

# Silicon Etching - TMAH

## Standard Operating Procedure

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### 1. Purpose and application

Preferential Silicon Etchants are preparations which have the greatest etch rate on a specific plane of orientation. The etching systems may also be used for chemical shaping of silicon and as etchants with photomask of Ag, Au, Ta, or SiO<sub>2</sub> as these materials are not etched.

Tetramethylammonium hydroxide (TMAH) is a quaternary ammonium salt with the molecular formula (CH<sub>3</sub>)<sub>4</sub>NOH. It is used as an anisotropic etchant of silicon. It is also used as a basic solvent in the development of acidic photoresist in the photolithography process. Since it is a phase transfer catalyst, it is highly effective in stripping photoresist.

**Precautions:** For long duration etching process the water level in the beaker should be monitored during the process. If it goes below the TMAH solution level then add slight amount of water to maintain its level above it [1].

Etch rate of TMAH is 0.5 μm/min at a temperature of 85 °C [2].

### 2. Equipment, Chemicals and Supplies

The mix 25 wt. % TMAH solution is composed out of 2 chemicals:

1. TMAH
2. DI Water

Mixture is available and purchased from Sigma Aldrich Chemie B.V.

<https://www.sigmaaldrich.com/catalog/product/sial/331635?lang=en&region=NL>

### 3. Personal Protective Equipment (PPE)

The following equipment should be used:

- Eye protection: Safety glasses and face shield required.
- Protective gloves: Black neoprene gloves. Check gloves for leaks before use.
- Protective clothing or equipment: Apron.

### 4. Operational Procedures

**Preparation of sample for etching (for bulk etching with SiO<sub>2</sub> as mask)**

1. Etch the oxide completely by putting it in BOE or HF solution to remove native oxide.

2. Strip (photo)resist from the sample by dipping it in e.g. acetone. The resist can pollute the solution if it is not removed.

### Procedure

1. Get three glass beakers or envelopes which will fit your sample and place them in the bench.
2. Write down your name and type of chemical for every beaker/envelope.
3. Carefully pour some TMAH solution (25%) in the first beaker/envelope such that it will cover your sample. If you need a low concentration (<25%) TMAH first pour the DI water according to your process and requirements and then carefully add your TMAH solution.
4. Fill the other two beaker/envelopes with DI water such that it will cover your sample. DI water is used for rinsing the etchant.
5. If you plan to heat the etch (recommended) set up an au bain-marie with a hotplate in the wet bench. Put the beaker/envelope filled with etchant in the au bain-marie (use a holder when you use an envelope) to bring it up to temperature. Use an temperature sensor housed within a glass enclosure to measure the temperature of the etchant. **Direct heating of inorganic mixtures at temperatures higher than 80 °C is only allowed in day time and only after personal approval of the set-up by the KN staff.**
6. Put your sample into the etchant and move your sample for the required time (fine bubbling from the surface of the sample indicates the etching process). *If etchant at the surface becomes saturated, and fresh etchant cannot reach the surface, then etching will slow down. Agitation can be used to bring etchant to the surface and promote etching.* In this case use a magnetic stirrer and carefully swirl your etchant to accelerate the etch and improve uniformity.

### DI Water rinse

1. When the etch is complete, transfer the sample carefully to the first DI water rinse beaker/envelope and move the sample for 5 mins in DI water.
2. If you use tweezers to move the sample, make sure you rinse your tweezers as well.
3. Transfer the sample to the second DI rinse beaker, and rinse for another 5 mins while moving your sample.

### Sample dry

1. After the water rinse is finished, remove your samples and blow them dry with the N<sub>2</sub> gun.

### Clean-up

1. Let the etchant cool down to room temperature.
2. When the used etchant is at room temperature, pour it carefully over the other two beakers/envelopes filled with DI water.
3. Fill the beaker/envelope where you had your etchant with DI water.
4. Use the venturi to remove the waste from all the beakers/envelopes.
5. Rinse all the beakers/envelopes three times with DI water.
6. Turn all the beakers/envelopes upside down, wash the outside with DI water and blow them dry with the N<sub>2</sub> gun.
7. Return all labware to its proper location.
8. Clean the area and rinse it with DI water.
9. Wash your black gloves and leave them in the bench.

## 5. Primary Hazards

TMAH solution is a strong base. The tetramethylammonium ion can damage nerves and muscles, causing difficulties in breathing and possibly death in a short period of time after exposure by contact, even with only a small amount. This structural similarity is reflected in its mechanism of toxicity - it binds to and activates the nicotinic acetylcholine receptors, although the response may subsequently desensitize in the continued presence of this agonist.

## 6. Engineering Controls to Prevent and Mitigate Hazards

Carry out the procedure in a wet bench. Store bottles of chemicals (sealed tightly) in the inorganic cabinets. Work area should contain an eye wash, safety shower and a bottle of diphoterine. Check where you could find this in your neighbourhood.

The chemical are in the high risk category (if the concentration of TMAH is >5%) :

- Working with HIGH risk inorganic chemicals is only allowed during office hours.
- A buddy must be in the same module within eye contact.

## 7. First Aid and Emergency Procedures

Eye Contact: Immediately flush with diphoterine while lifting upper and lower eyelids occasionally (use the complete 500 ml for one eye and remove contact lenses if possible). After using diphoterine, flush with water for at least 15 minutes. Get immediate medical attention. Press the evacuation button.

Skin Contact: Remove contaminated clothing, wash skin with diphoterine. After using diphoterine, flush with water for at least 15 minutes. If there is any irritation, get medical attention. Press the evacuation button.

Inhalation: Remove to fresh air. Resuscitate if necessary. Take care not to inhale any fumes released from the victim's lungs. The quick response team has to use the "Eerste Hulp Zuurstof Tas". Get immediate medical attention. Press the evacuation button.

Ingestion: Do not induce vomiting. Get immediate medical attention. Press the evacuation button.

In case of a spill: Press the evacuation button.

In case of a fire: Press the fire button. Use the CO<sub>2</sub> extinguisher to extinguish the fire.

## 8. Literature

- [1] „Standard Operating Procedures TMAH,” 22 July 2013. [Online]. Available: [http://www.cchem.berkeley.edu/rsgrp/SOPs2013/TetramethylammoniumHydroxide\\_Sarpong.pdf](http://www.cchem.berkeley.edu/rsgrp/SOPs2013/TetramethylammoniumHydroxide_Sarpong.pdf). [Geopend May 2018].
- [2] X. Duan, „Microfabrication Using Bulk Wet Etching with TMAH,” 31 August 2005. [Online]. Available: <http://www.physics.mcgill.ca/~peter/theses/xufeng.pdf>. [Geopend May 2018].