

Standard Operating Procedure (SOP)

Buffer Hydrofluoric Acid (BHF)

SECTION 1 – LAB-SPECIFIC INFORMATION

Department:	Mechanical Engineering
Date SOP was written:	7/31/2016
Date SOP was approved by PI/lab supervisor:	7/31/2016
Principal Investigator:	Sam Kassegne
Lab Phone:	(760) 402-7162
Emergency Contact:	Sam Kassegne/ (760) 402-7162
Location(s) covered by this SOP:	<i>Building A, Room 100/Cleanroom</i>

SECTION 2 – TYPE OF SOP:

Process Hazardous Chemical Hazardous Class

SECTION 3 – PHYSICAL / CHEMICAL PROPERTIES AND INTRODUCTION

Physical / Chemical Properties:

GHS Classification: Acutely Toxic, Skin Corrosive

Form (physical state): Liquid

Color: Colorless

Boiling point: 103 - 105° C

Introduction:

This Standard Operating Procedure (SOP) describes in detail the process flow of the Buffered Oxide Etch (BOE) of silicon dioxide on silicon wafers using buffered hydrofluoric acid. Due to the high health risk nature of the acid involved in this process, users are advised to heed the Material Safety Data Sheet carefully before carrying out the process. The MSDS are contained in a white binder located on the shelf directly underneath the fume hood in room 101 of the temporary structure, Building A. Three main uses of BOE are:

- 1) To remove the underlying sacrificial oxide layer of suspending microstructures on silicon wafers
- 2) To remove unwanted silicon dioxide on patterned silicon wafers
- 3) To remove native parasitic silicon dioxide on silicon wafers in preparation for thermal oxidation.

While the removal of parasitic oxide is relatively straight forward, the timing issue in releasing microstructures can be critical and requires great care.

The BOE process is based on the complex reaction:



where H_2SiF_6 is soluble in water

This reaction is performed in a dilute solution of HF. It has also been reported that this also lessens the attack of the photoresist by the hydrofluoric acid. Both thermally grown and deposited SiO_2 can be etched in buffered hydrofluoric acid. However, etching of deposited films is a lot faster than that of the thermal oxide.

SECTION 4 – POTENTIAL HAZARDS

Hydrofluoric acid (HF) is a highly corrosive liquid and is a contact poison. It should be handled with extreme care (i.e., beyond what is generally required to handle other mineral acids). Owing to its low dissociation constant, BHF as a neutral lipid-soluble molecule penetrates tissue more rapidly than typical mineral acids. Because of the ability of hydrofluoric acid to penetrate tissue, poisoning can occur readily through exposure of skin or eyes, or when inhaled or swallowed. Symptoms of exposure to hydrofluoric acid may not be immediately evident. HF interferes with nerve function, meaning that burns may not initially be painful. Accidental exposures can go unnoticed, delaying treatment and increasing the extent and seriousness of the injury.

HF is a calcium seeker. A person cannot sense when it comes in contact with the skin. But it dissolves the calcium in the bone. HF burns are often not evident until a day later. If not stored, handled and disposed of properly, HF can pose a serious threat to the health and safety of laboratory personnel, emergency responders and waste handlers. Hence, it is important to thoroughly understand the properties of HF and follow all safety protocols to properly store and handle HF.

Potential Health Effects:

Inhalation Toxic if inhaled. Material is extremely destructive to the tissue of the mucous membranes and upper respiratory tract.

Skin May be fatal if absorbed through skin. Causes skin burns.



SECTION 5 – PERSONAL PROTECTIVE EQUIPMENT (PPE)

Respirator Protection:

Respirators should be used only under any of the following circumstances:

- As a last line of defense (i.e., after engineering and administrative controls have been exhausted).
- When Permissible Exposure Limit (PEL) has exceeded or when there is a possibility that PEL will be exceeded.
 - Regulations require the use of a respirator.
 - An employer requires the use of a respirator.
- There is potential for harmful exposure due to an atmospheric contaminant (in the absence of PEL)
 - As PPE in the event of a chemical spill clean-up process

Lab personnel intending to use/wear a respirator mask must be trained and fit-tested by REM. This is a regulatory requirement.

Skin and Body Protection:

Lab coat & natural rubber apron, full-length pants, and closed-toe rubber or leather shoes are required.

NOTE: If HF is used in a cleanroom, the cleanroom gown will substitute for lab coat and full length pants. In addition, all the other PPE listed in this section is applicable.

Hand Protection:

White cleanroom Nitrile gloves are highly recommended. **Note:** It is recommended to layer two gloves on each hand, one underneath the sleeve of the lab coat/apron and the other, over the sleeve. Gloves must be inspected prior to each use. Use proper glove removal technique (without touching outer surface of the gloves) to avoid skin contact with HF on the contaminated gloves. Dispose of inner nitrile gloves after use as hazardous waste. Inner Butyl Viton gloves can be reused carefully (i.e., without touching the outer surface of the gloves). Wash hands thoroughly with warm water and soap.

NOTE: Consult with your preferred glove manufacturer to ensure that the gloves you plan on using are compatible with HF.



Eye Protection:

ANSI approved properly fitting safety goggles and face shield are required.

Hygiene Measures:

Avoid contact with skin, eyes, and clothing. Wash hands before breaks and immediately after handling the product.

SECTION 6 – ENGINEERING CONTROLS

HF can only be used in a properly functioning chemical fume hood or glove box.

SECTION 7 – FIRST AID PROCEDURES

First Aid Kit:

In case of spill and/or skin contact, the clean room stores the following items to help with care and treatment:

- Calcium Gluconate 2.5% Gel
 - Hydrofluoric Acid Spill Kit

If inhaled:

Dial 911. Move to fresh air. If the person is not breathing, give artificial respiration. Avoid mouth to mouth contact.

In case of skin contact:

Dial 911. Immediately (within seconds) flush affected area for at least 5 minutes. Remove all contaminated clothing. Wearing compatible gloves, massage calcium gluconate 2.5% gel into the affected area. Re-apply every 15 minutes until medical help arrives. **NOTE:** Hydrofluoric acid exposure is often treated with calcium gluconate, a source of Ca^{2+} that sequesters the fluoride ions. HF chemical burns can be treated with water and 2.5% calcium gluconate gel, or special rinsing solutions. However, because it is absorbed, medical treatment is necessary. Intra-arterial infusions of calcium chloride have also shown great effectiveness in treating HF burns.

In some cases, amputation has been required.

In case of small spills

A spill kit can be found on the last shelf of the silver cart. Instructions must be read before use of BHF.



SECTION 8 – SPECIAL HANDLING AND STORAGE REQUIREMENTS

- Ensure that you have all the PPE required for handling HF.
- HF must always be stored in plastic (nalgene / polypropylene) containers. Do not store HF in glass bottles/containers.
 - Store in corrosive/acid/lab storage cabinet within a secondary containment (nalgene/ polypropylene tray or tub).
 - Do not store in the top most shelf of the storage cabinet. In general, do not store chemicals at or above eye level.
 - Ensure the container is tightly closed at all times.
 - Do not store with oxides, organic chemicals, bases or metals.
- Carefully carry the stock bottle in a rubber maid bottle carrier/nalgene secondary container to the wet bench/chemical fume hood and pour out desired amount into a smaller container.
 - Place stock bottle back in corrosive chemical storage cabinet with cap tightly closed.
- Lab buddy system is highly recommended when handling HF. Lab emergency contact information must be readily available. The lab personnel must have easy access to a telephone (landline or cell phone).

SECTION 9 – SPILL AND ACCIDENT PROCEDURES

Chemical Spill Dial 911

Immediately evacuate area and ensure others are aware of the spill. If there is an imminent threat of a fire, pull the nearest fire alarm station to evacuate the building and **dial 911**.

Chemical Spill on Body or Clothes:

Remove clothing and begin first aid procedures (Section 7) immediately. Seek medical attention; **dial 911**.

Chemical Splash into Eyes:

Immediately rinse eyes and begin first aid procedures (Section 7) immediately. Seek medical attention; **dial 911**.

SECTION 10 – MEDICAL EMERGENCY

Life Threatening Emergency, After Hours, Weekends And Holidays:

Dial 911.

Non-Life Threatening Emergency:

Dial 911. All HF exposures should be considered an emergency.

SECTION 11 – WASTE DISPOSAL PROCEDURES

Label Waste:

Make sure the waste container(s) is properly labeled; label should indicate all of the contents of the container.

Store Waste:

Store hazardous waste in closed containers, and in a designated area (flammable cabinet is recommended). HF waste should be segregated from all incompatible chemicals such as caustics. DO NOT store in glass container.

Dispose of Waste:

Complete a Chemical Waste Pickup Request Form to arrange for disposal. Call EH&S for pickup.(619) 594-6778

SECTION 12 – SAFETY DATA SHEET (SDS)

A current copy of the BHF SDS is included in the Material Safety Data Sheet (MSDS) binder and made available to all personnel.

SECTION 13 – LOCATION OF EQUIPMENT, ACCESSORIES, TOOLS AND SUPPLIES

BOE should only be carried out in the fume hood located inside the cleanroom of the Microfabrication Laboratory.

Buffer HF-Improved that is in use can be found in the smaller fume hood inside the cleanroom. Extra BHF is stored in a covered pale blue polypropylene bucket behind the cleanroom, labeled “Acids: Inorganic”

Polypropylene containers must be used for submerging wafers/chips into the hydrofluoric acid and these are found in the larger fume hood.

Glassware must NOT be used because hydrofluoric acid corrodes glass.

Tweezers for wafer handling are stored in the middle compartment of the small white drawer next to the hot plates.



The hydrofluoric acid antidote for accidental skin contact is located in the same fume hood as the BHF (Labeled: Calgonate).

A hydrofluoric acid spill kit for up to one liter of spill is available on the bottom compartment of the silver cart.

SECTION 14 – MATERIAL COMPATIBILITY

Hydrofluoric acid is not compatible with glassware. Do NOT use glass beakers/containers. For long duration etching, such as under-etching of suspending MEMS structures, photoresist will be etched and is not a suitable masking material. A suitable masking material for that purpose can be silicon nitride.

SECTION 15 – PRIMARY HAZARDS & WARNINGS

Hydrofluoric acid is extremely hazardous (NFPA704M code = 4-0-0). It can cause severe burns of the respiratory, digestive tracts and permanent damage to the cornea. It is extremely dangerous to skin contact and can cause deep tissue and bone damage. The slight anesthetizing effect of the hydrofluoric acid makes the burn not immediately felt, but when it hurts, the pain will be intense. There is no real remedy for HF burns at present so use extreme caution in handling this acid. The antidote is for temporary relief of pain ONLY.