

Piranha Clean (Sulfuric Acid and Hydrogen Peroxide Mix)

Standard Operating Procedure

Faculty Supervisor: Prof. Robert White, Mechanical Engineering (x72210)

Safety Office: Peter Nowak x73246 (Just dial this directly on any campus phone.)

(617)627-3246 (From off-campus or from a cell phone)

Tufts Emergency Medical Services are at x66911.

Revised: May 5, 2017

Warning: Piranha is highly reactive, hot, and attacks organic materials. Process only in glass containers using PTFE or stainless steel tools. Piranha will burn you badly if it gets on your skin. Under no circumstances let it get in your eyes. Do not breathe the vapors. Work carefully in the hood with full personal protective equipment.

Extreme danger: Piranha reacts violently (explosively) with organic solvents such as acetone and isopropanol. If you somehow mix Piranha with acetone or isopropanol (for example by using the wrong waste bottle) it is going to explode violently. TAKE EXTREME CARE NOT TO MIX PIRANHA WITH ORGANIC SOLVENTS!

Pressurization danger for Piranha waste: Piranha waste evolves oxygen gas which can pressurize and break the waste bottle. Piranha must be fully cooled (1 hour cool) before being poured into the glass waste bottle. In addition, the waste bottle must have a vented cap to allow pressurization to be released.

1. Material Requirements:

- 1.1 **Equipment:** Three glass beakers (1 chemical, 2 rinse), stainless steel tweezers, PTFE (Teflon) wafer holders or sample holders.

Warning: Piranha attacks organics!! This includes most plastics. It will react violently with polyethylene and polypropylene tweezers, bottles, and containers. It will also react violently with organic solvents such as acetone and isopropanol. The only materials you should use as tools or containers are glass, stainless steel, and PTFE (Teflon).

- 1.2 **Chemicals:** Sulfuric Acid (H₂SO₄ 96%), Hydrogen Peroxide (H₂O₂ 30%). Note: These percentages are the dilutions as they arrive in the bottles from the chemical supplier. Just use the solution straight out of the bottle.

1.2.1 **Hazards associated with chemicals:**

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

1.2.1.2 **Hydrogen Peroxide:** Liquid or vapors are serious health hazards; and cause severe burns.

- 1.3 **Engineering Controls:** Conduct procedure in ventilated fume hood. Store bottles of chemicals (sealed tightly) in cabinets with secondary containment. Work area should contain an eye wash and safety shower.

- 1.4 **Personal Protective Equipment:** Trionic gloves on top of nitrile gloves, apron, goggles, and face-shield. Never work with Piranha without all this equipment.

2.0 Procedure:

Complete all processes in the fume hood. Keep the sash down as low as possible without restricting your motion.

2.1 Piranha Clean (3:1 96% H₂SO₄: 30% H₂O₂): 10-20 min

Note: Piranha attacks most plastics violently. PTFE (Teflon) is the only safe plastic to use with Piranha. You must do Piranha processing in glass containers using PTFE or stainless steel tools.

- 2.1.1 Get a water rinse beaker which will fit your samples (A 1000 mL beaker works for a single 4" wafer.) **Do this first.** If something goes wrong, you want the water available to quench the reaction.
- 2.1.2 Stand the rinse beaker on a few fab wipes in the hood, and fill it 80% full with deionized water.
- 2.1.3 Place 5 fab wipes in a pile in the hood. Get a second beaker that will fit your samples for processing (you should find one labeled "Piranha" on the shelves). Put it on the fab wipes in the hood. A 1000 mL beaker works for a single 4" wafer.
- 2.1.4 Fill the container ¾ full with 96% sulfuric acid (make sure to leave some space at the top of the container – so if you are using a 1000 mL beaker, for example, fill to the 750 mL mark with 96% sulfuric acid).
- 2.1.5 Cap the sulfuric acid bottle and put it away.
- 2.1.6 Bring the hydrogen peroxide bottle, and pour in 1/3 the volume used in the previous step of hydrogen peroxide. (So, for a 1000 mL beaker, add 250 mL of hydrogen peroxide, bringing the total volume of solution up to 1000 mL).

The solution will heat up and start to bubble.

- 2.1.7 Cap the hydrogen peroxide bottle and put it away.
- 2.1.8 Put your samples in the solution to etch. A PTFE (Teflon) or glass sample holder should be used.
- 2.1.9 Allow your samples to sit in the Piranha clean for 10-20 minutes to remove all organics.

2.2 DI Water rinse: 10 min:

- 2.2.1 When the Piranha clean is complete, transfer the sample carefully to the rinse beaker.
- 2.2.2 If you used tweezers to move the sample, make sure you leave them in the rinse beaker to rinse as well.
- 2.2.3 Let the sample and tools soak in DI water for 5 mins.
- 2.2.4 Fill the second rinse beaker with water.
- 2.2.5 After the 5 mins. are up, transfer the samples to the second rinse beaker. Rinse for an additional 5 minutes.

2.3 Sample dry:

- 2.3.1 Remove your samples and blow them dry with the N₂ gun.

2.4 Cleanup

- 2.4.1 **Leave the hot Piranha for at least 1 hour to allow it to cool before putting it into the waste container. If it is late, you can label it with your name, the date, and "Piranha", leave the container in the back of the hood, and dispose of it the next day.**
- 2.4.2 When the Piranha mixture is cool, dump it into the Piranha waste bottle. This must be a **glass** waste bottle **with a vented cap**.. Use the stainless steel funnel.

DO NOT use any plastic bottles or plastic funnels. DO NOT mix the waste with organic solvents such as acetone or isopropanol, they WILL EXPLODE.

- 2.4.3 Pour the 1st rinse water beaker into the piranha processing beaker, and then into the waste bottle (this is the first rinse).
- 2.4.4 Pour the 2nd rinse water beaker into the 1st rinse water beaker, then into the process beaker, and finally into the “dilute acid/base waste” 55 gallon HDPE jug. (This is the 2nd rinse).
- 2.4.5 Fill the 2nd rinse beaker with DI water again, pour it into the 1st rinse beaker, then into the process beaker, and finally dump this water into the “dilute acid/base waste” 55 gallon HDPE jug. (This is the 3rd rinse).
- 2.4.6 Return all labware to its proper location. The beakers can drip dry on fab wipes in the hood or on the bottom shelf of the storage shelving.
- 2.4.7 Wipe up any drips in the area with chemical wipes and dispose in the acid trash

2.5 Storage

- 2.5.1 Sulfuric acid should be stored in the acid cabinet.
- 2.5.2 Hydrogen peroxide should be stored in the base/oxidizer cabinet.

3.0 Waste Disposal:

3.1 Piranha waste:

- 3.1.1 Solid waste should go in the acid waste bin.
- 3.1.2 Liquid waste should go in the “Piranha” (that is, Sulfuric Acid and Hydrogen Peroxide) glass waste bottle in the hazardous waste accumulation area. It should only be added to the waste bottle when it has fully cooled to room temperature. The glass waste bottle must have a vented cap to avoid pressurization.

4.0 Accident Procedures:

4.1 Contact: Read MSDS prior to working with any chemical to familiarize yourself with the symptoms of exposure and recommendations for treatment.

- 4.1.1 Piranha mixture, straight sulfuric, or straight hydrogen peroxide:
 - 4.1.1.1 Skin contact: Remove contaminated clothing, rinse affected area with water for 10 minutes. **If there is a visible burn, get immediate medical attention. Don't be shy. Call the medical center if you got Piranha on your skin. Tufts Medical Services are at x66911.**
 - 4.1.1.2 Eye contact: Immediately flush with water for 20 minutes while holding the lids open. **Get immediate medical attention. Call Tufts Emergency Medical Services are at x66911.**
 - 4.1.1.3 Ingestion: Do not induce vomiting. **Get immediate medical attention. Call Tufts Emergency Medical Services are at x66911.**
 - 4.1.1.4 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. Call Tufts Emergency Medical Services are at x66911.**

4.2 Spill:

- 4.2.1 If a small, contained spill occurs, such as inside the hood, wipe it up with chemical wipes and dispose of in the acid trash container.
- 4.2.2 If a large spill occurs that you are not comfortable cleaning up:
 - 4.2.2.1 Evacuate the lab and notify the Tufts emergency services (x66911) immediately. Clean up should only be performed by authorized personnel according to MSDS guidelines. Notify the faculty advisor.

If at any time you feel a situation is dangerous, do not hesitate to call the safety office (x73246, Peter Nowak) or the faculty supervisor (x72210, Robert White).

Report all accidents (injuries, major spills, fires) to the safety office at x73246 (Peter Nowak) and the faculty supervisor at x72210 (Robert White). For emergencies, call Tufts Emergency Services at x66911.