

Standard Operating Procedure:

Hydrofluoric Acid

Table of Contents

Table of Contents..... 1

Principle of Operation..... 2

Material Requirements..... 2

Procedure..... 2

 Preparation..... 2

 HF Etch..... 3

 Cleanup..... 3

Emergency Response Procedure..... 3

 Skin Exposure..... 4

 Eye Exposure..... 4

 Inhalation..... 4

Revision History:..... 5

Principle of Operation

For isotropic wet etching of silicon dioxide. Etch rates depend on the concentration of HF, temperature, and type of silicon dioxide being etched with rates varying between a few nanometers to several hundred nanometers per minute. HF is also used to etch titanium.

Hydrofluoric (HF) acid has a number of chemical, physical and toxicological properties that make handling this material particularly hazardous. Anhydrous HF is a clear, colorless, fuming liquid or gas that is highly corrosive and toxic. All forms including the solution or the vapor can cause severe burns to tissue. The most widely known property of HF is its ability to etch glass, though it will also attack glazes, enamels, pottery, concrete, rubber, leather, many metals and organic compounds. As such, HF must be used and stored in polyethylene, polypropylene, Teflon, wax, lead or platinum containers.

***Danger:** Hydrofluoric acid is a contact poison, capable of penetrating skin and causing deep tissue damage, including severe burns and bone damage. If absorbed into the bloodstream, it will react with calcium and other electrolytes leading to hypocalcemia, causing cardiac arrhythmias and cardiac arrest. It is important to know the first aid procedure for treating HF exposure and to immediately call CCNY Public Safety so they can call an ambulance if there is an HF exposure. HF does not burn like other acids since it penetrates the skin and reacts in the body, leading to delayed reactions and pain. Depending on the concentration of HF, pain caused by the tissue damage may be delayed 1 to 24 hours. If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss and death, so it is important to wear the proper PPE and to get immediate medical assistance in the case of exposure.*

Material Requirements

Equipment:

Substrate, plastic (Teflon or polypropylene) beakers and vessels, plastic tweezers and/or any other HF-approved lab ware

Caution: HF etches glass, so glass containers are incompatible with HF.

Chemicals:

Hydrofluoric Acid, 48 to 51% solution in water

Transene Buffered Oxide Etchant [contains: hydrofluoric acid; ammonium fluoride]

- The etch rate will approximately double with every 10°C increase in temperature; stirring or agitation will increase the etch rate.
- The etch rate will be reduced by approximately 50% by adding 1 part DI water to 2 parts etchant.
- Recommended Operating Temperatures: 20-50°C (30-40°C most common)

- Etch Rate at 25°C: depends on ratio of HF
 - Buffered HF Improves: 800 Å/sec
 - BOE 6:1: 860-930 Å/sec
 - BOE 50:1: 125-145 Å/sec
- Select Compatible Materials: Gold, copper, nickel
- Select Incompatible Materials: Glass, titanium, alumina, silicon nitride
- Compatible Plastics: HDPE, PP, Teflon, PFA, PVC

Transene Titanium Etchant TFT [contains: hydrofluoric acid (8-15% solution in water); surfactant]

- The etch rate will approximately double with every 10°C increase in temperature; stirring or agitation will increase the etch rate.
- The etch rate will be reduced by approximately 50% by adding 1 part DI water to 2 parts etchant.
- Recommended Operating Temperatures: 20-50°C (30-40°C most common)
- Etch Rate at 25°C: 25 Å/sec
- Select Compatible Materials: Gold, copper, nickel, chromium
- Select Incompatible Materials: Glass, silicon oxide, silicon nitride, gallium arsenide
- Compatible Plastics: HDPE, PP, Teflon, PFA, PVC

Personal Protective Equipment:

Trionic gloves on top of nitrile gloves, vinyl apron with sleeves, safety glasses and face-shield

Procedure

Preparation

1. Review the first aid procedures for HF exposure with your chemical buddy, including identifying the location of the HF First Aid Kit and Calcium Gluconate Gel.
Note that you cannot use HF alone. When using HF, you must ensure that there is at least one other person (your chemical buddy) in the vicinity of the process at all times. That person must call Public Safety (212-650-7777) in the event of an emergency and then assist you with first aid.

HF Etch

1. Get two plastic beakers that will fit your samples for processing from the "HF Supplies" drawer in the glassware rack along the wall to the right of the hood – one should be labeled "Water Only" and the other should be labeled "HF Only".
2. Get a plastic measuring beaker from the "HF Supplies" drawer in the glassware rack.
3. Rinse all beakers with DI water prior to beginning the process.
4. Fill the "HF Only" labeled beaker with DI water so that the water level will submerge the entire substrate, and then pour the DI water from the "HF Only" container into the

measuring beaker to measure the amount of solution you'll need to submerge your sample.

5. Stand the beaker labeled "Water Only" to be used for rinsing the sample on a cleanroom wipe in the hood and fill it with DI water so that the water level will cover the entire substrate.
6. Blow the beaker labeled "HF Only" semi-dry with the N₂ gun and place it on a cleanroom wipe in the hood.
7. Pour the DI water from the measuring beaker into the sink, then blow it semi-dry with the N₂ gun and place it on a cleanroom wipe in the hood.
8. Prepare your HF solution:
 - a. If diluting hydrofluoric acid in water, determine the ratio of water to HF that you will be using. Fill the measuring beaker with DI water from the faucet to the volume needed, and then pour it into the "HF Only" container. Carefully pour hydrofluoric acid into the measuring beaker to the volume needed and then carefully add it to the water in the "HF Only" container. ***Acids should always be added to water when mixing solutions, and never the reverse.***
 - b. If using a premixed solution, such as BOE, carefully pour the BOE into the measuring beaker to the volume needed and then pour it into the "HF Only" container.
9. Rinse out the measuring beaker with DI water in the sink, then blow it semi-dry with the N₂ gun and place it on a cleanroom wipe in the hood.
10. If you plan to heat the HF solution for the duration of the etch, place the beaker of HF solution on the hotplate and set it to 40°C. **Never set the hotplate higher than 50°C.**
11. Stir the HF solution with plastic tweezers to ensure it is thoroughly mixed. Rinse the tweezers with DI water in the sink.
12. Calculate the etch time for your sample.
13. Place your sample into the HF solution using the plastic tweezers and allow it to soak in the HF solution for the appropriate amount of time calculated in the previous step. Agitation of the etchant will help to accelerate the etch

DI Water Rinse

1. When the etch time is complete, remove your sample from the HF solution with the plastic tweezers.
2. Transfer the sample carefully to the DI water rinse beaker. Make sure to leave the tweezers in the rinse beaker as well.
3. Let the sample and tools soak in DI water for 1 minute.
4. If you were heating the HF solution, turn off the hotplate so the solution can begin to cool down.
5. Remove the sample from the rinse beaker with the tweezers.
6. Rinse the sample with DI water in the hood sink, holding it in the water stream for approximately 10 seconds or more.

Sample Dry

1. After the water rinse is finished, blow the sample dry with the N₂ gun.

Cleanup

1. If you heated the HF solution, allow it to cool to close to room temperature before disposing of the solution. If you are going to leave the mixture unattended, make sure it remains properly labeled and the Badger slot is still enabled.
2. Carefully pour the HF solution into the waste container designated for HF waste in the back of the hood.
3. Rinse the beaker with DI water multiple times (typically 3 times or more) in the sink and then blow it as dry as possible with the N₂ gun. **DO NOT pour rinse water in the waste containers.**
4. Dump the DI rinse beakers into the sink in the hood. **DO NOT pour rinse water in the waste containers.**
5. Rinse the beaker with DI water multiple times (typically 3 times or more) in the sink and then blow it as dry as possible with the N₂ gun.
6. Return all containers and plastic tweezers to their proper storage location.
7. Wipe up any splashes or drops of fluid in the hood with wipes and dispose of them in the proper trash bin.
8. Store the HF or BOE in the HF Cabinet.
9. Inspect all of the PPE to ensure it did not come into contact with the chemicals before returning them to its storage location.

Accident Procedure

Emergency Response Procedure

In the event of an HF exposure your chemical buddy must call Public Safety (212-650-7777), and notify them of the nature of the emergency. When the ambulance arrives, the chemical safety buddy must explain to the emergency personnel the nature of the exposure, give them the MSDS, and request that the victim be transported to Columbia Presbyterian Medical Center, which is equipped to handle HF burns. **Note: The ambulance driver may not always comply with this request, in which case the proper emergency room should be left to the discretion of the driver.**

Skin Exposure

1. Move the victim immediately under an emergency shower or other water source and flush the affected area with large amounts of cool running water for at least 5 minutes. Clothing, shoes and jewelry should be removed while the water is flowing onto the victim. Goggles should be removed last while the victim is facing the water flow.

Colleagues must be EXTREMELY CAREFUL not to become contaminated while assisting the victim. Trionic gloves must be worn.

2. While the victim is being rinsed with water, call Public Safety (212-650-7777) and inform the emergency dispatcher of the HF exposure and request emergency transport. Ensure emergency responders and treating physicians are aware of the nature of the chemical exposure. Not all hospitals are equipped to deal with HF exposure, so emergency responders need to know to take the victim to the right hospital. Provide a copy of the MSDS to emergency responders.
3. After the affected area is flushed with copious amounts of water for at least five minutes, apply 2.5% calcium gluconate gel to the area of exposure. Massage gel into affected areas. If calcium gluconate gel is unavailable, flush skin surfaces with water for at least 15 minutes. In order to prevent cross contamination, the victim should self-apply the calcium gluconate gel. If the victim is unable to self-apply, anyone present can apply the gel after first putting on trionic gloves. Do not use regular nitrile gloves because they are not thick enough to provide an effective barrier against HF. Note the time when the calcium gluconate gel was first applied to the contaminated skin and provide this information to the emergency responders. Re-apply gel every 15 minutes until the victim arrives at the hospital and is treated by doctors.
4. After the emergency responders arrive they will call the Emergency Room doctor for instructions and may administer the calcium carbonate tablets (antacid tablets) in the HF First Aid Kit.

Eye Exposure

1. Immediately flush eyes for at least 5 minutes with copious cool flowing water. Call Public Safety (212-650-7777), inform the emergency dispatcher of the exposure and request emergency transport. The victim should then be transported to a medical facility. MEDICAL PERSONNEL may irrigate the victim's eyes with a sterile 1% calcium gluconate solution.
2. Ensure emergency responders and treating physicians are aware of the nature of the chemical exposure. Provide a copy of the MSDS to emergency responders.

Inhalation

1. *If a large volume of hydrofluoric acid gas is inhaled.* Immediately remove the victim to fresh air. Call Public Safety (212-650-7777) and inform the emergency dispatcher of the exposure and request emergency transport.
2. Ensure emergency responders and treating physicians are aware of the nature of the chemical exposure. Provide a copy of the MSDS to emergency responders.
3. Inhalation of hydrofluoric acid fumes may cause swelling in the respiratory tract up to 24 hours after exposure. Persons who have inhaled hydrofluoric acid vapors may need prophylactic oxygen treatment and must be seen by a physician as soon as possible.

Spills

Small Spill Within the Hood

If a small spill occurs and is fully contained within the hood:

- Wipe up the spill using appropriate wipes and dispose of them in the designated waste container.
- If wipes are insufficient, use the absorbent pads stored in the bottom right corner of the hood.
- If you are unsure how to clean up the material or feel uncomfortable doing so, **notify staff immediately**.

Medium or Large Spill Within the Hood - Always staff

If the spill requires neutralization or use of an absorbent pillow from the spill kit:

- **Notify staff immediately.**
- If the spill occurs **after hours**, contact cleanroom staff and post a message on Slack to alert other users **not to use the hood** until it has been properly cleaned and cleared by staff.

Any Spill Outside the Hood

If a spill occurs outside the hood:

1. **Notify cleanroom staff immediately.**
2. **Evacuate the immediate area** (typically the entire bay containing the hood).
3. If the spill occurs **after hours**, contact cleanroom staff and post a message on Slack to alert others. The cleanroom will remain closed until staff can safely manage the spill.

Revision History:

- Version 0.0 - Created September 6, 2017
- Version 1.0 - Revised November 20, 2024
- Version 1.1 - Revised May 22, 2025
- Version 1.2 - Revised July 14, 2025