ACID PIRANHA ETCH
STANDARD OPERATING PROCEDURE

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Section 1: Purpose

This document describes the standard operating procedures for utilizing an acidic piranha etch (30:70 30% H_2O_2:H_2SO_4). Specifically, the document aims to establish consistent operational procedures with the principal goal being safety.

Section 2: Application

An acidic Piranha etch is used for removing organics from the silicon surface, as well as forming a 15-18 Å chemical oxide layer. Piranha etches organics by first reducing them to carbon, which then reacts with free oxygen atoms in the solution to form CO_2. Only fresh solutions should be used.

Section 3: Equipment, Chemicals and Supplies

Piranha is composed of two chemicals:
1. Concentrated sulfuric acid (H_2SO_4)
2. 30% hydrogen peroxide (H_2O_2).

They are typically mixed in a 3:1 acid:peroxide mixture.

Section 4. Personal Protective Equipment

Due to the extreme corrosiveness of acidic piranha, all possible precautions must be taken to ensure safety. This includes ensuring that no skin is exposed. The following equipment should be used:

- **Safety glasses and laboratory coat are mandatory.**
- Gloves:
  - For use of <20 ml of etchant **doubled** acid-compatible nitrile gloves. Check gloves for leaks before using. Discard immediately on contact with acid or peroxide.
  - For use of >20ml of etchant:
    - Thick neoprene gloves. Check for leaks before using.
    - Face mask and chemically resistant acid-compatible lab apron.
- Closed-toe shoes (no sandals) and pants (no shorts).

Section 5: Operational Procedures

Note: Piranha etch is extremely aggressive, and can foam out of its container or explode if given sufficient organic fuel. NEVER let anything plastic/organic come in contact with hot piranha. This includes plastic tweezers, solvents, non-glass beakers, etc. Metals are also completely non-compatible with piranha, as the metals will be quickly etched and hydrogen will be evolved which could result in explosion.

1. **To use Piranha solutions you must have specific laboratory safety training and be authorized by the lab safety officer prior to doing any work.**

2. Wear proper safety attire (described in section 4) and prepare working area in the hood.

3. Locate the safety shower, and eye wash.

4. Clear the working area of ALL solvents. Remove methanol and acetone bottles, etc.

5. Prepare proper container for piranha and place in secondary containment. Remember, *piranha MUST be used in quartz/pyrex beakers, and never plastic*. Teflon is OK *chemically*, but the initial reaction generates enormous heat and can cause the Teflon to melt. Prepare a proper waster disposal container: a glass funnel situated on a glass Erlenmeyer flask to temporarily store spent etchant.

6. Generally, acids are always added to water, since acids are heavy and water on top could cause splattering. ***Piranha, however, is the exception!*** Adding sulfuric acid to H_2O_2 could cause an explosion (oxygen concentration becomes too high). Thus add H_2O_2 to the acid. Spattering is still a danger, however, and the solution should be stirred following the addition of the H_2O_2 to ensure mixing.

7. Note that the reaction of sulfuric acid and H_2O_2 is very exothermic, and the solution will likely quickly reach temperatures around 100 C.

8. Pour 9 mL of sulfuric acid slowly into the glass centrifugation tube. Close the lid on the sulfuric acid bottle and return the bottle to storage.

9. Add 3 mL of the H_2O_2 solution. Take care to ensure that the addition does not result in a layer of H_2O_2 on top of the sulfuric, which could result in spattering. Stir the solution quickly with a Pasteur pipette.

10. Place sample in the solution.

11. Empty centrifuge tube into glass funnel on waste Erlenmeyer after desired etch time, being careful to let all excess piranha drip off into the funnel.

12. Rinse the sample collected in the funnel with water. The water from at least the first two rinse cycles should be treated as piranha waste and disposed of accordingly. The beaker used to hold the tweezers should also be rinsed in the same manner.

13. Piranha should NEVER be sealed in a waste container when hot, since it continues to evolve gases. It should therefore be allowed to cool (overnight, if at all possible), before sealing the lid of the waste container.

14. Examine the workspace carefully to ensure that there are no wet spots. Clean up any wet spots as if they were piranha. Also inspect gloves and lab coat.

Section 6. Primary Hazards

Piranha is extremely corrosive and can quickly cause extreme burns to skin and severe damage to eyes. As described above, it reacts violently with organics, and can explode if given sufficient fuel. By themselves, its constituents are also reactive:

30% Hydrogen Peroxide:

H_2O_2 is a strong oxidizer, and is rated a 3 (severe) on the health scale. Contact with other materials can cause fire. It is corrosive to skin. Inhalation can damage the respiratory tract.

Concentrated Sulfuric Acid (98%):

Rated 4/4 on the health scale. Concentrated sulfuric acid is a strong dehydrating agent that will quickly damage human tissue, especially if heated (which happens when preparing piranha etch). Inhalation of mists can damage respiratory tract and lungs. Eye injuries can be severe and permanent.

Section 7. Engineering Controls to Prevent and Mitigate Hazards

All operations with piranha are performed in a fume hood, which is close to an eye wash and shower. All containers which contain piranha must have secondary containment at all times.

Section 8. First Aid and Emergency Procedures

Eye contact:

Immediately flush eyes with plenty of running water for at least 15 minutes. Speed is extremely important. Obtain medical attention as soon as possible.

Skin contact:

Immediately flush affected areas with water, removing contaminated clothing while under the safety shower. Continue washing and get medical attention.

In case of a spill:

Minor spills can be diluted and neutralized with soda ash, lime or caustic. Large spills should be contained. EH&S should be notified.

In case of fire:

Do not use water. If water is added to concentrate acid a severe eruption may result. Use a carbon dioxide or dry chemical extinguisher.