratory irritant. Can get hot when reacting with water, or any base. Compatible with glass, HDPE, polymethylpentene (PMP), polyethylene (PE), and Teflon (PTFE).

**1.2.3** Glacial Acetic Acid (>98%): Acute burns to skin and eyes. Severe respiratory irritant. Can get very hot when reacting with water, or any base. Compatible with glass, HDPE, polymethylpentene (PMP), polyethylene (PE), and Teflon (PTFE).

**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.

## **2.0** Procedure:

This etch is intended as an isotropic etch for silicon and polysilicon. It will also attack silicon dioxide and some metals (Titanium, Aluminum, etc). You can mask an HNA etch with photoresist for a short etch (~1 min or so). Use a 40 min, 120°C hardbake on your resist. If you etch longer, the photoresist will start to peel off.

For information on preparing a photoresist mask, see the SOPs on Standard Lithography, the OAI Aligner, and the Spinner.

### **Complete all processes in the fume hood.**

#### **2.1 HF/Nitric/Acetic (HNA) etch**

**Warning: HNA etches glass. Therefore, you must do HNA processing in polyethylene or polymethylpentene containers only.**

**2.1.1** Place some fab wipes in the hood. Get a three polyethylene beakers or polymethylpentene jars that will fit your samples for processing (you should find containers labeled “HF”, “HNA”, “HF Rinse” and “HNA Rinse” on the shelves... any of these are acceptable). Put them on the fab wipes in the hood. Try to use the smallest containers that will work for your sample size to reduce waste.

**2.1.2** Use graduated cylinders to measure the following chemicals into the first container.

**2.1.2.1** Use a glass graduated cylinder for the acetic acid and nitric acid. Use a plastic graduated cylinder for the HF.

**2.1.2.2** Add the acetic acid first, then the nitric acid, and finally the HF.

Use the following ratio:

55 mL Glacial Acetic Acid

35 mL Nitric Acid

20 mL Hydrofluoric Acid (49%)

**2.1.3** Cap the bottles and put them away.

**2.1.4** Fill the second and third process containers with deionized water.

**2.1.5** Transfer the sample into the HNA mixture carefully with tweezers or PTFE wafer tools.

**2.1.6** Let the sample etch for the required length of time (depending on etch depth). Expect approximately **3-5 $\mu$ m/minute** etch rate, although this may vary considerably. (See the Schwartz & Robbins paper for more information, the citation is listed at the top of this document)

**2.1.7**

### **2.2 DI Water rinse: 2 x 5 min:**

**2.2.1** When the etch time is up, transfer the sample carefully to the first rinse beaker with tweezers or PTFE wafer tools.

**2.2.2** Leave the tweezers/tools (which have HNA solution on them now) to soak in the DI water with the sample.

**2.2.3** Let the sample and tweezers soak for 5 mins.

**2.2.4** Transfer the sample and tools to the second rinse beaker, and soak for 5 minutes.

**2.2.5** 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.

### **2.3 Sample dry:**

**2.3.1** After the third waste rinse is finished, 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.

## **3.0 Cleanup**

**3.1** If you do plan to do another HNA etch in the near future (next 2 days), cap the etchant container or cover it with aluminum foil, label it with "HF/Nitric/Acetic", your name, and the date, and place it in the back of the hood.

**3.2** If you do not plan to do another HNA etch in the near future, dump the used HNA solution into the HF waste bottle. Refill the HF container with DI water and again dump it into the HF waste container. The waste container should be an HDPE bottle. Use a plastic funnel.

**3.3** Rinse the HNA container with DI water again and dump it into the HF waste bottle.

**3.4** Dump the first water rinse container into the HF waste bottle.

**3.5** Dump the water from the second rinse beaker into the dilute acid/base water waste container. (5 gallon jug)

- 3.6 Rinse all the containers one more time with DI water and dump them into the dilute acid/base water waste container. (5 gallon jug)
- 3.7 Return all labware to its proper location. The beakers can drip dry on fab wipes in the hood or on the storage shelving.
- 3.8 Wipe up any drips in the area with chemical wipes and dispose in the acid trash.

#### **4.0 Storage:**

- 4.1 Hydrofluoric acid, nitric acid, and glacial acetic acid should all be stored in the acid cabinet in tightly capped polyethylene bottles.

#### **5.0 Waste Disposal:**

##### **5.1 Acid waste:**

- 5.1.1 HNA contaminated fab wipes are disposed of in the acid trash can.
- 5.1.2 HNA 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 5 gallon HDPE tank.

#### **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.**

##### **6.1.2 Nitric Acid or Glacial Acetic Acid:**

- 6.1.2.1 Skin contact: Rinse affected area with water for 15 minutes, removing contaminated clothing during the rinse. **If a burning sensation persists, or a large area or large amount of exposure occurred, get immediate medical attention. Call the Tufts Emergency Medical Services at x66911.**
- 6.1.2.2 Eye contact: Immediately flush with water for 20 minutes while holding the lids open. **Get immediate medical attention. Have your lab partner call Tufts Emergency Medical Services are at x66911 while you are flushing your eyes.**

**6.1.2.3 Ingestion: Do not induce vomiting. Get immediate medical attention. Have your lab partner call Tufts Emergency Medical Services at x66911.**

**6.1.2.4 Inhalation: Remove to fresh air. Resuscitate if necessary. Take care not to inhale any HNA fumes released from the victim's lungs. If dizziness or other neural symptoms, or respiratory problems are evident, or if the exposure was severe, get immediate medical attention. Have your lab partner call Tufts Emergency Medical Services 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.

**If at any time you feel a situation is dangerous, do not hesitate to call the safety office (x73246, Peter Nowak) or the faculty supervisor (x72210, Robert White).**

**Report all accidents (injuries, major spills, fires) to the safety office at x73246 (Peter Nowak) and the faculty supervisor at x72210 (Robert White). For emergencies, call Tufts Emergency Services at x66911.**