KOH ETCHING AND DECONTAMINATION PROCEDURES

Note: Adapted for use from http://snf.stanford.edu/Equipment/wbgeneral/KOHEtch.html

1. OVERVIEW

Heated KOH solutions can be used for preferential etching of silicon along crystal planes. The etch rate will depend on the doping and crystal orientation of the silicon and the type of KOH solution used, but is typically on the order of about a micron per minute. Potassium (K+) is an extremely fast-diffusing alkali metal ion, and a lifetime killer for MOS devices. Lab members using KOH absolutely must observe proper procedures to avoid contaminating any metal-ion sensitive processes and equipment elsewhere in the lab. KOH-etched substrates, however, may be later processed in "Clean" equipment, but only providing that the procedures for decontamination described here are strictly followed.

2. SAFETY

2.1 Chemical Hazards

KOH solutions are caustic. The primary hazard classifications (Appendix A) for KOH solutions are: Corrosive, air/water reactive. If you are using Isopropyl Alcohol in your KOH solution, remember that it is a solvent and that it is Flammable.

The 1:1:1 H_2O:H_2O_2:HCl and 5:1:1 H_2O:H_2O_2:HCl solutions are used for decontamination of wafers and labware following KOH etching. The primary hazard classifications (Appendix A) for these solutions are: Corrosive, oxidizer, air/water reactive.

2.2 Process Hazards

General process hazards involve handling of chemicals, and materials which come into contact with chemicals, used at this station. Wet benches are potentially the most dangerous operations in the lab. Be sure you understand all hazards and proper handling procedures before working at any wet bench. Be aware that KOH etching solutions and the H_2O:H_2O_2:HCl decontaminating solutions are heated, and not only present thermal hazards, but also chemical hazards that are more severe than what may be listed in the typical MSDS.

3. QUALIFICATION CHECKLIST: N/A

4. OPERATION/PROCESS

4.1 KOH Etching of Silicon

KOH Etching is done in the constant temperature bath station. KOH decontamination (see section 4.2) may be performed at a general work bench (with appropriately clean *quartz* containers).

1. **Fill the constant temperature bath.**
   Fill the bath with water, leaving a couple of inches at the top so that it does not overflow when the beaker is placed inside.

2. **Select the appropriate labware.**
   KOH etching requires an etch beaker with a lid, a rinse beaker, and teflon wafer holder (either a boat & handle or single wafer holder). There is a designated set "Clean" labware consisting of a *quartz* etch beaker with a Pyrex condensor lid, a Pyrex rinse beaker, and various wafer holders/boats. The "Clean" labware is specifically for processing material that will be KOH-decontaminated for subsequent processing in "Clean" equipment. These are stored in the labeled roll-around cart at wbgeneral and may **not** be used for any

materials that have (or have ever had) any metals. (For more information about "Clean" labware, including decontamination procedures, see section III below.) There is also a designated set of "Metal- and Gold-Compatible" labware (beaker, beaker lid, and wafer handling tools) for KOH etching of all other materials. These are located on the shelf at wbgeneral.

3. **Mix up your KOH solution in the beaker and place it in the bath.**
   Pour the desired amount of KOH into the beaker. The KOH solution supplied in the lab is 45%. Depending on your process, you may want to dilute with water or water and isopropanol (although processing of materials using solvents is not allowed at wbgeneral, KOH etching is an exception). A ruler placed against the side of the beaker will help with determining the correct proportions. People tend to use 30% KOH in water, which etches at ~60 mm/hr. Carefully place the KOH beaker into the constant temperature bath.

4. **Assemble the condensor.**
   Place the condensing unit on top of the beaker with the lower hose connected to the industrial water connection and the upper hose going down the drain. Turn on the water to obtain a slow, steady flow. The actual temperature of the bath can be monitored by placing a thermometer in the constant temperature bath (do not place a thermometer inside the KOH etching beaker!) The thermal capacity of the bath is much higher than that of the beaker and its contents, so you may assume that the etching solution is at the same temperature as the surrounding bath.

5. **Heat the bath.**
   Using the on/off toggle, turn on the heater on the constant temperature bath and set the temperature desired. The temperature setting should not be set above 90°C (water boils at 100°C). Set the Limit Adjust knob at about 130°C (if it is too low it will trip the breaker and cool down the bath.) It takes about 3 hours to heat the bath to 80°C. Check the water level and add water to the bath as needed.

6. **Etch your wafers.**
   Place your wafers in the designated Teflon wafer boat or holder. When the bath/beaker has come up to temperature, carefully remove the condensing unit from the beaker. Place your wafers into the solution. Replace the condensing unit and proceed with etching.

7. **Check the water level frequently**.
   Add water to the bath as needed. The temperature will be more stable if small amounts of water are added frequently (rather than large amounts, less often.) Do not leave the bath heating and unattended for more than four hours (and certainly not overnight) as it will boil dry.

8. **Finish etching and clean up.**
   Remove your wafers and thoroughly rinse in the appropriate rinse beaker. Turn off the heater to the bath. Disassemble, remove, and rinse the condenser lid. **Pour the KOH in a gold contaminated beaker and aspirate the KOH from this beaker. The tip of the aspirator is dirty and should not contaminate the *quartz* beaker**. Log the KOH into the station checklist. Thoroughly rinse the beaker. Clean up labware. Make sure the bench is left clean and dry.

4.2 DECONTAMINATING KOH-ETCHED SUBSTRATES

Decontamination is required only if you plan on processing your KOH-etched materials in any "Clean" equipment. KOH-cleanup/decontamination may be performed at a general work bench (section 4.2.1) or at wbsilicide (section 4.2.2).

4.2.1 At wbgeneral (aka general work bench)

1. **"Clean KOH" labware should have been used for KOH etching.**
   You should have performed your KOH etching in the appropriate, designated "Clean KOH" labware at wbgeneral. Note that in this case "Clean KOH" is not the same as the lab definition of "Clean" -- because the labware is used for KOH etching, it is contaminated with potassium, an alkali metal which is a lifetime killer in devices.

2. **Obtain metal-free labware.**
   Labware for decontamination must be quartz or Teflon. Pyrex is not acceptable, as it contains ~5% sodium. Polypropylene is not acceptable, because it has a low melting temperature. The quartz and Teflon labware used for KOH etching is acceptable. If you wish to use a separate beaker for rinsing your substrates, it must also be quartz or Teflon. Place your wafers in the Teflon holders.

3. **Decontaminate wafers (and labware).**
   Twenty minutes of immersion in a self-heating solution of 1:1:1 H_2O:H_2O_2:HCl is used to decontaminate wafers and labware. Mix up the solution by pouring H_2O, then 30% H_2O_2, and then finally adding the concentrated HCl. Add the HCl slowly. Be careful, as this mixture self-heats and boils. If you are using a rinse beaker, you must also decontaminate it with this solution, and then rinse thoroughly. Place the wafers into the HCl acid solution, while still hot. Leave the wafers in solution for 20 minutes. Remove the wafers and rinse thoroughly.

4. **Clean up.**
   Aspirate the H_2O:H_2O_2:HCl solution. Rinse beakers thoroughly. Log acid on the logsheet. Leave the bench clean and dry.

4.2.2 At wbsilicide:

KOH-wafer cleanup/decontamination may be done only in the HCl hotpot at the wbsilicide station. Following wafer cleanup, the hotpot and cassette/handle must be decontaminated again to prevent any possibility of cross-over. As a courtesy to others, make sure to reserve wbsilicide in advance. Allocate enough time to clean your wafers and to decontaminate the hotpot. Until final decontamination of the station, normal use of wbsilicide cannot resume.

1. **Before starting, put a note on over the bench.**
   The note should have the following information:
   - "KOH Contamination clean-up in progress in the HCl hot pot"
   - your name
   - the date
   - the time
   - the time you expect to be finished using the wetbench

2. **Pour fresh 5:1:1 H_2O:H_2O_2:HCl solution.**
   Aspirate the old solution, and pour fresh solution, as described in the wbsilicide operating instructions. Heat the solution to 70°C.

3. **Load your wafers into a wbsilicide cassette.**
   Observe proper use of designated tweezers. Use KOH-contaminated wafers to load wafers into the wbsilicide cassette. Do not use these tweezers after this point. The cassette with KOH-etched wafers is now considered KOH-contaminated. Do not put this cassette into the dump rinser, spin/rinse dryer, or any other hot pot, at this point.

4. **Place the cassette with wafers into the HCl hotpot.**
   Use a dedicated wbsilicide cassette handle to place the cassette in the hotpot. Leave the wafers in the heated HCl solution for at least 20 minutes.

5. **Rinse wafers in the dump rinser, then in the spin/rinse dryer.**
   After the HCl hotpot, the wafers and cassette are no longer considered KOH-contaminated.

6. **Remove wafers and store.**
   Use "Non-metal/photoresist" tweezers to remove wafers from the silicide cassette. Store the wafers in a non-metal, non-KOH storage box. The wafers are now considered clean enough to be processed at wbnonmetal. If you wish to process these wafers in one of the "Clean" Tylan furnaces, the wafers must be cleaned first at wbnonmetal, and then through wbdiff.

7. **DECONTAMINATE wbsilicide.**
   This must be done immediately after cleaning your wafers.

   - Aspirate the KOH-contaminated HCl solution.
   - Fill the hot pot (nearly to the top, so the whole pot is cleaned) with 5:1:1 (H_2O:H_2O_2:HCl).
   - Heat to 70°C.
   - Place the cassette and handle you used into the solution.
   - Let the solution sit for 60 minutes.
   - Remove the handle and cassette. Dump rinse and spin/rinse dry the cassette.
   - Aspirate the hotpot.
   - Rinse the hot pot thoroughly by completely filling and aspirating four times with DI water.
   - Be sure to log the clean-up on the chemical change sheet. Note the fact that the silicide cassette and handle were both cleaned, too.

5. ROUTINE MAINTENANCE: N/A

6. SHUTDOWNS: N/A

7. TROUBLESHOOTING: N/A

8. BACKUP EQUIPMENT: N/A

9. ADDITIONAL PROCESS INFO

9.1 KOH Etching of Silicon

Hot, concentrated solutions of KOH (and other alkali metal hydroxides) will etch along the (100) crystal plane several hundred times faster than along the (111) plane. KOH etching through mask openings >1mm will result in a V-shaped pit that can go all the way through a (100) wafer of standard thickness. MEMS engineers frequently design structures which exploit this etch preference, thus making KOH the most common method of machining silicon.

Photoresist will not hold up to KOH etching. Silicon oxide can serve as a mask, although it still etches somewhere on the order of about 1 nm/min (oxide to silicon selectivity is a bit better in TMAH solutions). Silicon nitride is the prefered mask material (as little as 250 A is sufficient for masking (100) etch all the way through a wafer). For detailed process info, including references and recipes, consult Greg Kovacs' indispensable book, "Micromachined Transducers Sourcebook."

Because potassium (K^+) is a lifetime killer for MOS devices, extensive decontamination procedures are defined here, for those applications which require later processing in "Clean" equipment. If you wish to avoid the decontamination process, you may use the TMAH etch process instead. TMAH etching must be performed entirely in quartz beakers; Pyrex is unacceptable because it contains about 5% sodium, another fast-diffusing, MOS lifetime killer. If you use TMAH, all quartzware and Teflon wafer ware must be decontaminated before processing your wafers. To decontaminate, use the 1:1:1 H_2O:H_2O_2:HCl procedures outlined in section 4.2.1.

9.2 About the decontamination procedure

The HCl decontamination solution mixtures described here are derived from the SC-2 step of the industry standard RCA clean. This specific mixture was developed to remove trace metal ions. The standard mixture used here at SNF is 5:1:1 H_2O:H_2O_2:HCl, which is heated to 70°C (this is what is used in the HCl hotpots at wbsilicide and wbdiff.) The 1:1:1 H_2O:H_2O_2:HCl mixture described in this document is used only at wbgeneral; these proportions results in a self-heating solution (HCl is air/water reactive (Appendix A) and thus generates heat when added to water). HCl solution must be heated to be active; because the 1:1:1 mixture is self-heating, it is also self-limiting in temperature, and so is safer than heating on a hot plate. For more detail about the RCA clean, see section 9 of the wbsilicide (Appendix B) operating instructions.

The standard hydrogen peroxide solution stocked by the lab is 30% H_2O_2 in water. The concentrated hydrochloric acid solution is approximately 38% HCl in water. These are weight, not volume percentages. Roughly speaking, however, a 1:1:1 H_2O:H_2O_2:HCl solution contains about: 13% hydrochloric acid, 10% hydrogen peroxide, and 77% water (33% v/v concentrated HCl, 33% v/v 10% H_2O_2 in water, 33% v/v water.)

Appendix A

Stanford Nanofabrication Facility (SNF) Primary Handling Hazard Classes for Wet Benches

At SNF, we define the Primary Hazards for each of the liquid chemicals or chemical mixtures that are handled at the wet benches. Although virtually all the chemicals at SNF pose a health risk due to inhalation, according to standard laboratory practice all direct chemicals handling must take place in properly exhausted areas. So, the Primary Hazards are the concerns (other than inhalation, which is a given) that the wet bench user must be aware of when handling these chemicals. Handling risks include contact with skin, mixing with other chemicals, contact with combustibles like cleanroom wipes, etc. -- in general, things that should be avoided at all costs, but may happen when, for example, a beaker is tipped over.

The Primary Hazards as described here should noted on the "In-use Hazardous Materials" blue card which is required for any container (other than designated hot pots or tanks.) The Hazard classes are as follows:

1= Corrosive
2= Flammable
3=Oxidizer
4=Air/Water Reactive
5=Toxic
6=Non-hazardous

1. **"Corrosive"** is used to describe acids and bases; direct contact with skins will usually results in burns. Never mix with flammables.

2. **"Flammable"** generally covers most all solvents. These should never be mixed with corrosives or oxidizers.

3. **"Oxidizer"** generally covers chemicals which have oxygen as an elemental component; thus, they sustain fires by providing a nice, ready supply of oxygen. Never mix with flammables.

4. **"Air/Water Reactive"** generally means that heat is generated when this chemical is mixed with air and/or water. Corrosive/oxidizing acids are included in this hazard class.

5. **"Toxic"** indicates that even low levels of direct exposure pose a health risk.

6. **"Non-hazardous"** is generally used to refer only to water.

Note: Adapted for use from http://snf.stanford.edu/Safety/WBHazards.html

Appendix B

Note: Adapted from (wbsilicide operating instructions) http://snf.stanford.edu/Equipment/wbsilicide/OpInstrct.html#9

B. ADDITIONAL PROCESS INFO

B.1 Photoresist Strip/Piranha Clean

This solution consists of 90% concentrated sulfuric acid (H_2SO_4) and 10% hydrogen peroxide (H_2O_2) and is heated to 120 +/- 10 °C. Sulfuric acid is about 95%-98% pure; the hydrogen peroxide in the lab is 30% in water.
This combination is excellent for removing organics. The sulfuric acid converts organic compounds to elemental carbon (which is why the solution may darken temporarily when loaded with photoresist). The peroxide then oxidizes the carbon to carbon dioxide and water (which is why the solution boils and fumes, and eventually clears again.) When the piranha mixture has been around for a while or has been used extensively, the hydrogen peroxide all turns to water, which is a lousy oxidant in this system. So, additional hydrogen peroxide can be added on an as-needed basis to increase the active lifetime of the piranha. However, for the temperatures that we run, additional peroxide can help only so much before the acid becomes diluted and then needs to be changed. For regular usage levels in our lab, a change frequency of about once/week is generally sufficient.
Wafers with photoresist or if they have just been scribed must undergo a 20 minute clean in the 90% sulfuric before proceeding to pre-diffusion or pre-deposition cleans.

B.2 About the "RCA" clean (from the MIT MTL website)

"Contaminants present on the surface of silicon wafers at the start of processing, or accumulated during processing, have to be removed at specific processing steps in order to obtain high performance and high reliability semiconductor devices, and to prevent contamination of process equipment, especially the high temperature oxidation, diffusion, and deposition tubes. In 1970, the RCA Laboratories developed a cleaning procedure for silicon semiconductor device fabrication technology, which has become the industry standard; it uses several reagents containing hydrogen peroxide.

"The RCA cleaning procedure has three major steps used sequentially:

I. Removal of insoluble organic contaminants with a 5:1:1 H_2O:H_2O_2:NH_4OH solution (SC-1).

II. Removal of a thin silicon dioxide layer where metallic contaminants may accumulated as a result of (I), using a diluted 50:1 H_2O:HF solution.

III. Removal of ionic and heavy metal atomic contaminants using a solution of 6:1:1 H_2O:H_2O_2:HCL (SC-2).

"The RCA cleaning technique does not attack silicon, and only a very thin layer of silicon dioxide is removed (in II) in the process. The procedure was also designed to prevent replating of metal contaminants from solution back to the wafer's surface."

At SNF, the procedure has been modified slightly. Instead of SC-1, we use a low temperature, highly oxidizing 4:1 sulfuric: peroxide clean which serves the same purpose in removing trace organics. For ease of use, we also use a slightly different formulation of SC-2 (5:1:1). And for cleans which precede film deposition, the order is switched so that the last dip is the 50:1 HF, to minimize any native oxide that might form.

B.3 4:1 Sulfuric/Peroxide Piranha Clean

This solution consists of 80% concentrated sulfuric acid and 20% hydrogen peroxide. The 4:1 piranha clean is run at 90°C, which is lower than the standard process temperature for 90% clean for photoresist removal. At this station, this dip serves the same purpose as the first SC-1 step of the RCA standard clean process, in removing any trace organics.

B.4 5:1:1 H_2O:H_2O_2:HCl

This solution is heated to 70°C. This HCl clean is a variant of the SC-2 step of the standard RCA clean procedure (the standard SC-2 uses slightly different proportions). This formulation is excellent for removing trace metal cations from silicon surfaces.

B.5 HF-based Etchants

There are several varieties of HF-based etchants, different in acid strength and in composition. HF-based etchants include the BOE etchants, Pad etch, and ammonium fluoride (NH_4F). Before working with any HF-based etchant, read the information and the links provided in Appendix C.

B.5.1 HF/Water Mixtures: 50:1 HF and 49% HF

SNF stocks two "straight HF" mixtures (which contain only HF and water): 50:1 HF and 49% HF.
Concentrated hydrofluoric acid is approximately 49% HF and 51% water. 50:1 HF is approximately 2% HF in water, about 25-fold less than 49%. Do not confuse these two (yes, this mistake has been made). The 49% HF bottles should have an eye-catching magenta-colored ty-rap around the neck of the bottle.
The etch rate of thermal oxide in 50:1 HF is generally nominal (about 50 Å/min.) Because this acid is not buffered, the etch rate may vary with acid lifetime or usage. More detailed etch rate info is available on the Processes section of the SNF website.

B.5.2 Buffered Oxide Etchants: BOE

BOE is the acronym for "Buffered Oxide Etch", which is a mixture of ammonium fluoride, HF, and water. Ammonium fluoride is normally a solid with a low temperature of sublimation, but is very soluble in water (concentrated ammonium fluoride is approximately 40% by weight in water.) In the BOE etchants, the ammonium fluoride acts as a buffer, maintaining the pH of the solution which keeps the etch rate stable/constant over time. High concentrations of ammonium fluoride are used in BOE; in fact, the total fluoride ion content is nearly that of concentrated 49% HF, and so BOE etchants are considered to pose the same toxic hazards as 49% HF.
The temperature of BOE etchants is not controlled in SNF. Depending on the manufacturer, BOE acids may also have an added surfactant to help circumvent surface tension, which can prevent etching in small geometries or in areas with high aspect ratios. The exact formulations of BOE's are generally proprietary, but here is a general summary is below.

B.5.2.1 20:1 BOE

20:1 BOE is approximately 20 parts of 40% ammonium fluoride and 1 part of 49% HF. Thus, 20:1 BOE is approximately 38% NH4F, 2.5% HF, and 60% water. The etch rate of thermal oxide is approximately 300 Å/min. More detailed etch rate info is available on the SNF website.

B.5.2.2 6:1 BOE

6:1 BOE is approximately 6 parts of 40% ammonium fluoride and 1 part of 49% HF. Thus, 6:1 BOE is approximately 34% NH4F, 7% HF, and 59% water. The etch rate of thermal oxide is approximately 900 Å/min. More detailed etch rate info is on the SNF website.

Appendix C

HF (and Ammonium Fluoride)

Note: Adapted for use from http://snf.stanford.edu/Safety/AboutHF.html

C.1 A Word about HF (and Ammonium Fluoride)

There are a lot of horror stories about HF. Take them seriously. (See Section C.2 for First Aid procedures for HF). In brief:

1. Concentrated HF is considered "extremely" toxic (4, on the health hazard scale of 0-4). However, any solution containing a source of free fluorine ions is also hazardous. A plain, concentrated ammonium fluoride solution is considered "very" toxic (3, on the health hazard scale), yet becomes "extremely" toxic when made more acidic, such as in the BOE mixtures we use at SNF. So, even though 20:1 BOE has much less HF (about 7% of volume) than 49% HF, because it also has about 38% NH4F and it is acidic, it presents the toxic hazards as 49% HF.

2. On contact, very HF easily passes through skin and tissue. Because its action can be delayed for many hours, it can distribute throughout the body.

3. Negatively charged fluorine ions bind very easily to positively charged calcium and magnesium ions to form insoluble salts (CaF_2 and MgF_2 salts form some natural gemstones.) In the body, Ca and Mg ions are used to mediate a variety of physiological processes, such as muscle movement. Calcium is also a chief component in bone.

- Local tissue damage (and the point of contact) results from free hydrogen ions which cause corrosive chemical burns and free fluorine ions which cause deep tissue damage including erosion of bone.
- Systemic damage can occur when fluorine becomes distributed throughout the body. These conditions include hypocalcemia (loss of calcium) and hyperkalemia (too much potassium). Since calcium and potassium regulate the heart, irregular beating and cardiac arrest are manifestations. "Deaths have been reported (see link in part 6) from concentrated acid burns to as little as 2.5% BSA [body surface area exposed to skin contact]."

4. Calcium gluconate is used as an antidote. This provides extra calcium ions which can scavenge free fluorine ions before they penetrate and damage tissue. In cases of skin contact, calcium gluconate gel must be applied immediately to the area of contact. In cases where systemic damage is a risk, calcium gluconate is administered by a healthcare professional in an IV.

5. Pure hydrogen fluoride is an extremely toxic gas which very easily dissolves in water. "Hydrofluoric acid" describes this solution form. HF easily passes between gas and liquid phases; so HF- (and NH_4F-) containing solutions will emit toxic fumes. Although SNF lab safety precautions tend to emphasize protection against skin contact with fluoride-containing solutions, remember to avoid inhalation of the fumes by always working under fully exhausted areas of the wet benches.

6. Concentrated HF solutions are used in many household items, such as rust removers.

For more detailed medical info about HF, check the following links:

http://www.emedicine.com/emerg/topic804.htm

C.2 First Aid for HF Exposure

C.2.1 HYDROFLUORIC ACID FIRST AID FOR SKIN CONTACT

1. IMMEDIATELY rinse the contacted skin area with copious quantities of water, being careful to wash the acid away from other parts of your body, especially finger/toe nails.

2. Remove all clothing exposed to the HF.

3. Continue rinsing for 1-2 minutes. Do NOT dry the skin.

4. Puncture the Calcium Gluconate Gel tube using the inverted tube cap.

5. Squeeze the Calcium Gluconate Gel on the contacted area; cover the entire area with gel.

6. Use a double gloved hand to spread the gel, and gently massage it into the skin. Take the gel with you and continue to apply fresh gel while enroute to the Emergency Room.

7. Elevate burned extremities, if possible.

8. Immediately go to the Emergency Room.

9. Tell them you have Hydrofluoric Acid on you.

10. Continue to apply fresh gel (and gently massage it in) while waiting to be treated.

NOT FOR USE IN THE EYES

[safety/hf first aid, dermal/2-1-95]