

PIRANHA CLEANING – GLASS SURFACES

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BACKGROUND

- This protocol details how to clean small amounts of organic residues from glassy surfaces (oxides) and render them hydrophilic using a highly oxidative acid bath.
- The Piranha clean is a mixture of H_2SO_4 (concentrated): H_2O_2 (30%) (5:1). Because it is a strong oxidant solution, it removes metals and organic contaminants, and will hydroxylate most surfaces (add OH groups) rendering them hydrophilic.
- The piranha clean is suitable for putting samples in a furnace or evaporation instrument without contamination.
- A few observations must be made to ensure the best possible cleaning of the surface and the safe operation of the piranha bath:
 - a. If a sample has a large amount of organic impurities (e.g. photoresist) the piranha etch will form an insoluble organic layer that can't be removed. It is recommended to follow a suitable photoresist cleaning procedure (hot strip bath or acetone-IPS solvent rinses) first if photoresist was used on the sample.
 - b. Due to the self-decomposition of H_2O_2 , piranha solution should be used freshly-prepared. Piranha solution should not be stored.
 - c. Immersing a substrate (such as a wafer) into the solution should be done slowly to prevent thermal shock that may crack the substrate material.
 - d. Piranha solution can be **explosive** near or in contact with Acetone, Isopropanol, or any organic solvents.
 - e. 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 splashing** of the extremely acidic solution.
 - f. Also, **explosions may occur** if the peroxide solution concentration is more than 50%.
 - g. As a rule of thumb, treat the piranha solution with great care, do not pour or squirt organic solvents into it or immerse samples that contain large amounts of organic materials, prepare the piranha bath in a large beaker that allows enough room for any bubbling of the solution without splashing, and **under no circumstances must piranha solution be left unattended, unlabeled or in an open container if not in use.**

A. MATERIALS

- Dedicated crystallization dishes (3) large enough to hold wafer and stir bar so they do not interfere with each other (pyrex or quartz) or dedicated Teflon bench dip slots
- Hot plate with electronic stirring
- Magnetic, Teflon coated stir bar
- Thermometer that goes up to 150°C
- Concentrated sulfuric Acid (H_2SO_4)
- 30% Hydrogen Peroxide (H_2O_2)
- DI Water
- Acid safe gloves
- Face shield
- Acid Apron
- Fume hood
- Teflon wafer/substrate dipper
- Graduated cylinder (pyrex or quartz)

B. PROTOCOL

NOTE: Wear acid safe gear at all times during the Piranha clean.

1. Fill two large rinsing beakers with DI water.
2. Place magnetic stir bar in bottom of third beaker.
3. Place beaker on hot plate/stirrer.
4. 5:1 H_2SO_4 : H_2O_2 Piranha solution
 - a. Pour sulfuric acid into beaker, enough to cover the top of the wafer/samples in Teflon dipper completely when immersed (Do not put wafer/samples in the solution yet!). For 125 mm crystallization dish use about 75 mL H_2SO_4 .
 - b. Heat sulfuric acid to approximately 60°C.
 - c. Measure out H_2O_2 in a graduated cylinder so that it is 1/5 the volume of the H_2SO_4 . For 125 mm crystallization dish use about 15 mL H_2O_2 .
 - d. Very slowly add the H_2O_2 to the H_2SO_4 . NOTE: H_2O_2 reacts with H_2SO_4 exothermically. The solution will start to bubble and heat up. Allow the solution to cool down if it starts bubbling too vigorously. (The use of 5:1 H_2SO_4 : H_2O_2 solution is intended to

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- keep the temperature in the appropriate range. Extra H_2O_2 can be added later (up to a ratio of 3:1) to increase the temperature or regain the solution's reactivity).
- e. Turn on stirrer. Stir the mixture slowly. If the H_2O_2 floats on top of the H_2SO_4 , use a stirring rod to mix the two. BE CAREFUL, this will cause the two to react more quickly and violent bubbling can lead to acid splashes.
 5. Heat solution to 100-110°C. The solution should begin to bubble vigorously as it approaches 100°C. NOTE: The solution can heat up very quickly, even when you think nothing is happening. Watch it carefully so it does not overheat. If it does overheat, turn off the hot plate or, if safe, remove the beaker from the hot plate until it cools down.
 6. Keep solution between 100 to 110°C for the entire clean.
 7. Immerse wafer in H_2SO_4 : H_2O_2 for 10 minutes.
 8. Carefully remove wafer from solution. Be careful of dripping of the highly acidic solutions.
 9. Immerse wafer in rinse beaker with DI water for 5 minutes.
 10. Immerse wafer in second rinse beaker with DI water for 5 minutes.
 11. Dry wafer with nitrogen gun.
 12. Piranha solution can be used many times before its efficacy is spent.
 - a. If the solution is still hot and bubbling, just continue using it to clean additional wafers.
 - b. If the solution has cooled and is not more than 12 hour old, it can be refreshed by heating and adding H_2O_2 until it starts to react again.

C. PIRANHA SOLUTION DISPOSAL

1. Allow solution to cool to room temperature. Dilute solution at least 1:5 before disposal.
2. Slowly pour solution into waste piranha solution container. If neutralization is used, it is important to first dilute the solution at least 1:20 so that addition of a concentrated base, and the ensuing exothermic reaction does not cause the contents to boil overflow and spill.

NOTE: One time when I was disposing of Piranha solution it reacted with something in the waste acid container (sometimes people put things in acid waste containers that do not belong there). If this happens, keep the waste bottle cool by running water on the outside and DO NOT seal the bottle. Watch the bottle until the reaction stops and the bottle cools down. Get a new acid waste bottle and dispose of the remaining Piranha solution. Notify the person in charge of the lab that this happened.