JILA SAFETY MODULE
Clean Room Safety
with David Alchenberger

Introduction

Use of the JILA Clean Room poses its own set of unique safety issues. By its very nature, the clean room is a positively pressurized, closed environment using partially supplemented, recirculating filtered air. Approximately one-third of the air in the room is vented to the outside and the remaining two-thirds is mixed with fresh air and returned to the room through High Efficiency Particulate Air (HEPA) filters. Noxious fumes not captured by the wet processing stations could be reintroduced for several minutes, albeit diluted with each room air exchange.

The lithography bay of the clean room is lighted with amber safe lights to prevent pre-exposure of the photoresists used in the room. The amber color makes true color rendering difficult, so special care must be taken to correctly identify storage containers.

Hydrogen fluoride-bearing solutions, such as Buffered-Oxide Etchant, are used for some processes in micro/nano fabrication. Peroxide-bearing solutions such as peroxymonosulfuric or Caro's acid, often referred to as "piranha" solution, is a strong oxidizer used for cleaning and etching. Both are occasionally used in the lithography bay. These dangerous chemicals require special care and attention, both by the user and by others working in the area. A special section in this module titled Extraordinary Hazards is dedicated to these materials.

Users should also be aware that there are two radioactive Polonium-210 alpha-emitter sealed sources in the lithography and, on occasion, fabrication bay.

Clean-room users come from varying disciplines, with some people being more familiar with chemistry than others.

General Safety Policies and Protocols Regarding the Use of the Clean Room

Access to the clean room will be granted only to those who complete the requirements as outlined in the JILA Clean Room New User Cover Sheet, which includes JILA Safety and EH&S training and quiz obligations. An initial walk-through with the cleanroom manager is also required. There are no exceptions to this policy.

The gowning protocol is not only meant to maintain the low-particle integrity of the area, but also provide some personal protection.

The cleanroom manager is not responsible for keeping users current on EH&S requirements regarding Hazardous Material/Waste Management. Before using the clean room, you must consult with the HMWM proctor for your lab and complete appropriate training and documentation to be in compliance with EH&S rules governing Hazardous Waste Generators.

Due to the static eliminators, users of the lithography bay and those wishing to use the eliminators in the fabrication bay must complete the EH&S Radiation Safety training and quiz.

In general, it is good practice to let someone know that you are going to work in the clean room and when, approximately, you will return. In addition to the advice set forth in UCB's EH&S Laboratory Safety Guidelines and JILA's Safety Handbook and Chemical Safety brochure, the following rules for the use of the clean room must be observed:

Do not use HF anywhere other than the wet processing station designated for HF use only. Do not use this station for anything else. A one-person-at-the-bench policy for the other stations applies for processes and chemicals deemed especially hazardous. Piranha use is subject to this policy. Use the stainless steel station is for solvent cleaning, spin coating, and developing only. Solvents are not to be used at the acid station and vice versa.

Except for small solvent squirt bottles, all chemicals are sequestered to the lithography bay, Room X121D. The chemical inventory for that room is posted in the front section of the MSDS binder. Chemicals other than those in the room's inventory are not to be introduced, used, or stored without approval of the lab manager.

Approved, but non-inventoried, chemicals must be removed from the room at the end of the work session.

Chemical compounds or solutions made from inventoried constituents must be brought to the attention of the lab manager.

Chemical containers must be covered and labeled using lab-approved labels with the chemical name, date, and user's name. Unattended containers, such as Petri or crystallization dishes used during a lift-off process, for example, must be similarly covered and labeled.

Chlorinated solvents are not allowed in the room.

Containers of used chemicals ready for disposal are to be clearly labeled and placed in the agreed collection site for transfer to the Satellite Accumulation Area. Use the word "Used" instead of "Waste" on labels for containers in the lithography bay. The SAA is the only place where waste chemicals can reside.

Heated vapor deposition (HMDS) and passive vapor etching (XeF_2) are not allowed without permission of the lab manager.

No glass or metal closed-vessel reactors are permitted.

Lecture bottles, whether full or empty, need to be stored in the gas cabinet beneath the reactive-ion etcher.

Use prudent judgment on whether to work in the clean room when it is crowded.

Repeated violations of rules and policies or consistent lapses of common sense and courtesy to others will result in a loss of the privilege to use the facility. All users are within their right to question another person's unsafe practice or unauthorized access. Reporting infractions in person or anonymously by means of the notice board located in the gowning room is encouraged.

Standard Safety Procedures

Know your environment.

- Familiarize yourself with the location of the first-aid kit, fire extinguisher, eye washer, face shield, calcium gluconate antidote, isotonic skin and eye wash bottle, the yellow Material Safety Data Sheet (MSDS) binder, and telephone. These are pointed out in the initial walk-through.
- In the event of a chemical splash to the face, for example, you may need to "feel" your way to the eye washer.

Know your circumstance.

- Take note of any spills and containers on the bench before you get started.
- pH test paper located under the acid processing station can help identify spills.
- Give yourself plenty of space to work in, even if it means moving hot plates or other devices you won't need.
- If your process allows you to work with another person at the bench at the same time, know what they are using.

Know your process.

- Do not undertake any chemical process or mixing without knowing what to expect and what might go wrong. For example, diluting a large amount of acid in water may heat the beaker or evolve fumes to a surprising level.
- Become familiar with the materials you are about to use by reading each MSDS.
- Wear safety garments, accessories, and gloves appropriate for the materials used.

Avoid using incompatible materials at the same time.

- Keep acids away from solvents and bases.
- Store chemicals in their designated cabinets, keeping incompatible materials well separated in the "Used Chemicals" cabinet.
- Acids, whether used or bulk, are always stored in the acids cabinet.
- Peroxides are stored in the vented cabinet within the acid bench.

Extraordinary Hazards

The dangers of using hydrogen fluoride-bearing and peroxide-bearing solutions cannot be overstated. Ad-hoc instruction provided by lab personnel in the preparation, use, and storage of these materials is required.

Hydrofluoric Acid

HF is a contact poison, and the most toxic compound in the clean room. It is used almost exclusively for etching silicon dioxide. Because it affects nerve function, contact with the skin may not be immediately noticed as with the strong acids. It is readily absorbed into the skin and can cause deep-tissue damage. The fluoride ion reacts with calcium in bone, resulting in osteoporosis, and it can react with calcium and magnesium ions in the blood, causing cardiac arrest. The fumes can be just as harmful as contact with skin. This material is potentially lethal. The death of a custodial staff member at a research lab was directly attributed to negligent disposal of cleaning materials used in wiping up an HF spill. The lithography bay has a bench dedicated exclusively to HF processing.

Given its toxicity, one may want to consider alternatives to using HF such as reactive ion etching or a lift-off technique that involves selective deposition rather than etching of silicon dioxide.

Protocol for using HF:

- Familiarize yourself with the properties of HF by reading the MSDS.
- Use only in the designated HF processing station. Avoid the fumes at all cost.
- Always wear protective barrier garments and a face shield when handling or using HF. Latex or nitrile gloves can be thought of as first-order protection only for diluted (<5%) HF. Silver Shield gloves must be used when handling concentrated (48%) HF. Silver Shield gloves and a plastic apron are located in the storage area under the acid processing station. The face shield is stored on the wall beside the first aid kit.
- Tuck coat sleeves into the gloves to prevent any liquid from wicking onto the sleeves.
- HF etches silicon dioxide, a primary component of glass. Do not use glassware with HF. Instead use nalgene or fluoroware vessels.
- When finished, carefully pour the used HF in a properly labeled nalgene container and store in the secondary container labeled “Hydrogen Fluoride Containing Solutions Only” in the acids cabinet.
- At the end of the HF session, check for holes in the gloves and any of dampness on clothing.

In the event of exposure to HF:

- Remove any affected clothing and set aside it as hazardous material.
- Rinse the contact site with water immediately.
- Liberally apply calcium gluconate to the site immediately after the rinse. The antidote will begin to draw the fluoride ions out of the skin, so prompt application is imperative.
- Seek immediate medical attention. All cases of HF exposure require medical attention. Assistance can be provided by the lab manager or any lab safety person.

- If you inhale fumes, seek medical attention immediately.

HF Spills:
You must wear Silver Shield gloves and a plastic apron when managing an HF spill.

- For spills within the hood or small amounts outside the hood, wipe up the spill with disposable toweling, such as Kimwipes, that is more absorbent than clean-room wipes. Sequester any disposable materials that come or may have come into contact with the HF from normal trash by placing them in a plastic bag labeled with a EH&S Hazardous Material/Waste tag. Let the lab manager know about the spill because the deck plates in the bench may need to be removed to clean the lower catch basin.
- Large spills outside the hood require evacuation of the clean room and adjacent metrology area. Immediately notify the lab manager of the situation so that hazmat procedures can be implemented.

Piranha Solution
Acid piranha solution is a solution of sulfuric acid and hydrogen peroxide. It is used primarily as a glass and sapphire substrate cleaner. Occasionally it is used as an etchant. Piranha is one component of a two-part high-explosive that is unstable above 10° C. As a strong oxidizer, it is important to keep organic solvents away from it. In a chemistry lab at Cornell, circa 1986, piranha solution aspirated into a tape-wrapped glass flask containing only a trace amount of acetone caused an explosion that hospitalized and permanently impaired a graduate student with lacerations to the face, hands and arms. A chemist at the scene estimated the force of the blast to be equivalent to a quarter of a stick of dynamite.

Protocol for using piranha solution:

- Although oxygen and carbon dioxide are the only two gases evolved from piranha solution, small amounts of sulfuric acid may be aerosolized and cause irritation to skin and mucous membranes. Avoid the fumes by using piranha solution only in the hood with the sash down and the HEPA blower off. Wear a double set of latex or nitrile gloves. A plastic apron is also recommended.
- Familiarize yourself with the properties and cautions of sulfuric acid, the main component of piranha solution, by reading the MSDS.
- Do as much pre-cleaning of the substrate as possible, including stripping any resists with acetone or an oxygen plasma before you prepare the piranha solution. Do not immerse a hydrocarbon-coated object directly into the solution. If it doesn't blow up, it will certainly boil over.
- Make sure there are no organic solvents in the immediate vicinity of the location where the solution will be made and used.
- Make only as much as piranha solution as you think you might need. The shelf life of this material is on the order of days.
- Slowly pour the hydrogen peroxide into the sulfuric acid. The solution gets very hot remarkably fast; one can easily exceed its safe operating temperature just in the mixing process.

- Use only fluoropolymer utensils, such as Teflon, for manipulating the substrate in the solution. Piranha readily corrodes most metals.
- The action of piranha is optimal at 100 °C. Do not exceed this temperature.
- Immerse objects slowly into the solution to prevent thermal shock and to get a feel for the interaction of the two materials.
- When finished, allow the solution to cool before pouring it into a properly labeled and clean nalgene container or a container already labeled for piranha storage. Because oxygen is continuously dissociating from the peroxide, use only a cap that is vented, or the bottle will burst within a few hours.
- Immediately place the storage container in the peroxides cabinet.
- Piranha has to be aspirated and neutralized before disposal. Do not leave active piranha solution out for disposal. In some cases, depleted solution can be replenished.

In the event of exposure to piranha solution:
Heated piranha will dissolve rubber gloves in seconds. If any should splash or spill on the gloves, quickly remove them and place in the sink for neutralizing and rinsing later. Thoroughly rinse your hand at the site, just in case some solution penetrated. Splashed or spilled piranha on cloth will be evident as black spots. By the time the solution has reacted with the natural or synthetic fibers of clothing, the peroxide has been depleted and the temperature mitigated to a safer level. However, the sulfuric acid is still an issue of concern.

Contact with skin will be immediately apparent. Flush the contact area with water for at least 15 minutes while removing any affected clothing. Excessive acid on skin can be neutralized with a 2% solution of bicarbonate of soda (baking soda) located in the grey “Used Chemicals” cabinet. Medical attention may be required if the exposure is severe.

If contact with the eyes should occur, immediately flush the eyes with a gentle but large stream of water for at least 15 minutes, lifting lower and upper eyelids occasionally, using the eye washer beneath the first aid kit. Irrigate the eye with the sterile, isotonic solution located just above the washer. Call a physician at the Wardenburg Health Center immediately.

Piranha Spill:
- Wear Silver Shield gloves when managing a sulfuric acid spill.
- Slowly neutralize the spill with bicarbonate of soda.
- Wipe spill with absorbent cleanroom wipes and rinse the wipes in the sink before bagging them and disposing of them in the trash.

After you have finished reviewing the Clean Room Safety Module
please complete the Clean Room quiz in the Quiz Packet.