

Piranha Cleaning Standard Operating Procedure

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1. Purpose and application

Piranha solution, also known as piranha etch, is a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) , is used to clean organic residues from the substrates. Because the mixture is a strong oxidizer, it will remove most organic matter, and it will also hydroxylate most surfaces (add OH groups), making them extremely hydrophilic (water compatible). Piranha solution is used frequently in the microelectronics industry, e.g. to clean photoresist residue from silicon wafers.

Piranha solution can be an explosive. Mixing the solution is exothermic. The resultant heat can bring solution temperatures up to 120°C. One must allow the solution to cool reasonably before applying any heat. The sudden increase in temperature can also lead to violent boiling, or even splashing of the extremely acidic solution. Also, explosions may occur if the peroxide solution concentration is more than 50%. The maximum concentration for peroxide in water solution is 35%.

Many different mixture ratios are commonly used, and all are called piranha. A typical mixture is 3:1 concentrated sulfuric acid to 30% hydrogen peroxide solution; other protocols may use a 4:1 or even 7:1 mixture.

The traditional piranha solution is a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide. The solution may be mixed before application or directly applied to the material, applying the sulfuric acid first, followed by the peroxide. Piranha solutions are extremely energetic and may result in explosion or skin burns if not handled with extreme caution.

Pressurization danger for peroxide waste: Peroxide waste evolves oxygen gas which can pressurize and break the waste bottle, the bottle must have a vented cap to allow pressurization to be released.

Due to the self-decomposition of hydrogen peroxide, piranha solution should be used freshlyprepared. Piranha solution should not be stored. Waste piranha solution should be neutralized and disposed *in situ*, instead of being accumulated in containers. Oxygen given off during the self-decomposition, as well as the oxidation products of organic compounds can cause the container to rupture.

Cleaning usually requires about 10 to 40 minutes, after which time the substrates can be removed from the solution [1].



2. Equipment, Chemicals and Supplies

This Piranha solution is a 3:1 mixture of:

- 1. Concentrated sulfuric acid (>96%)
- 2. Hydrogen peroxide (31 %)

Concentrated sulfuric acid (>96%) is purchased from Honeywell. <u>https://shop-lab-honeywell.com/sulfuric-acid-30743/</u>

Hydrogen peroxide (31%) is purchased from VWR International B.V. <u>https://nl.vwr.com/store/product/708930/waterstofperoxide-31-unstabilised-vlsi-selectipur-for-</u> <u>the-electronics-industry</u>

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

Piranha solution is very energetic and potentially explosive. It is very likely to become hot, more than 100°C, when you prepare the mixture. Handle with care. Maximum temperature for this process is 80°C. Picking up a beaker that is this hot will be very painful, might melt your gloves, and may cause you to spill it!

- 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. Use your first beaker/envelope for making the Piranha solution. When preparing the piranha solution, always add the peroxide to the acid very slowly. The H₂O₂ is added immediately before the etching process because it immediately produces an exothermic reaction with gas (pressure) release. If the H₂O₂ concentration is at 50% or greater, an explosion could occur.
- 4. Fill two beaker/envelopes with DI water such that it will cover your sample. DI water is used for rinsing the etchant.
- 5. Substrates should be rinsed and dried before placing them in a piranha bath. Piranhas are used to remove photoresist and organic residues, not the compounds themselves. Mixing hot piranha with organic compounds may cause an explosion. This includes acetone, photoresist, isopropyl alcohol, and nylon.
- 6. Put your sample into the etchant and move your sample an appropriate amount of time. *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 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 piranha solution 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

Piranha solution is a strong oxidizer. Both liquid and vapour forms are extremely corrosive to skin and respiratory tract. Direct contact will create skin burns and will be extremely destructive to mucous membranes, upper respiratory tract and eyes [1].

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 <u>high risk</u> 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

<u>Eye Contact</u>: 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 30 minutes. Get immediate medical attention. Press the evacuation button.

<u>Skin Contact</u>: 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. Get immediate medical attention. Press the evacuation button.

<u>Ingestion</u>: 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.

<u>In case of large exposure</u>: Press the evacuation button. The victim should be removed from the contaminated area, and placed under a safety shower while emergency personal is contacted.

8. Literature

- [1] "Piranha solution safety guidelines," November 2016. [Online]. Available: https://www.concordia.ca/content/dam/concordia/services/safety/docs/EHS-DOC-019_PiranhaSolutionGuidelines.pdf. [Accessed May 2018].
- [2] "Standard Operating Procedure Piranha Solution," [Online]. Available: https://ehs.ucr.edu/laboratory/SOP/Piranha%20Solution.doc. [Accessed 2018].