KOH Etchant
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. A mask material solution of Ag, Au, Ta,SiO_2 or Si_3N_4 can be used [1].

KOH is an etchant which attacks silicon preferentially in the <100> plane producing a characteristic anisotropic V-etch with sidewalls that form a 54.7 degree angle with the surface (35.3 degree from the normal). This etch process is independent of the doping concentration for As, P and Sb [2].

Etch rate of KOH (40 %) is approx. 0.6 – 1 µm/min at a temperature of 80 ˚C. See appendix for more information.

Ask for introduction if you want to use the standard setup.

2. Equipment, Chemicals and Supplies

Our standard setup consist out of a 3 L reaction vessel and is located in TU07-01.

The 40 wt.% KOH solution *e.g.* for our standard setup is composed out of 2 chemicals:

1. 1 kg KOH pellets
2. 2.5 L DI water

The KOH pellets are purchased from VWR.
https://nl.vwr.com/store/catalog/product.jsp?catalog_number=26668.296

HCl (37%) is used for stopping the reaction and is purchased from Sigma Aldrich.
https://www.sigmaaldrich.com/catalog/substance/hydrochloricacid3646764701011?lang=en&region=NL

3. Personal Protective Equipment (PPE)

The following equipment should be used:

- Eye protection: Safety glasses (optional with face shield).
- Protective gloves: Black neoprene gloves. Check gloves for leaks before use.
- Protective clothing or equipment: Apron.

4. Operational Procedures at 80˚C (40 wt.% KOH)

Preparing the solution for our standard setup (only when solution in reaction vessel needs to be refreshed)

1. Use the venturi to remove the etchant out of the reaction vessel.
2. Rinse the vessel with DI water till it is clean.
3. Carefully add KOH pellets to the required amount of water (2.5 L of DI water for every 1 kg of KOH pellets) using a magnetic stirrer in the reaction vessel for making a homogenous solution.

Process

1. Switch the heater of the KOH reaction vessel on for at least one hour in advance, so that final solution will stabilize at 80˚C. *Be careful with this step… keep careful watch on the solution temperature as it heats up, do not let it exceed 90˚C.* **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.**
2. Use the temperature indicator and controller (VT5) with a temperature sensor housed within a glass enclosure (be careful!) to measure the temperature of the etchant. **If you want to use other temperatures you should ask the KN staff.**
3. Get four glass beakers or envelopes which will fit your sample and place them in the bench.
4. Write down your name and type of chemical for every beaker/envelope.
5. Fill three beaker/envelopes with DI water such that it will cover your sample. DI water is used for rinsing the etchant.
6. Fill the other beaker with a H_2O: HCl (37%) (4:1) solution. *Adding the acid carefully to the water.*
7. Fix your wafer using 4” PEEK sample handling tools. *Fixing the wafer is done because gas is created during the etch process which tilts up your sample.*
8. After the 40% KOH solution has reached equilibrium at 80˚C, hang your holder on the lid and close the vessel with that lid to catch most of the evaporating solution and return it to the vessel using a condenser. **The condenser connected to the KOH reaction vessel works automatically and is turned on from 7.00 A.M. till 7.00 P.M.**
9. Etch for the desired length of time. Expect approximately 0.6 – 1 µm/min etch rate of silicon in the <100> direction, and undercut rate at convex corners of about 3 µm/min. *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. *You can find a marker next to the rotary knob for the right spin speed.*
10. **Keep in mind that if you do not use the 4” PEEK sample handling tool, you also need to protect the back of your wafer with a coating (e.g. SiO_2, Protek, PMMA, Mounting wax). For more information ask the KN staff.**

DI Water rinse and H_2O:HCl rinse

1. When the etch is complete, transfer the sample carefully to the first DI water rinse beaker/envelope and move your sample for 5 mins in the 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 H_2O:HCl beaker/envelope and rinse for 5 mins moving again the sample.
4. Transfer the sample to the second DI rinse beaker, and rinse for another 5 mins while moving your sample.
5. Transfer the sample to the third DI rinse beaker, and rinse for another 5 mins while moving your sample.

Clean-up

1. After turning off the heater, allow the KOH solution to cool to room temperature.
2. When you are finished pour carefully the H_2O:HCl solution over the last two beakers/envelopes filled with DI water.
3. Fill the beaker where you had your H_2O:HCl 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

Potassium Hydroxide: Causes severe eye and skin burns. Causes severe digestive and respiratory tract burns. Heats upon dissolution in water.

Hydrochloric Acid: Liquid or vapours are serious health hazards; and cause severe burns. Hydrochloric acid is much more viscous than water, be prepared for this when you pour it.

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 chemicals are in the medium risk category:

- Processing during afterhours requires the presence of a buddy, mixing of chemicals is not allowed (prepare your solution beforehand) and the maximum quantity of liquid is 100 ml.
- If one of these points is not fulfilled the process is considered to be high risk and it must be done during office hours.

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, wash with water. 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. 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.

8. Literature

[1] "Preferential Silicon Etchants," 2018. [Online]. Available: http://transene.com/si/. [Accessed 2018].

[2] "Anisotropic Silicon Etch Using KOH," [Online]. Available: https://www.inrf.uci.edu/wordpress/wp-content/uploads/sop-wet-anisotropic-si-etch-using-koh.pdf. [Accessed 2018].

[3] K. Sato, M. Shikada, Y. Matsushima, T. Yamashiro, K. Asaumi, Y. Iriye and M. Yamamoto, "Characterization of orientation-dependent etching properties of single-crystal silicon: effects of KOH concentration," *Sensors Actuators,* vol. 64, pp. 87-93, 1998.

9. Appendix

Table 1 Orientation-dependent etch rates (μm/min) as a function of KOH concentration at an etching temperature of 70˚C [3].

Crystallographic Orientation	Rates at different KOH Concentration		
	30%	40%	50%
(100)	0.797 (0.548)	0.599 (0.463)	0.539 (0.619)
(110)	1.455 (1.000)	1.294 (1.000)	0.870 (1.000)
(210)	1.561 (1.072)	1.233 (0.953)	0.959 (1.103)
(211)	1.319 (0.906)	0.950 (0.734)	0.621 (0.714)
(221)	0.714 (0.491)	0.544 (0.420)	0.322 (0.371)
(310)	1.456 (1.000)	1.088 (0.841)	0.757 (0.871)
(311)	1.436 (0.987)	1.067 (0.824)	0.746 (0.858)
(320)	1.543 (1.060)	1.287 (0.995)	1.013 (1.165)
(331)	1.160 (0.797)	0.800 (0.619)	0.489 (0.563)
(530)	1.556 (1.069)	1.280 (0.989)	1.033 (1.188)
(540)	1.512 (1.039)	1.287 (0.994)	0.914 (1.051)
(111)	0.005 (0.004)	0.009 (0.007)	0.009 (0.010)