



## University at Buffalo Laboratory Standard Operating Procedure

<b>Title of Experimental Procedure:</b> Preparation of Porous Silicon: Electrochemical Etching of Silicon	<b>Date:</b> 8/22/14
<b>Principle Investigator:</b> Frank V. Bright	<b>Department</b> Chemistry
<b>Lab Building &amp; Room</b> Natural Sciences Complex 513	<b>Lab Telephone</b> (716) 645-4177
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<b>Responsible Person:</b> Frank V. Bright	
<b>Approved by EH&amp;S:</b>	<b>Date:</b>

**This Standard Operating Procedure is for a:**

- (  ) Specific laboratory procedure or experiment
- (  ) Generic laboratory procedure that covers several chemicals
- (  ) Generic use of specific chemical or class of chemicals with similar hazards
- (  ) Other \_\_\_\_\_

- 1) **Project Overview:** *Provide a brief overview of the experimental protocol including its purpose.*

Project Overview:  Electrochemically etch crystalline silicon using hydrofluoric acid and current in the preparation of porous silicon.
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- 2) **Risk Assessment:** *What are the risks to personnel handling this material?*

Risks:  <b>Small spills on skin:</b> If hydrofluoric acid spills on skin in small amounts, wash affected area for a minimum of 15 minutes, apply calcium gluconate liberally, and seek medical attention.  <b>Large spills on skin:</b> If hydrofluoric acid spills on skin in large amounts, remove affected clothing, use safety shower, apply calcium gluconate liberally, and seek medical attention.
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**Exposure to eyes:** If hydrofluoric acid splashes in eyes, remove contact lenses, wash eyes for a minimum of 15 minutes, and seek medical attention.

**Inhalation:** If hydrofluoric acid is inhaled, please seek fresh air and medical attention.

**Ingestion:** If hydrofluoric acid is ingested, **DO NOT INDUCE VOMITING**, drink water, milk, or milk of magnesia, and seek medical attention.

If you are assisting a person with an emergency, please wear neoprene gloves, laboratory coat, and goggles.

Hydrofluoric acid is corrosive, has a high vapor pressure, dissolves glass, ceramics, and natural rubbers, reacts with metals to form explosive hydrogen gas, and can react violently with organics.

Ethanol and pentanes are toxic, limit exposure to body.

Ethanol and pentanes are flammable, keep away from ignition source.

Risk of electrical shock is possible, please use extreme caution.

3) **Step-by-Step Description of Experiment:** Give a detailed description of each step in the procedure, including:

- What personal protective equipment to wear
- What safety equipment is available and how to check for proper working condition
- How hazardous solvents, solutions, mixtures, reaction residues, etc. are manipulated and disposed of
- How the work area and equipment is to be cleaned up
- How to remove PPE and wash up
- Lab specific rules that need to be followed

Experimental Protocol Step-by-Step Procedure:

**Please read Safety Data Sheet for hydrofluoric acid, ethanol, pentane, gallium-indium eutectic, copper, and platinum and Laboratory Safety Manual (NSC 510) before beginning.**

ALL persons participating must NOT electrochemically etch alone.

ALL persons participating must wear personal protective equipment which includes eye protection, laboratory coat, pants, closed toes shoes, and nitrile AND neoprene gloves.

ALL persons participating must work ONLY in a specially designated hood for hydrofluoric acid and determine that hood is ventilating properly before use by checking flow meter (red and alarm sounding when improperly venting – call Customer Services and DO NOT USE).

ALL persons participating must familiarize themselves with the laboratory safety equipment which includes safety shower, eye wash station, fire extinguisher, hydrofluoric acid spill kits (NSC 513), first aid kit (NSC 507), calcium gluconate (NSC 513), and phone.

Dispose of and store chemical waste as stated in the “Waste Disposal” section of this standard operating procedure.

#### Electrochemical Etching of Crystalline Silicon Procedure:

1. Cut crystalline silicon wafers into 1.6 cm x 1.6 cm squares using a TLC plate cutter.
2. Sand the etched side of the crystalline silicon wafer in a figure eight pattern (5 cm x 15 cm) five times by applying light pressure to the center of the wafer to remove surface oxides.
3. Rinse organics and silicon dust from the sanded crystalline silicon wafer by placing the silicon wafer in 20 mL of ethanol for 150 s.
4. Remove crystalline silicon wafer from ethanol and wipe free any remaining dust and ethanol with a lint free tissue.
5. Coat the sanded side of the crystalline silicon wafer with a thin layer of gallium-indium eutectic using a cotton swab to provide an ohmic contact between the copper contact electrode and the silicon anode.
6. Place the gallium-indium eutectic coated side of the crystalline silicon wafer in contact with the copper contact electrode and assemble the electrochemical etching system as shown in Figure 1.
7. Fill the electrochemical etching cell with 4.5 mL of 1:2 (v:v) 48% hydrofluoric acid:ethanol solution using a pipette and let sit for 60 s to remove surface oxides from the polished side of the crystalline silicon wafer. The ethanol allows the hydrophilic hydrofluoric acid to react with the hydrophobic silicon surface and allows the hydrofluoric acid to enter the pore network.
8. Place the platinum ring cathode (1.7 cm diameter) 1.9 cm above polished side of the crystalline silicon wafer so that the platinum ring is submerged in the 1:2 (v:v) 48% hydrofluoric acid:ethanol solution.
9. Apply 50 mA of current to the electrochemical etching system for 150 s. The current density will change based on the size of the crystalline silicon wafer. The measured potential will change based on differences in system resistance. (Measured potential: 3 to 7 V for optimal electrochemical etch to avoid electropolishing)
10. Use a pipette to remove the 1:2 (v:v) 48% hydrofluoric acid:ethanol solution from the electrochemical etching cell and place the 1:2 (v:v) 48% hydrofluoric acid:ethanol solution and pipette in their respective waste containers.
11. Place the porous silicon wafer in 20 mL of a 1:2 (v:v) water:ethanol solution for 150 s to remove hydrofluoric acid from the porous silicon pore network.
12. Place the porous silicon wafer in 20 mL of ethanol for 150 s to remove water from the porous silicon pore network, increase the miscibility with the final rinsing solvent, and lower the solvent surface tension.
13. Place the porous silicon wafer in 20 mL of pentanes for 150 s to further lower the solvent surface tension and allow quicker drying.
14. Clean the indium-gallium eutectic coated side of the porous silicon wafer with ethanol and a cotton swab to remove the residual indium-gallium eutectic from the porous silicon wafer completely.
15. Place the porous silicon wafer in an evacuated desiccator (125 torr) for 900 s to remove any residual organics from the porous silicon pore network.

16. Please leave the area clean for the next person, refill and cap all reagent bottles and put the bottles in proper storage cabinet or secondary containment, cap all waste bottles and put in secondary containment (authorized graduate student must dispose of if full), restock supplies if needed, turn off power source, close hood, dispose of gloves immediately, and wash hands thoroughly.

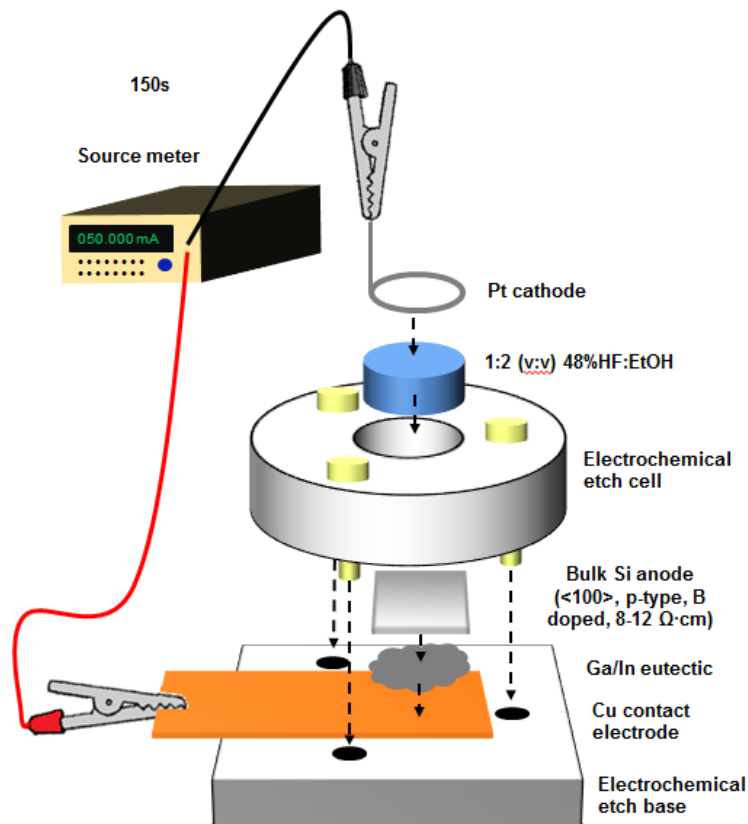


Figure 1: Electrochemical etching system (Not drawn to scale)

4) **Training Required for this Procedure:** List the training that is required in order to safely perform this procedure:

- ( x ) Selection and proper use of personnel protective equipment
- ( x ) Basic Lab Specific Safety Procedures
- ( x ) Advanced Lab Specific Safety Procedures
- ( x ) EH&S Laboratory Safety & Hazardous Waste Disposal
- ( x ) Overview of SOP, including the mixing & manipulation of chemicals and the use of any hazardous materials.

Other: Annual hydrofluoric acid safety training

5) **Safety Equipment:** Check those materials available for the procedure:

Safety Equipment & Items Available in the Lab	Available
Laboratory Hazard Signage posted on entrance door:	Yes
Hazard Signage posted on equipment as needed:	Yes
Chemical Fume Hood:	Yes
Certification Date of Chemical Fume Hood:	Yes
Containment Centrifuge:	No
Vacuum lines protected by in line filters:	No
Waste flask in secondary containment:	Yes
Biological Safety Cabinet: ( ) Class I ( ) Class II ( ) Class III	No
Certification Date of Biological Safety Cabinet:	No
Autoclave ( ) in Laboratory ( ) on Same Floor ( ) in Building	No
Other Safety Equipment Used/Needed: Personal protective equipment (eye protection, laboratory coat, nitrile and neoprene gloves) Calcium gluconate Hydrofluoric acid spill kit	Yes

6) **Waste Disposal** - Describe the quantities of waste you anticipate generating and appropriate waste disposal procedures. Include any special handling or storage requirements for your waste. Contact EH&S at 829-3301 for questions and additional guidance.

Waste Disposal:

Hydrofluoric acid – 4 L waste container (Hydrofluoric acid is toxic, handle with extreme care)

Hydrofluoric acid waste must be stored in a high density polyethylene waste container within secondary containment, capped when not in use, and disposed of properly.

Pipettes exposed to hydrofluoric acid – 4 L waste container (Hydrofluoric acid is toxic, handle with extreme care)

All pipettes exposed to hydrofluoric acid must be stored in a high density polyethylene waste container, capped when not in use, and disposed of properly.

Ethanol and pentanes – 4 L waste container

All ethanol and pentanes waste must be capped when not in use and disposed of properly. (

Gallium-indium eutectic and copper – 500 mL waste container

All copper and gallium-indium eutectic waste must be capped when not in use and disposed of properly.

Silicon – 500 mL waste container

All silicon waste must be capped when not in use and disposed of properly.

- a) *Has a Regulated Medical Waste Disposal Program compliant with New York State Regulations been implemented in the laboratory and applicable animal use areas?*  
( ) Yes                      ( ) No                      ( x ) Not applicable
- b) *Is a Sharps Disposal Program in place in the Laboratory?*  
( ) Yes                      ( ) No                      ( x ) Not applicable

7) **Small Chemical Spill Procedures:** *(the instructions below are general guidelines – modify as necessary).*

Small Chemical Spill Procedures: The following steps should be taken in the event of a hazardous chemical spill:

- 1) Small, low hazard spills should be absorbed, neutralized, and collected immediately. Consult the MSDS for specific instructions on spill response.
- 2) Liquids should be covered with spill universal absorbent pads, vermiculite or equivalent absorbent to contain and absorb the material. DO NOT use a combustible absorbent for cleaning up oxidizer spills! Absorb all liquid in the pads or absorbent and put the absorbent into a heavy-walled plastic trash bag or other suitable container and seal. Put the plastic bag or container in a second plastic bag or the 5-gallon pail that is part of the spill kit and seal. Treat the contents as a hazardous waste.
- 3) Solids should be carefully pushed with absorbent pads or swept into a pile and transferred to a plastic trash bag or other suitable container and sealed. Put the plastic bag or container in a second plastic bag or the 5-gallon pail that is part of the spill kit and seal. Treat the contents as a hazardous waste.
- 4) Decontamination of the spill area with a mild soap solution or sodium bicarbonate (for acid neutralization) may also be necessary. Questions regarding procedures can be directed to EH&S at 829-3301.

If you have any doubt about whether a spill can be safely and effectively cleaned up by staff in the lab, call the University Police at 645-2222 immediately.

8) **Chemical Spill Emergency Procedures:** *(the instructions below are general guidelines – modify as necessary).*

Chemical Spill Emergency Procedures:

- 1) **Evacuate:** Remove People From The Area: As you leave an area involved in a chemical spill, assist people exiting the area. Never enter a chemical spill area where you may place your health in jeopardy – Call the University Police at 645-2222 for assistance.
  - a) Evacuate personnel from the spill area and close doors

- b) If safe to do so, shut off electrical equipment as you leave the area
  - c) Direct personnel to nearest fire exit. Do not use elevators
  - d) Attend to victims
  - e) Alert neighbors
- 2) **First Aid:** Remove victims from spill area to fresh air, but do not endanger your own life by entering areas with toxic gases
- a) Immediately remove contaminated clothing
  - b) Flush skin or eyes with running water for 15 minutes
  - c) Get medical attention for victims
  - d) Chemicals spills over large body areas:
    - Remove contaminated clothing while under shower
    - Flush affected body area with water for at least 15 minutes
    - Resume water wash if pain returns
    - Wash off chemicals with mild detergent and water; do not use neutralizing chemicals, unguents, creams, lotions or salves
    - Get immediate medical help
    - Make sure medical personnel understand exactly what chemicals are involved
- 3) **Confine:** Close fire doors and isolate the area
- a) Establish exhaust ventilation, if possible
  - b) Vent fumes only to outside of building
  - c) Open windows, if possible, without exposing yourself to fumes
  - d) If vapors or gases are in a room which is not vented to outside of building, close off the room
- 4) **Report:** Call the University Police at 645-2222 for all chemical spills that
- a) Involve injury requiring medical treatment
  - b) Involve fire or explosion hazards
  - c) Are potentially life threatening
  - d) Are larger than one liter or cover a large area
- 5) **Secure:** Until emergency responders arrive on the scene, you and your staff will need to block off entrances to the spill location and prevent people from entering the contaminated area:
- a) Lock doors leading to the chemical spill (while keeping keys handy for emergency personnel) and post signs on doors warning of the spill
  - b) Tape or rope off stairwells, corridors, and elevators leading to the spill and hang signs on the tape
  - c) Post staff by commonly used entrances to the spill location, so they can warn people to use other routes

## References

- 1) EH&S Chemical Hygiene Plan
- 2) EH&S Hazardous Waste Management Guidebook
- 3) Commitment to Safety
- 4) Other:

Kraut, N.D.; Brattlie, J.D.; Deuro, R.E.; McGoorty, M.M.; Bright, F.V. High-Throughput Screening System for Creating and Assessing Surface-Modified Porous Silicon. *Appl. Spectrosc.* **2012**, *66*, 1171-1178.

<http://www.ubbrightgroup.com/safety/>

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