BOE / HF – Silicon dioxide Etching Standard Operating Procedure

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1. Purpose and application

Buffered Oxide Etch (BOE) or just hydrofluoric acid is used for etching silicon dioxide on silicon wafers. Buffered oxide etch is a mixture of hydrofluoric acid and ammonium fluoride. Ammonium fluoride containing etches give silicon surfaces with an atomically smoother surface than HF. Due to the high health risk nature of the acid involved in this process, users are advised to read the Material Safety Data Sheet carefully before carrying out the process [1].

Three main uses of BOE / HF 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.
4) 40% HF is used for fast removal of oxide.
5) BOE gives a slower removal of oxide, but can extend the lifetime of a photoresist mask. Etch rate typically 30 – 80 nm/min.
6) Diluted HF etches - say 5% HF - is used for removal of native oxide in about 30 seconds. The surface becomes highly hydrophobic [1, 2].

The BOE process is based on the complexing reaction:
$SiO_2 + 6\ HF \rightarrow H_2SiF_6 + 2\ H_2O$
where H_2SiF_6 is soluble in water.

This reaction is performed in a dilute solution of HF, buffered with NH_4F to avoid depletion of the fluoride ions. It has also been reported that this also lessens the attack of the photoresist by the hydrofluoric acid [2].

Both thermally grown and deposited SiO_2 can be etched in buffered hydrofluoric acid or just hydrofluoric acid. However, etching of deposited films proceeds a lot faster than that of the thermal oxide. Densification of the deposited films, by heat treatment at 1000 - 1200˚C for about 15 minutes, results in a fall in the etch rate to approximately the same as that for the thermally grown oxide [2].

This etch will remove silicon dioxide. It will only attack silicon and silicon nitride at a very slow rate. Some metals etch in BOE (Titanium, Aluminium) some do not (Chromium, Gold, Platinum). You can mask a BOE etch with photoresist for a short etch (20 mins or so). If you etch longer, the photoresist will start to peel off. You can also mask BOE etches with silicon nitride or Cr/Au [3].

- HF (40%) has an etch rate of approximately 833 nm/min at a temperature of 21 ˚C [4].
- BOE 7:1 has an etch rate of approximately 80 nm/min at a temperature of 21 ˚C [1].
- BOE 20:1 has an etch rate of approximately 30 nm/min at a temperature of 21 ˚C [1].
- BOE with surfactant has an etch rate which is identical to BOE without surfactant [5].

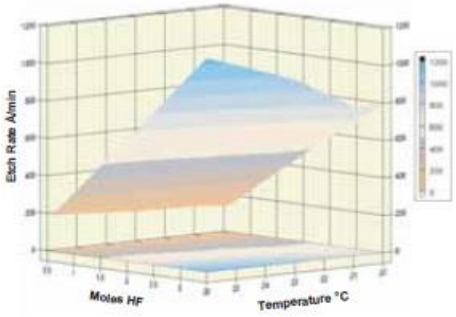

Figure 1 Etch rate vs. Temperature and Concentration: Identical Data With/Without Surfactant [5].

More etch rates for BOE can be found in appendix 9.

2. Equipment, Chemicals and Supplies

- BOE (buffered oxide etch) 7:1 is composed out of three chemicals:

1. 87.5 wt.% Ammonium fluoride (40 %)
2. 12.5 wt.% Hydrofluoric acid (49 %)
3. Water

Mixture is already purchased from Microchemicals.
https://www.microchemicals.com/products/etchants/buffered_hf_boe.html

- BOE (buffered oxide etch) 20:1 is composed out of three chemicals:

1. 95.2 wt.% Ammonium fluoride (40 %)
2. 4.8 wt.% Hydrofluoric acid (49 %)
3. Water

Mixture is purchased from Honeywell.

- BOE (buffered oxide etch) 20:1 with surfactant is composed out of three chemicals:

1. 30 – 50 wt.% Ammonium fluoride
2. 0.5 – 10 wt.% Hydrogen fluoride
3. 40 – 70 wt.% Water

Mixture with surfactant is purchased from J.T. Baker.
http://www.cen.iitb.ac.in/inventory/Chemical-MSDS/9_BOE_etchant_7_1.pdf

- HF (40 %) is purchased from Sigma Aldrich.

https://www.sigmaaldrich.com/catalog/product/mm/100335?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

1. Get three polypropylene (PP) or polytetrafluoroethylene (PTFE) beakers or envelopes which will fit your sample and place them in the bench.
2. Write on process card that you will work with HF or HF containing products. NOT ON THE BEAKERS.
3. Carefully pour some BOE in the first beaker/envelope such that it will cover your sample.
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. Cap the BOE/HF bottle, clean it according to the KN procedure and put it away.
6. Transfer the sample into the BOE carefully with PTFE tweezers or PTFE wafer tools.
7. Let the sample etch for the required length of time. Etch rate will vary with oxide composition and depositions method. You should verify etch rate with your own experiments on your own samples.
8. If the silicon dioxide has not been completely etched away, you will observe a film of the DI water wetting or sheeting across the whole surface of the wafer. If the layer of SiO_2 has been etched off, the DI water will not adhere to the back, except for a few isolated drops, and the wafer will appear dry and dull gray. This happens because SiO_2 is hydrophylic as opposed to silicon which is hydrophobic. Observe the backside of the wafer to confirm this effect for a few seconds. If the oxide is not thoroughly etched or removed, immerse the substrate or the wafer back into the BOE solution. Etch for an additional 30 seconds.
9. Recheck back of wafer as mentioned in step 8 after the substrate has been rinsed with DI water. Repeat this step until SiO_2 is completely etched and removed.

DI Water rinse

1. When the etch is complete, transfer the sample carefully with PTFE wafer tools to the first DI water rinse beaker/envelope and move the sample for 5 minutes 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 minutes while moving your sample.

Sample dry

1. After the water rinse is finished, remove your samples and blow them dry with the N_2 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_2 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

HF acid is very dangerous and HF burns are particularly hazardous. An insidious aspect of HF burns is that there may not be any discomfort until long after exposure. These burns are extremely serious and may result in tissue damage. If you contact HF, flush the area well and be sure to work under and around your finger nails. Finger nails and cuticles are the classic areas where people receive burns, having washed off the HF without washing under their nails. If washed off immediately after exposure, HF may do no harm [6].

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 hexafluorine. Check where you could find this in your neighbourhood.

The chemical are in the high risk category:

- 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 hexafluorine while lifting upper and lower eyelids occasionally (use the complete 500 ml for one eye and remove contact lenses if possible). After using hexafluorine, flush with water for at least 20 minutes. Do not apply calcium gluconate. Get immediate medical attention. Press the evacuation button.

Skin Contact: Remove contaminated clothing, wash skin with hexafluorine. After using hexafluorine, flush with water for at least 5 minutes. Apply generous amounts of calcium

gluconate gel to the area. 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_2 extinguisher to extinguish the fire.

8. Literature

[1] "Technical data: BOE Buffered Oxide Etchants," [Online]. Available: http://www.smfl.rit.edu/pdf/productinfo/productinfo_General_Chem_BOE.pdf. [Accessed 2018].

[2] B. Darling, "Buffered Oxide Etch," 7 June 1999. [Online]. Available: http://www.phas.ubc.ca/~ampel/nanofab/sop/BOE.pdf. [Accessed 2018].

[3] R. White, "Silicon Dioxide Etch using Buffered Hydrofluoric Acid," 22 September 2016. [Online]. Available: http://engineering.tufts.edu/microfab/documents/SOP_OxideEtch-BHF.pdf. [Accessed 2018].

[4] P. Gennissen and P. French, "Sacrificial oxide etching compatible with Aluminum metallization," 19 June 1997. [Online]. Available: https://ieeexplore.ieee.org/stamp/stamp.jsp?arnumber=613624. [Accessed 21 August 2018].

[5] J. McFarland, Honeywell and M. Parent, "Evaluation of Buffered Oxide Etch Solutions with Fluorinated Surfactants," 2003. [Online]. Available: http://www.honeywell.com/sites/docs/doc128e30a-f9d1a9a0f6-e0df9bfada07602278603c6cb43673fb.pdf. [Accessed July 2018].

[6] "Wet Oxide Etch," [Online]. Available: http://inside.mines.edu/impl/BOE.html. [Accessed 2018].

9. Appendix

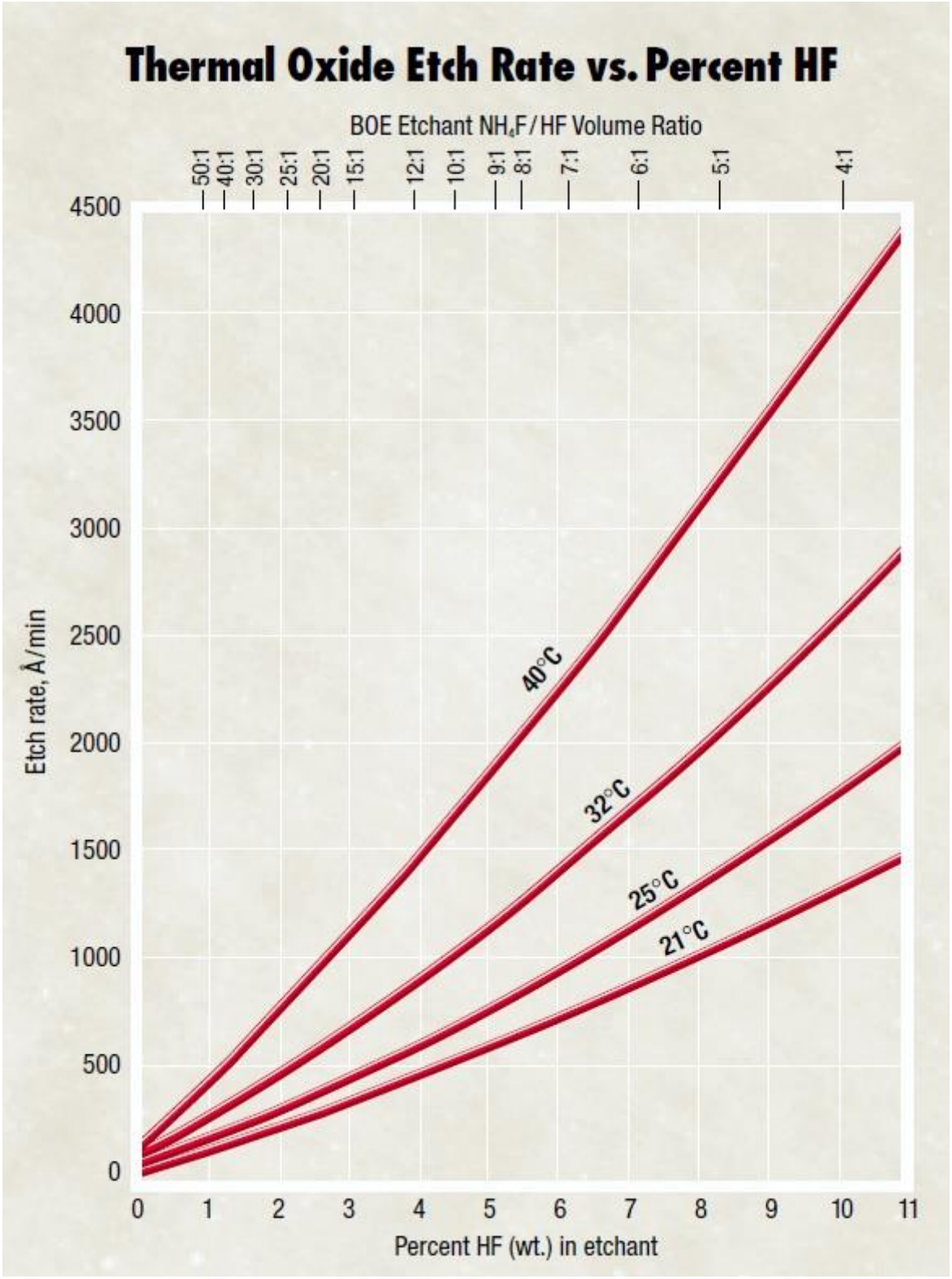

Figure 2 Thermal Oxide Etch Rate vs. Percent HF [1].