



Safety
with
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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, primarily via the processing benches, 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. Because the pressure in the lithography bay is positive relative to the other bays and corridor, these fumes could also find their way into adjacent sections of the cleanroom.

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 color coded labels.

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, along with a short discussion on KOH use.

Users should also be aware that there are occasionally two radioactive Polonium-210 alpha-emitter sealed sources in the lithography and 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 Clean Room Use

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.

With the possible exception of a water bottle kept in the gowning area, food and beverages are not allowed in the cleanroom.

The gowning protocol, which entails donning a gown, head and facial hair covers, gloves, booties and safety glasses, is not only meant to maintain the low-particle integrity of the area, but also provides 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 for Sealed Sources 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 module, the following rules for the use of the clean room must be observed:

Do not use HF or KOH anywhere other than the wet processing station designated for these materials only. Do not use this station for anything else. A one-person/one process bench policy applies to the HF/KOH station. Piranha use in the acid bench is subject to this policy. 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.

All metal etching should be performed on the acid bench, even if the etchants are not acidic. This applies to potassium iodine solution for etching gold and sodium hydroxide for etching aluminum. Ensure no acids are present when using alkaline solutions on the acid bench. Do not use the stainless steel bench for metal etching.

Except for small solvent squeeze 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 by lab personnel. 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 (XeF₂) are not allowed without permission of the lab manager.

No glass or metal closed-vessel reactors are permitted unless a variance is approved.

There is to be no heating of hydrofluoric acid or BOE.

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

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 by means of dropping by the office or email is encouraged.

Standard Safety Procedures

Always wear safety glasses/goggles when in the lithography bay (X121D).

Know your environment.

- Familiarize yourself with the location of the first-aid kit, fire extinguisher, eye washer, face shield, calcium gluconate antidote, isotonic and saline eye wash bottles, the yellow Material Safety Data Sheet (MSDS) binder, telephone, intercom, and fire extinguishers. 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/face 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. Used solvents and bases can be stored in the same cabinet.
- All acids are to be kept in the storage area beneath the acid bench.
- Peroxides are stored in the vented box within the acid bench.

Extraordinary Hazards

There are three aqueous compounds used in the cleanroom that pose particular safety hazards: Hydrofluoric acid (HF and vendor prepared Buffered Oxide Etchant or BOE), Piranha solution (and its more stable derivative Nano-Strip), and, to a lesser extent, Potassium hydroxide (KOH). The dangers of using hydrogen fluoride-bearing and peroxide-bearing solutions cannot be overstated. *These materials are to be used only during normal business hours when assistance is more forthcoming and because of longer response times of emergency responders when called after hours.* Ad-hoc instruction provided by lab personnel in the preparation, use, and storage of these materials is required.

Hydrofluoric (HF) Acid

HF acid 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 substitute the calcium and magnesium ions in the blood, causing cardiac arrest. The fumes can be just as harmful as contact with skin, however at room temperature and atmospheric pressure, the amount of vapor from an open container of aqueous HF will not pose a health hazard if used on the vented bench. This is why heating of open containers of HF acid is strictly forbidden. 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. All HF-bearing solutions are to be stored in the locked area in the lower left part of this bench.

Given its toxicity, should 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.
- Request the HF cabinet key from the lab manager. Leave the cabinet unlocked until all HF solutions are returned to the cabinet. Lock the cabinet and return the key.
- Use only in the designated HF processing station with the hinged sash down.
- Never prepare more than a 10% HF solution. Container labeling is imperative.
- When handling or using HF, always wear protective barrier garments and a face shield (face shield optional when working with the sash between you and the solution) when handling or using HF. Nitrile gloves can be thought of as first-order, short duration protection only for diluted (<5%) HF. MAPA (a nitrile, neoprene, natural rubber blend) gloves must be used when handling all other concentrations of HF. Three sizes of the vinyl coat aprons, which

should be worn with the open side to the back, are located in the rack beside the acid bench. Multiple sizes of MAPA gloves and optional face shield can be found on the wire shelf by the phone.

- HF etches silicon dioxide, the primary component of glass. Do not use glassware for HF. Instead use nalgene or fluoroware vessels and tools.
- When finished, carefully pour the used HF in a properly labeled nalgene container and place in the secondary container labeled “Hydrogen Fluoride Containing Solutions Only” in the lower left part of the HF/KOH bench.
- At the end of the HF session, check for holes in the gloves and any of dampness on clothing.
- A summary of these instructions is posted on the bench’s head-case door.

In the event of exposure to HF:

- Remove any affected clothing and set aside as hazardous material. Under these circumstances, modesty is going to have to be set aside.
- Rinse the contact site with water immediately for at least 5 minutes using either the faucet in the sink, the eye/face washer, or, in the event of a significant exposure, the emergency chemical shower beside the bench. A towel and gown can be found in the Plexiglas storage box just above the eye/face washer.
- Immediately after the rinse, liberally apply the 2.5% “Calgonate” calcium gluconate gel to the site. This antidote will begin to draw the fluoride ions out of the skin, so prompt application is imperative. Tubes of calcium gluconate can be found on the green eye wash dispenser on the wall to the immediate right of the acid bench.
- In the event of eye exposure, immediately irrigate the eye first with the small blue isotonic and then the large green sterile saline solutions located on the wall just beside the acid bench, followed by rinsing with water in the eye washer for at least 15 minutes. Do not put calcium gluconate on the eyes.
- Anyone assisting the exposed person needs to wear nitrile or MAPA gloves.
- Seek immediate medical attention. **All instances of HF skin exposure require medical evaluation***. Assistance in getting to a medical professional can be provided by the lab manager or any lab safety person. If exposure is to a moderate skin area (1-2 square inches), call 911 and have the EMT’s assist. If exposure is to an area larger than 2 square inches, the situation may be life-threatening and 911 needs to be called immediately so that intravenous calcium gluconate can be administered as soon as possible.
- Although the vapor should not pose a hazard if used in the bench with the hinged sash down, do not ignore any signs of possible vapor exposure such as eye, nose or throat irritation and/or coughing. Seek medical attention immediately.
- A summary of these instructions is posted on the towel/gown dispenser above the eye washer.

* By the advice of a toxicologist at the Rocky Mountain Poison and Drug Control Center

HF Spills:

- Always wear MAPA gloves and a vinyl coat 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 the 12” x 12” absorbent wipers. Isolate any disposable materials that come or may have come into contact the HF from normal trash by placing them in a

sealable plastic bag which will be labeled with a EH&S Hazardous Material/Waste tag. Let the lab manager know about the spill because the deck plate in the bench may need to be removed to clean the lower catch basin.

- Large spills outside the hood require evacuation of the whole clean room area. Anyone in the vicinity of the spill needs to leave their gown on the floor in the gowning area before leaving. No one is to enter the cleanroom unless a life-threatening situation exists. Immediately notify lab personnel of the situation so that a request for an EH&S HazMat team can be initiated.

Piranha Solution

Acid piranha solution, and a more stable, premixed derivative known commercially as Nano-Strip, is a solution of sulfuric acid and hydrogen peroxide. It is used primarily as a glass, sapphire and silicon 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. Wear MAPA gloves or double layer of nitrile gloves and a vinyl coat apron. A face shield 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 introducing it to 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 anywhere near where the solution will be made and used. This especially includes solvents resident on the substrate.
- Make only as much as piranha solution as you think you might need. The shelf life of this material is on the order of weeks.
- When mixing, 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. Nano-Strip is premixed and should be used as it is.
- 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 storage box.
- 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 upper left tray of the acid bench. 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 between the acid and HF benches. Irrigate the eye first with the small blue isotonic and then the large green sterile saline solutions located on the wall just beside the acid bench. Medical attention is highly advised.

Piranha Spill:

- Wear MAPA 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.

Potassium Hydroxide

Potassium hydroxide (KOH) is a strong base typically used for crystal-plane anisotropic etching of silicon and occasionally SiO₂. Although KOH does not inherently pose any greater health and safety hazard than the strong acids in the acid bench, it is included in this section because it is typically used at elevated temperatures, which make it far more caustic and dangerous, especially due to vapors.

Protocol for using KOH solution:

- This material is to be used at the HF/KOH bench only and stored only in the right-hand storage area beneath that bench. There is a one-person/one process policy on this bench. Put the hinged sash down.
- Wear MAPA gloves when preparing and using KOH.

- Long etching times are inevitable with KOH, so please put a sign announcing a KOH etch in progress when unattended.

In the event of exposure to KOH solution:

- You will know right away if you get KOH at any temperature on your skin. Rinse thoroughly with water for 15 minutes using either the faucet or eye/face washer beside the bench. Should there be significant exposure to cloths and skin, remove affected clothing and use the emergency chemical shower.
- For eye exposure, rinse with the eye/face wash and use the saline and isotonic solutions from the green dispenser box. Get immediate medical attention or blindness may result.
- Vapor exposure will manifest itself with strong irritation of mucous membranes around the eyes and in the nose and throat. Move to a place with fresh air, preferably outside. If symptoms persist, seek medical attention.

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