COSINC-Fab Facility
Safety Manual

Version 1.0
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This safety manual contains information and procedures specific to the COSINC-FAB. The purpose of this manual is to instruct all FAB users of the correct safety procedures that are to be followed at all times while conducting work at the FAB.

The rules described here have evolved from experience and exist to protect you and your fellow researchers. Failure to follow them may result in expulsion from the facility. If you have any questions, feel free to ask a staff member. Remember, there is no excuse for not following these safety procedures outlined or described in this manual.

[*Sections of the Fab safety manual have been reproduced from the University of Minnesota, Minnesota NanoCenter's Laboratory Safety Plan and the Stanford Nanofabrication Facility Laboratory Manual]

About COSINC

The Colorado Shared Instrumentation in Nanofabrication and Characterization (COSINC) is a multidisciplinary core research facility and service center, within the College of Engineering and Applied Science, that provides access to state-of-the-art equipment in the areas of micro and nanofabrication, nanomaterials characterization and metrology and offers expertise and advanced hands-on training in the same related areas. It is an open-research facility serving the academic, industrial and governmental researchers across campus and beyond. The facility offers a common platform for the convergence of multiple scientific and engineering disciplines and facilitates collaborative research with strategic partners and information exchange.

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1.0 GENERAL

1.1 Safety training requirements

All users must complete the following before beginning work in the Fab

- Environmental, Health, and Safety (EH&S) online courses
  - Hazardous waste generation
  - PPE
- Fab-specific online safety quiz
- Sign a Fab-specific safety form
- Fab lab tour with a FAB staff member
- Equipment-specific training—users are not allowed to use equipment and tools for which they have not received training.

1.2 Lab behavior

As in any area in which chemicals are used, eating and drinking are prohibited. Users may use cell phones in the clean rooms but headphones are not allowed.

Users should minimize clutter and remove or store everything brought into the lab. It is prudent that users are always aware of their work area and are sensitive to what others are doing around them.

Users should immediately report all accidents or tool malfunctions to a FAB staff member

1.3 Clothing

Full-length pants and fully enclosed shoes (no sandals, open toe, or sling-back shoes) must be worn at all times. Clothes should be light and comfortable to allow free movement underneath clean room gowns.

Clean room gowning protocols must be followed at all times. Instructions for gowning procedures are located near the entrance to each clean room.

1.4 Buddy system

For safety reasons, users are strongly discouraged from working alone in the lab. If a user anticipates working after hours (after 5:30 PM during the workweek and on weekends), the user must arrange for a buddy (preferably a FAB user) to be in the lab or in close proximity when working in ECEE 271 and at the acid and solvent benches in ECEE 271. To facilitate this, users are required to fill-out the "After-Hours and Weekend Buddy Log" sheet posted near each lab entrance. This log must include the buddy's name and time in the lab. This requirement is enforced by security and safety cameras installed in each lab.

1.5 Hazards overview

1.5.1 Gas hazards

Compressed gases pose both chemical and physical hazards. Some of the gases used at the FAB are inert; others are toxic, corrosive, flammable, or explosive. The primary health risks posed by gases are the physical hazards (fire, explosion) and inhalation (toxics and corrosives.) General information about some gases used at the FAB can be found in Section 7.0 (for more detailed

hazard information, please refer to the pertinent MSDS.) Because of these potential hazards, safe use of these gases is strictly determined by state and local regulations, and university policy. Although potential hazards are minimized by use of engineering controls, users must always be aware of the types gases and the hazards posed in the equipment being used.

1.5.2 Liquid chemical hazards

Liquid chemicals present the greatest potential risk for injury. They can cause severe burns, tissue, and organ damage, and can ignite and explode. The greatest health risks posed by liquid chemicals are physical (fire, explosion), direct contact with skin and eyes (tissue damage), and inhalation (pulmonary damage or long-term chronic effects). General information about some of these chemicals and their uses can be found in Section 2.6. For detailed hazard information, consult the pertinent MSDS—users should make every effort to understand the chemical processes in use. Knowing the general rules for how to safely transport, pour, use, and dispose of these chemicals is every user's responsibility.

1.5.3 Electrical hazards

Although equipment and tools are interlocked to prevent operator exposure, users should be aware of the electrical hazards for the tools they plan to use. Burns occur wherever the body completes a circuit connecting the power source with ground. Although the resistance of dry, unbroken skin to electric current is relatively high, the amount of current needed to kill a person is small. It is easy to exceed lethal levels of current, especially if the skin is broken, wet, or damp with sweat. Unless it is in your training, never open electrical enclosures or cabinets on equipment, even when the power is off.

A FAB staff member should be immediately notified of any potential electrical hazard that arise while working in the facility. With the exception of most personal electronics devices, any electrical equipment brought into the lab must have prior approval by a FAB staff member.

1.5.4 Other hazards

UV exposure through UV lamps is a potential risk in the FAB. UV-blocking safety glasses should be worn to prevent eye damage when using the mask aligner, UV/ozone cleaners, and UV light hammer. Always turn off the power source for the UV lamp and unplug the vacuum pump on the mask aligner when finished working. As UV lamps are mercury-based, they pose a chemical risk. If a UV lamp should break or explode users should not clean up the lamp, instead, isolate the immediate area and notify a FAB staff member.

Electromagnetic radiation may be generated by equipment using RF (primarily plasma etch and plasma deposition tools.) Users with pacemakers should be aware that RF sources are present in the lab. All equipment is shielded to prevent exposure; users should report any damage to shielding on the equipment or cables.

Cryogenic hazards are presented by liquid nitrogen and helium. Liquid nitrogen is 77 degrees K (196 degrees C below freezing) and will cause freezing burns. Users are not allowed to handle liquid nitrogen unless their equipment training covers it. Users must always wear protective gear (thermally insulated gloves and goggles) when handling liquid nitrogen.

2.0 CHEMICALS AND CHEMICAL STORAGE

2.1 FAB-stocked chemicals

The FAB will stock the following chemicals; use of these chemicals is included in the instrumentation hourly user fees.

- Solvents, strippers, developers
  - Methanol
  - Isopropanol
  - Acetone
  - Ethanol
  - Methyl isobutyl ketone (MIBK)
  - Remover PG (>99% n-methyl-2-pyrrolidinone (NMP))
  - AZ 400 K Developer (>85% water, <15% postassium borates)
  - AZ 400 T
  - MF319
  - RD6
  - RR2
- Resists
  - AZ4210
  - AZ9260
  - NR9
  - NR71
  - SU8-10
  - SU8-3050
- Acids
  - Hydrochloric acid
  - Nanostrips
  - Sulfuric acid
  - Nitric acid
  - Hydrofluoric acid
  - Various metal etchants
- Bases
  - Potassium hydroxide
  - Ammonium hydroxide

2.2 User-purchased chemicals

Users may purchase and store their own chemicals at the FAB by following the labeling and storage procedures outlined in Sections 2.3 and 2.5. Users should notify a FAB staff member before a new chemical is brought into the facility. Custom or in-house created chemical mixtures, reagents, and buffers cannot be stored in FAB without prior approval by FAB staff. Any chemical or chemical mixture that is not in its original container and not labeled per Section 2.3 will be disposed immediately.

2.3 Chemical labels

Users who store their own chemicals at the FAB must label their chemicals with a FAB provided labels as can be found above the sash of the solvent and acid hoods. This label should include the contents of the container (even if the chemical is its original container), the date, lab group, and name. Any non-FAB-purchased chemicals that are not labeled correctly will be disposed immediately. All non-FAB-purchased chemicals will be disposed of 18 months after their listed date. Do not use hazardous waste labels to label unused chemicals.

2.4 Material safety and data sheets (MSDSs)

Users should be familiar with a chemical's MSDS before using that chemical. The FAB will keep hard copies of all MSDSs on site. Electronic versions may be searched for online or by going to the manufacturer's web site.

2.5 Chemical storage

2.5.1 Liquid chemical storage

Acids must be stored in their respective bin underneath the acid bench fume hood in ECEE 271. Mixed, user-created acids that have been approved by a FAB staff member may be stored in the appropriate secondary containment bin near the acid bench as shown in Figure 2.2B. Bases must be stored in their respective bin underneath the solvent bench fume hood in ECEE 214. Opened containers of flammable solvent stocks, strippers, and developers may be stored in the yellow flammable cabinet at the entrance of the yellow clean room in ECEE 271. Unopened bottles of solvent stocks, etc. must be stored in a flammables cabinet in ECEE 214.

2.5.2 Solid chemical storage

All solid chemicals must be stored in the cabinet shown in Figure 2.2A which is located in ECEE 271; user-purchased chemical solids must be labeled per Section 2.3.

Figure 2.2 Chemical storage locations for common solvents and developers

2.6 Specific hazardous chemicals

2.6.1 Peroxides

All peroxides are highly oxidizing materials; energy is released when they are reacted. Some peroxides are unstable, and can explode. 30% hydrogen peroxide in water is stocked the ECEE 271 lab. Extreme care should be used in mixing solutions containing peroxides. Peroxides are incompatible with all forms of organic solvents and flammable materials.

A FAB staff member should be notified BEFORE a user begins generating ANY hydrogen peroxide (H_2O_2) waste. Hydrogen peroxide mixed with acids or bases may continue to produce oxygen gas after a user has finished an experiment and disposed of the H_2O_2 waste in a hazardous waste bottle. For this reason, all users who generate H_2O_2 waste must handle their H_2O_2 waste seriously and responsibly to avoid excessive pressure build-up in the waste bottle and subsequent explosion.

All H_2O_2 waste mixed with a bench acid must be placed in a glass bottle. To prevent waste bottles from exploding or bulging, users should make sure their waste bottle is in a secondary containment bin and leave the lid slightly loose to relieve oxygen gas build-up. All H_2O_2 waste bottles should be stored in the corresponding red bin located near the front of the lab. If the H_2O_2 waste is also

mixed with chemicals that give off toxic vapors (e.g. hydrofluoric acid, hydrochloric acid, etc.), these bottles should be stored in a secondary containment bin in a fume hood. Again, please consult a FAB staff member for appropriate handling of your H_2O_2 waste.

2.6.2 Acids

Nanostrips, i.e. “piranha” solution

The heated mixture of concentrated sulfuric acid and 30% hydrogen peroxide is commonly referred to in the semiconductor industry as "piranha clean." This mixture is an extremely aggressive oxidizer, used primarily for removing photoresist and, in sequence with other chemical mixtures, to remove contaminants (i.e., the "RCA" or pre-diffusion clean process). The proportions of sulfuric acid and hydrogen peroxide used will depend on the particular application.

The FAB stocks a commercially available brand of piranha solution called Nanostrips which is a stabilized formulation of sulfuric acid and hydrogen peroxide. The Nanostrips or piranha solution destroys organic materials it contacts (photoresist, cleanroom wipes, vinyl or latex gloves, skin.) Nanostrips/Piranha vapor is extremely caustic, so the piranha mix should be used only in a fume hood. Boiling Nanostrips/piranha spatters, so always wear protective gear when working over a hot plate. Piranha is incompatible with all solvents and flammable materials. It reacts violently when mixed with base. Do not add water directly to piranha to try to cool it; sulfuric acid is water reactive, so adding water will cause heating (not cooling!) and can lead to an explosion.

Nitric acid

Nitric acid is also water reactive (heating upon addition of water). Nitric and acetic acids are components of pre-mixed aluminum and nickel etchants. All oxidizers should be kept away from solvents, bases, and flammable materials.

Hydrofluoric acid and fluoride containing chemicals

See Section 8.0 for all hydrofluoric acid handling, storage, and safety.

2.6.3 Liquid etchants

Liquid etchants for etching metals are stored underneath the acid bench fume hood and should only be used in this fume hood.

2.6.4 Solvents

Flammable solvents

Acetone, isopropanol, and methanol may be found in the solvent wet benches. Acetone is often used to dissolve photoresist and other polymers. Isopropanol and methanol are often used for cleaning.

These chemicals are all flammable solvents with low flash points. This means that at sufficiently high vapor concentrations, they can be easily ignited at room temperature and, therefore, pose significant fire hazard. Thus, solvents should not be used on or near hot plates or near any electrical system. Solvents may also ignite or explode when brought into contact with chemical oxidizers (such as many acids) and so should not be mixed with, nor collected in the same waste container as these compounds. Solvents may be used only in designated solvent hoods.

Chlorinated solvents
Chlorinated solvents (such as chlorobenzene, trichloroethane, and methylene chloride) may be present in some special resist processes. Long term, repeated exposure to some chlorinated solvents is correlated to cancer and liver and nerve damage. Because of environmental hazards, chlorinated solvent waste must be collected in a waste container, separate from other kinds of liquid solvent waste.

Removers and strippers (PG remover, AZ-300T stripper, and related chemicals)

These are organic base mixtures, which are used for removing photoresist from wafers containing metal films (which are corroded by conventional piranha clean.) Unlike other acids and bases used in the lab, these strippers are not water-based and are combustible; by some criteria, they may be considered solvents. These strippers must never be directly mixed with strong oxidizers.

Glycol ether solvents
Methyl- and ethyl- glycol ethers may be present in some photoresists . These have been implicated in reproductive problems in semiconductor workers. In addition, some specialty chemicals, such as imported high performance resists, may contain methyl- or ethyl- glycol ethers. Glycol ethers may be referred to generically as "Cellosolve", but the following names also refer to glycol ether compounds: Methyl Cellosolve, 2-methoxyethanol, Ethyl Cellosolve, 2-ethoxyethanol (2EE), Ethylene glycol mono ethyl ether. Acetate salts of glycol ether compounds may also appear in some specialty photoresist formulations as: Cellosolve Acetate, Ethyl cellosolve acetate (ECA), Ethylene glycol mono ethyl ether acetate, 2-Ethyoxy ethyl acetate.

2.6.5 Alkali/Bases
Alkaline compounds, or bases, are the chemical opposite of acids, and may react violently when mixed with them. They are most commonly used in the lab in lithography and etch. Alkalis are caustic, so protective gear should always be worn when working with them to prevent contact with skin and eyes.

Heated solutions of 25%-30% potassium hydroxide (KOH) or tetramethyl ammonium hydroxide (TMAH) are commonly used to chemically etch silicon. TMAH presents special hazards (see next section.)

2.6.6 Tetramethylammonium hydroxide (TMAH)
Tetramethyl ammonium is a nerve agent (specifically, a ganglion blocker) and is found in MF-CD-26 developer, AZ-300 MIF developer, and AZ-300T stripper which are all stocked in the FAB. Its hydroxide form can allow rapid penetration through corrosive damage to the skin. Deaths have resulted in an industrial accident where 25% TMAH spilled onto workers even though they rinsed within a minute of exposure. TMAH is used at lower concentrations (2-3%) in most photoresist developer solutions. Health effects have been documented for large area exposure at these concentrations, so PPE should always be worn when handling developer solutions directly.

2.6.7 Gallium arsenide

All users should contact a FAB staff member before working with gallium arsenide materials. Gallium arsenide (GaAs) and its by-products are extremely toxic. All persons working with GaAs should develop especially good "housekeeping" habits and be constantly aware of how arsenic might be generated during processing. Avoid direct physical contact with GaAs and anything that comes into direct contact with GaAs. When breaking and scribing GaAs wafers, work in the solvent fume hood and wipe down all surfaces afterwards to prevent spreading of GaAs dust.

Any GaAs waste, no matter how small, must be considered hazardous, including GaAs-contaminated labwipes and old proximity-cap silicon wafers. Place GaAs waste in an airtight zip-lock plastic bag and place in the "Solid GaAs Waste" container underneath the solvent bench fume hood.

3.0 SPILL RESPONSE PLAN

3.1 General

Users must be prepared for proper response in the event of a spill. A detailed spill response plan is outlined in the Chemical Hygiene Plan; instructions for spill clean-up are located in the spill kits specified in Section 3.2. After a spill has been contained, notify a FAB staff member if not already present.

3.2 Spill kit locations

General-purpose spill kits for most acid, solvent, and mercury spills are located in ECEE 271. All work with acid is limited to ECEE 271. A hydrofluoric acid spill kit is located at the entrance of ECEE 271 as outlined in Section 8.1.

4.0 HAZARDOUS WASTE

4.1 Waste container compatibility

Know your waste and your waste container compatibility! Inorganic bench acids such as hydrochloric and sulfuric must be disposed in clear glass bottles. Hydrofluoric acid should be stored in polyethylene, Teflon, or polypropylene bottles. If the HF is also mixed with a bench acid, you must first neutralize the pH to 6 – 8 and then store the waste in a polyethylene, Teflon, or polypropylene bottle. Mixed solvent waste must be stored in glass containers, clear or brown. Bases can be stored in glass or plastic bottles. If you're not sure which container should be used to store your hazardous waste, search online for a compatibility chart or ask a FAB staff member.

4.2 Storage

Make sure a waste bottle does not already exist for your waste before creating a new one. Do not fill waste bottles completely full—leave approximately 2-3 inches of head space. Once a bottle is full, place it in the appropriate waste pick-up cart located at the back of the lab in ECEE 271. A FAB staff member will contact EHS for pick-up of the hazardous waste bottle

4.2.1 *Hazardous waste storage in ECEE 271*

Hazardous waste bottles are stored below the solvent bench hood in ECEE 271 as shown in Figure 4.1A. Empty bottles for new waste may be located to the left of the solvent bench. Acid waste should not be generated in ECEE 214.

4.2.2 *Hazardous waste storage in ECEE 271*

Common solvent, etchant, developer, photoresist stripper and acid hazardous waste is kept between the acid hood and the development hood in room ECEE 271. Each waste has its own bottle, if you cannot find the bottle for the waste you have generated ask FAB staff. Hydroflouric Acid waste is kept underneath the acid hood as in figure 4.2.

Figure 4.2 Hazardous waste collection sites in ECEE 271

5.0 WET BENCHES

5.1 General

Liquid chemicals may only be used at wet benches. The exception is squeeze or spray bottles containing mild solvents for cleaning (see Section 5.4). Wet benches are designed for the safe use of chemicals; only designated chemicals or classes of chemicals may be used at each wet bench. Every wet bench contains an exhausted area. There are two general types of wet benches in the lab: those used for processes which use solvents/bases and those used for acids. To use a wet bench, users must book time on the bench using the online scheduler. Bench space and all labware should be cleaned and put away after a user has finished their work. Users must label all containers and experiments at the wet bench with contact info and date if the user is not present for the entire duration of the time booked at the wet bench.

5.2 Solvent benches

Solvent benches are located in ECEE 271. Squeeze bottles of isopropanol, methanol, acetone, and water are stored at these benches at all times. A one gallon, glass, hazardous chemical waste bottle is kept in both fume hood benches at all times for disposing isopropanol, methanol, acetone, and water waste only. All other solvent/base waste should be disposed in its own bottle labeled per Section 4.3; these waste bottles may be stored underneath the solvent bench fume hoods per Section 4.2. Two hot plates and spin coaters are kept permanently in the acid bench in ECEE 271; users must be trained on this equipment before use.See Section 5.5 for correct hot plate usage procedures.

5.3 Acid bench

The acid bench in ECEE 271 should be used for all acid work. This includes Nanostrips/piranha solutions, hydrofluoric acid, metal etchants, etc. Hydrofluoric acid waste and calcium hydroxide HF neutralizing solutions and creams are stored at this acid bench in the fume hood; see Section 8.0 for HF safety and handling. All acid and hydrogen peroxide waste generated at this bench should be labeled per Section 4.3 and stored in the appropriate waste accumulation site per Section 4.2.

5.4 Squeeze bottles

Bottles containing mild solvents (acetone, isopropanol, or methanol) are the only chemicals that may be used outside of wet benches. They still should, however, be stored at the solvent benches, and they must be properly labeled. They should be used only very sparingly outside of solvent wet benches, because of their low vapor pressure, and they should never be used at non-solvent wet benches nor near any electrical equipment.

5.5 Hot plates

Do not leave an experiment on a hot plate overnight, even if the hotplate is turned off; NEVER leave a hot plate turned on overnight. If you must leave a hot plate unattended, please label your experiment with your contact information and chemicals/materials that are on the hot plate. Label with lab tape affixed to the hotplate or dish. Do not label hot plates/experiments with paper towels as these will easily fall to the floor or blow away. Consistently monitor your hot plate temperature. Fluctuations in the airflow in the fume hoods across the hot plate surface will affect its surface temperature if you are not using a programmable hot plate equipped with a thermocouple for feedback control.

6.0 PERSONAL PROTECTIVE EQUIPMENT (PPE)

6.1 General

While operating certain equipment, PPE will be required. Use of any wet benches or the normal handling or transportation of any chemicals in the lab requires the use of PPE. Disposable gloves, safety glasses, and lab coats are stocked in all labs at the FAB. Please consult the Chemical Hygiene Plan for more specific PPE requirements. Contact a FAB staff member if you require additional PPE for work at the FAB. Users who handle hydrofluoric acid require additional PPE and should refer to Section 8.0.

6.2 Eye protection

Eye protection in the form of safety glasses or goggles should be worn at all times in the lab. The exception is when using a microscope or equipment with eye pieces. For users requiring corrective lenses, impact-resistant prescription safety glasses with side shields may be purchased from most prescription glasses suppliers. Contact lenses are allowed, but safety glasses are still required for normal lab activities. Most safety glasses are designed to protect only against flying fragments, however, not chemical splash hazards. So full face shields should be worn in addition to glasses when handling chemicals or working at chemical wet benches.

7.0 COMPRESSED GASES

7.1 Hazardous gases

Boron trichloride and chlorine gas are the only toxic gases in the FAB which pose a significant health hazard. Both gases are highly corrosive and are stored in an exhausted gas cabinet in ECEE 271C which is equipped with an alarm in case of loss of air flow from the exhaust manifold. The following is an instruction manual for working with Chlorine and BCl3 at the COSINC-FAB.

7.1.1 Toxic Gas Detection Systems in COSINC-FAB

The COSINC-FAB cleanroom (ECEE 271) contains a plasma etcher that utilizes both chlorine (Cl_2) and boron trichloride (BCl_3) gas. The gases are supplied via compressed gas cylinders which are housed in a toxic gas cabinet near the etcher. The gases are connected to a control system in the gas cabinet and delivered to the etcher as needed via stainless steel tubing. The exhaust gases from the etcher flow to a toxic gas scrubber which reacts the toxic gases away before the exhaust is ejected from the building.

BCl_3 gas readily hydrolyzes in ambient air and forms hydrochloric acid (HCl) and boric acid. Due to the health risk of exposure to Cl_2 or HCl, toxic gas detection and alarm systems have been installed in the COSINC-FAB. There are two distinct systems – one detection system measures airborne Cl_2 and HCl levels in the ambient air around the etcher and the other system monitors inside the toxic gas cabinet. The ambient air gas detection system is connected to four light trees – two are mounted on the cleanroom wall across from the gas cabinet and the other light trees are mounted on a wall inside the gowning room.

The light trees have 4 modes:

- Green light = Everything okay
- Amber light = Warning Alarm
- Red light (+ sounding horn) = High level alarm
- No light illuminated = Fault or malfunction in detection system

Personnel working in the COSINC-FAB should read and understand these procedures to be prepared in the event of an emergency.

1. Before entering the COSINC-FAB, inspect the light trees and ensure the ambient air toxic gas detection system has no warnings or faults (the green light on the light trees is illuminated).
2. Ensure the doors to each room in the COSINC-FAB remain closed at all times, except when entering or leaving.
3. If possible, perform work with the plasma etcher only during regular business hours and when others are present in the lab. Use of the plasma etcher is limited only to properly trained users.

The detection systems have 2 levels of alarms which are dependent on measured Cl_2 or HCl levels:

--WARNING ALARM (LOW LEVEL) (AMBER LIGHT)—
Gas concentrations measured at the low level alarm threshold are safe for most individuals to be exposed for a limited time (i.e., 5 minutes) However a thorough inspection of the equipment is warranted any time a warning alarm sounds. Follow the emergency procedures listed below for a warning alarm before continuing work with the plasma etcher.

- 0.4 ppm Cl_2
- 2.0 ppm HCl

--HIGH LEVEL ALARM (DANGER) (RED LIGHT & SOUNDING HORN)—
Gas concentrations measured at the high level alarm threshold are approaching levels that are unsafe for human exposure for any amount of time. Immediately inform others in the lab, pull the fire alarm and exit the building. WAIT outside for fire fighters to arrive and ADVISE them of the issue.

- 0.8 ppm Cl_2
- 4.0 ppm HCl

7.1.2 Emergency Procedures: Ambient Air Gas Detection System

If the ambient air toxic gas alarm activates, immediately take the following steps:

a. Look at an alarm light tree. If a RED LIGHT is illuminated and a horn is sounding (high level alarm), take the following steps:
   i. Stop work. If safe to do so, shut down the plasma etcher and/or other lab equipment.
   ii. Inform other lab members about the alarm, leave the room and close the door.
   iii. Exit the building and activate a building evacuation by pulling the building fire alarm on your way out of the building.

iv. Wait for the Boulder Fire Department in a safe location outdoors. When the fire department arrives, approach a firefighter and explain the situation. This is important to ensure the situation is accurately communicated to emergency response personnel.
v. The COSINC-FAB should not be re-entered until the "all clear" is issued by the Boulder Fire Department. The plasma etcher cannot be used until the issue that caused the high level alarm to activate is determined.
vi. The high level alarm is non-latching, meaning it will automatically reset once a measured gas concentration drops below the set threshold

b. If an AMBER LIGHT is illuminated (warning alarm), take the following steps:
   i. Attempt to determine why the gas was detected by inspecting the equipment, piping and valves (only if it is safe to do so).
   ii. The warning alarm is a non-latching alarm, meaning it will automatically reset if gas concentrations drop below the set threshold.
   iii. If the cause of the leak cannot be determined after 5 minutes, ensure there are no toxic gas alarms sounding in the toxic gas cabinet and then manually close the valves on the CL_2 and BCL_3 cylinders.
   iv. Place signage indicating an equipment malfunction on the plasma etcher and that it should not be used. Immediately notify the COSINC-FAB manager of the problem.
   v. Do not leave the building until the concentration of gas has subsided and the alarm resets. If the alarm remains activated after 5 minutes has passed, notify others and exit the COSINC-FAB. Remain in the hallway outside of the COSINC-FAB and call the lab manager or EH&S for help.

c. Any time a serious toxic gas leak or system malfunction is suspected, follow the instructions for a high level alarm and evacuate the building.

Any time an alarm has been activated or a problem with the toxic gas detection system is suspected, call the lab manager (Alex Cell) 303-718-1831 building manager (Bret Moreland cell) 303 503-7939 and EH&S 303-492-6025 (after-hours call CUPD 303-492-6666).

7.1.3 Emergency Procedures: Gas Cabinet Toxic Gas Alarm

If the gas cabinet toxic gas alarm activates, immediately take the following steps:

a. Always give close attention to the Ambient Air Gas Detection System and follow the emergency procedures for this alarm. If at any time a RED LIGHT on a light tree is illuminated, the lab and the building must be immediately evacuated.
b. Stop work. If safe to do so, shut down the plasma etcher and/or other lab equipment.

c. Look at a gas monitor on the toxic gas cabinet. If a RED LIGHT is illuminated on a gas monitor and a HORN IS SOUNDING on the cabinet, this is a high-level alarm. Take the following steps:
    i. The gas cabinet controls will automatically turn off the gas supply when a gas monitor goes into a high level alarm. Ensure the toxic gas cabinet doors are securely closed and do not open the access windows.
    ii. If there is an obvious failure due to the rupture of a valve or a pipe leak (loud hissing noises and a cloud of white smoke (hydrogen chloride) or yellow-green gas (chlorine) within the gas cabinet, the lab and the building must be immediately evacuated.
    iii. Observe the gas monitor in alarm. If the concentration on the readout is below 10 ppm for Chlorine or 50 ppm for Hydrogen Chloride, stay and observe the trend of the concentration. Is it rising or falling?
    iv. If gas concentration exceeds 10 ppm for Chlorine or 50 ppm for Hydrogen Chloride, the lab and the building must be immediately evacuated.
        1. Immediately inform others in the lab, pull the fire alarm and exit the building. WAIT outside for fire fighters to arrive and ADVISE them of the issue.
    v. If gas concentration is falling, wait until the concentration on the readout falls to below 0.4 ppm Chlorine or 2 ppm Hydrogen Chloride.
        1. Open an access window into the cabinet and manually close the valves to the Chlorine and Hydrogen Chloride cylinders.
        2. To silence the gas cabinet alarm, press the “ACK” button on the control panel.
        3. Shut down the plasma etcher and the gas scrubber. The plasma etcher cannot be used until the failure that caused the leak is discovered and repaired. Label the plasma etcher and the gas cabinet as ‘Out of Order’.
        4. Notify the lab manager of the leak.
d. Look at a gas monitor on the toxic gas cabinet. If a RED LIGHT is illuminated on a gas monitor but a HORN IS NOT SOUNDING on the gas cabinet, this is a low-level alarm. Take the following steps:
    i. Observe the gas monitor in alarm. Is the gas concentration rising or falling?
    ii. If the concentration is rising and exceeds 10 ppm for Chlorine or 50 ppm for Hydrogen Chloride follow the instructions above on line iv.
    iii. If the gas concentration is falling, wait until the concentration on the readout falls to below 0.4 ppm Chlorine or 2 ppm Hydrogen Chloride and follow the instructions above on line v.
    iv. Attempt to determine why the gas was detected by inspecting the equipment, piping and valves (only if it is safe to do so).
e. Any time a serious toxic gas leak or system malfunction is suspected, follow the instructions for a high level alarm and evacuate the building.

f. Any time an alarm has been activated or a problem with the toxic gas detection system is suspected, call the lab manager (Alex Denton) 303-718-1831 and EH&S 303-492-6025 (after-hours call CUPD 303-492-6666).

	8-hr TWAs (PPM)				Low-Level Alarms (PPM)*	
	ACGIH	**NIOSH**	**CAL/OSHA**	**OSHA**	**Current Alarm**	**Sensor Limit**
Chlorine	0.1	N/A	0.5	N/A	0.4	0.25
Hydrogen Chloride	N/A	N/A	0.3	N/A	2	0.95

	Short-Term Exposure Limits (PPM)				High-Level Alarms (PPM)**	
	ACGIH	**NIOSH**	**CAL/OSHA**	**OSHA**	**Current Alarm**	**Sensor Limit**
Chlorine	0.4	0.5	1	1	0.8	0.25
Hydrogen Chloride	2	5	2	5	4	0.95

	IDLH			
	ACGIH	**NIOSH**	**CAL/OSHA**	**OSHA**
Chlorine	N/A	10	N/A	N/A
Hydrogen Chloride	N/A	50	N/A	N/A

7.2 Non-toxic gases

7.2.1 Nitrogen and clean dry air (CDA)

House nitrogen and CDA are plumbed throughout the facility for general use in equipment and other utilities. The supply can run up to 80 psi, which can pose a hazard: do not direct a nitrogen or air gun toward your own body (especially the face and eyes) or toward anyone else.

7.2.3 Etch gases

Tetrafluoromethane (CF_4), Oxygen (O_2), and Trifluoromethane (CHF_3) are commonly used in dry etching. Although the gases themselves generally pose low health risk, their by-products in etch systems are less benign. Make sure to follow proper operating procedures for pumping down or purging etch chamber systems following processing.

8.0 HYDROFLUORIC ACID

This section describes injury prevention, personal protective equipment (PPE), safe working practices, spill cleanup, and waste disposal for users who work with hydrofluoric acid (HF). All users must undergo hands-on HF training with a FAB staff member prior to any work with HF.

HF is a unique inorganic acid and needs to be treated differently than other strong inorganic acids such as sulfuric and hydrochloric acids. The major route of occupational exposure in research labs is skin contact with HF solution or droplets. The fluoride ions are very rapidly absorbed through the skin and eyes and cause systemic toxicity.

HF progressively releases fluoride ions and the 'free fluoride ions' penetrate and spread into the deepest tissues and form insoluble salts with calcium and magnesium, resulting in liquefactive necrosis (also known as colliquative necrosis, tissue death that liquefies the affected cells), hypocalcaemia (low calcium levels), hypomagnesaemia (low magnesium levels), and hyperkalemia (high potassium levels). The liquefactive necrosis mechanism differentiates HF from other strong acids which cause damage via the 'free hydrogen ions', thus causing coagulation necrosis with precipitation of the tissue proteins.

Injury and illness prevention is the most significant part of HF management in research labs because internal damage can occur before symptoms appear. Pain associated with exposure to solutions of HF (1-50%) may be delayed for 1-24 hours. If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss or death. HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid.

8.1 First aid and spill kit

An HF first aid and spill kit is located to the left of the acid bench fume hood on the floor in an orange bucket as shown in Figure 8.1. The content of this HF first aid and spill kit should be verified by all users prior to their first work with HF. FAB staff will verify the contents of this kit at the start of each work week.

Figure 8.1 HF first aid located to the right of the entrance of ECEE 271

Figure 8.2: Spill response kit located on the far wall of ECEE 271

The contents of the FAB's HF first aid and spill kit (with descriptions) include:

- PPE (use PPE in HF PPE cabinet if possible):
  - Apron
  - Gloves
  - Goggles
  - Boot covers
  - Respirator with 2 cartridges (NOTE: respirators are not to be used by untrained users; if a respirator is needed due to an HF spill >250 mL and >40 wt% HF outside of the acid bench fume hood, evacuate all personnel from the lab space and call 911)
- 4 Hydrofluoric acid neutralizer shaker bottles (labeled as Kolor-Safe® / Kolor-Lock ®) for sprinkling on HF spills
- pH test paper for testing pH of spill after neutralization (should be between 6 and 8)
- Scrapers for mixing slurry spill to assure all HF is neutralized
- Scoop with brush to clean up slurry / solid after cooling and neutralization
- 2 Hazardous waste bags for disposal of neutralized HF waste
- Calgonate® calcium gluconate (CG) gel for treating HF skin exposure (see section 8.2)

- Calgonate® emergency eyewash for treating HF eye exposure (see section 8.2)

Additional tubes of 2.5% calcium gluconate (CG) gel may be found on the back shelf of the acid bench fume hood.

8.2 Emergency/medical treatment

- **First aid measures MUST BE started within seconds in the event of HF contact in any form or concentration!**
- **If HF is not rinsed off immediately after the exposure, severe burns and skin damage will definitely occur.**
- **Even at very low concentrations, HF can be irritating to the respiratory tract, eyes, and skin.**

Without delay, rinse the affected skin area with water for at least 20 minutes and apply CG gel to neutralize the fluoride ions and prevent further tissue destruction. Even if the affected user feels no pain, the affected area must be immediately rinsed off with copious amount of cold water at least for 20 minutes, followed by application of CG gel to the affected skin area. For HF exposure on the hand, users may inject CG gel into a clean nitrile glove and then place their hand in the glove for better CG gel/skin contact. Researchers must then seek immediate medical attention for HF burns BY GOING TO THE HOSPITAL.

If the spill has occurred near the eye, eyelid, or eyelash, irrigate exposed or irritated eyes with cold water for at least 20 minutes. The 20 minutes may be limited to 5 minutes only if a CG eye wash solution is readily available and is used immediately after the 5 minutes of cold water rinse, and the individual proceeds to ETC without delay.

Ingestion of HF can cause severe mouth, throat and stomach burns. In case of ingestion, dilute the acid by giving large quantities of water and eight to twelve antacid tablets, and proceed to ETC without delay. DO NOT induce vomiting.

If no one is immediately available to assist you or drive you to ETC, call 911 and let them know you have a medical emergency with HF exposure such as splatter near the eyelid or other parts of the body.

A medical evaluation is necessary for any exposure to HF. Additional medical treatment/consultation should follow with appropriate medical specialists for eyes and/or skin burns. For detailed medical treatment, please review the Honeywell reference document, "Recommended Medical Treatment for HF Exposure."

8.3 Personal protective equipment (PPE)

When working with HF, safety glasses with side shields are NOT adequate. Outer neoprene, nitrile, or butyl rubber gloves (14 mil or thicker), inner double nitrile gloves (4 mil thick), butyl rubber apron, face shield, chemical splash goggles, lab coat, long pants, and closed-toed shoes must all be worn at all times.

Hydrofluoric acid-specific PPE for work at the ECEE 271 acid bench can be found on top of the flammable cabinet at the entrance of ECEE 271. Face masks can be found to the left of the Acid hood.

Additional PPE practices when handling HF include the following

- Silver shield gloves with inner double Nitrile gloves can be used for spill cleanup work
- If dexterity of silver shield gloves impacts the handling of HF, review chemical resistance charts for other glove options.

8.4 Safe working practices

- Users are not permitted to store their own HF at the FAB and are strongly discouraged from transporting open HF bottles between labs in IATL. If your HF requirements are not being adequately met, please inform a FAB staff member
- Users must be informed of all storage locations for both stock and waste HF solutions
- Never store or use HF with glass materials/containers or place HF containers in a location that has not been designated for HF storage by a FAB staff member
- All tools and labware that come in contact with HF during an experiment should be made of polyethylene, polypropylene, or polytetrafluoroethylene plastic
- All work involving HF or other HF-containing reagents must be performed inside the acid bench fume hood in ECEE 271
- Users must reserve the acid bench fume hood using the online scheduler before anticipated work with HF
- Users are strongly discouraged from working alone with HF in the lab. At a minimum, a second individual should be informed of your anticipated work with HF
- Users are not permitted to leave the acid bench area wearing PPE used to work with HF nor leave open containers/labware with HF unlabeled or unattended
- When finished working with HF, inspect all gloves and apron for HF droplets and place these items back in their appropriate storage location; see Section 8.3. Place all disposable PPE in the red biohazardous waste bin located in the acid bench work area
- Wipe any suspected HF droplets with a Kolor-Safe®-soaked-towel followed by clean-up with DI water to remove any calcium fluoride residue; refer also to Section 8.5.1.
    - A fresh, 1 L bottle of 12 wt% Kolor-Safe® is located on the back shelf of the acid bench fume hood and can be used for clean-up with towels. Dispose of all towels in the red biohazardous waste bin.
- Researchers must thoroughly wash their hands after handling HF bottles and reaction vessels

8.4.1 Standard operating procedures (SOPs)

Before a user can begin any work with HF, they must submit an SOP for their work and experiments to be performed at the FAB. This SOP should include the following sections and must be submitted to a FAB staff member.

1. Purpose of experiment
2. Reagents and labware items

    a. List all reagents and equipment needed for the experiment including concentrations and anticipated volumes of chemicals per experiment
3. Experimental method
    a. Describe the experimental steps to be performed in the acid bench fume hood at the FAB
4. Waste disposal
    a. Include method for neutralizing and cleaning all tools that have come in contact with HF. This typically includes rinsing tools in a calcium hydroxide bath prior to final rinsing and drying; see Section 8.4.2
    b. List out anticipated waste mixtures including all components and their approximate concentration in the waste mixture in weight percent
    c. Include anticipated volume of waste per experiment
    d. If HF waste contains hydrogen peroxide (H_2O_2), please refer to Section 2.6.1 and list appropriate methods for handling HF/H_2O_2 waste

Any updates or revisions to a user's SOP that pertain to new chemicals or chemical mixtures and corresponding waste must be submitted to a FAB staff member.

8.4.2 Additional prudent work practices

Make sure the acid bench fume hood is on and working and that the protective sash has been lowered to protect all users from splashes.

Proper PPE must be worn anytime HF is to be poured from a stock solution or when working in the acid bench and an open vessel containing HF is in use by yourself or another user; see section 8.3 Personal protective equipment (PPE).

A plastic bottle carrier should be used for transporting HF bottles between the storage cabinets, the acid bench, and hazardous waste pick-up locations.

8.5 Spill cleanup

- HF is a unique inorganic acid and does not completely dissociate. Therefore, researchers should allow sufficient time for the neutralizing agents to neutralize the acid
- An HF specific spill kit is located next to the acid bench as described in Section 8.1
- Spill kits containing silica such as sand, vermiculite, Floor-Dri or kitty litter should not be used because HF reacts with silica to produce a toxic silicon tetrafluoride (SiF_4) gas
- Properly dispose of waste from an HF spill using polyethylene containers or the hazardous waste bags provided in the spill kit
- HF spillage should be contained—avoid allowing the spill to go down the drainage sink in the acid bench fume hood, if possible. If necessary, neutralized liquid within the fume hood should be diluted with copious amount of running water
- Surfaces and equipment should be thoroughly wiped down with calcium-hydroxide-soaked-towels as a final measure following any HF spill clean-up
- Inform a FAB staff member after clean-up of any HF spill incident

8.5.1 Spills inside acid bench fume hood

- Small spills (< 2 mL and 40% HF) may be cleaned with a paper towel or wipe.

- Place all towels/wipes used to clean-up HF spills in the Kolor-Safe® bath container briefly and dispose in the red biohazardous waste tub.
- Soak a towel/wipe with Kolor-Safe® solution and wipe all areas where an HF spill was located. Clean-up any neutralized solid residue left behind from wipe with DI water

- Larger HF spills in the acid bench fume hood can be neutralized using the Kolor-Safe® / Kolor-Lock® calcium hydroxide powder from the HF spill kit (orange bucket shown in Figure 8.1) as shown in Figure 8.4 and by following these instructions while wearing the appropriate PPE
  - Sprinkle Kolor-Safe® on the spill. The spill will change color during neutralization as indicated on the Kolor-Safe® bottle. Exercise caution in applying the powder to avoid splashing the spilled acid and thus enlarging the affected area
  - Use the scrappers in the spill kit to mix the slurry to be sure that all liquid is thoroughly neutralized; add more powder if color does not stay the color indicated on the Kolor-Safe® bottle
  - Allow neutralized solid to cool
  - Observe the spill area for remaining pools of liquid
  - Once the residue has cooled and uniformly changed color, check the pH of the solution using pH test strips in the HF spill kit. Assure you have reached a pH between 6 and 8
  - Sweep or shovel the neutralized solid using the scoop, brush, and heavy duty disposal bags provided in the spill kit. Seal bags with ty-raps provided in the kit. Place the bags in a well-taped cardboard box and label with a correctly filled out hazardous waste lab
  - Soak a towel/wipe with Kolor-Safe® solution and wipe all areas where the HF spill was located.
  - Clean-up any neutralized solid residue with DI water and paper towels
  - Notify a FAB staff of the spill incident and cleaned-up waste

Figure 8.4 Kolor-Safe® / Kolor-Lock® Solidifier for hydrofluoric acid neutralization

8.5.2 Spills less than 250 mL outside acid bench fume hood with HF < 40%

- Follow same procedure as outlined in Section 8.5.1

8.5.3 Large spills greater than 250 mL outside acid bench fume hood with HF > 40%

- Evacuate all personnel from the lab and call 911 immediately

8.6 Waste disposal

In addition to these practices for handling HF waste, all users should follow standard hazardous waste storage practices and labeling procedures as described in Section 4.3. HF on labels should be written out as hydrofluoric acid, not "HF."

- Never pour HF waste down the drain. If small amounts of HF are accidently spilled in the acid bench sink, sprinkle with Kolor-Safe® (see Section 8.5.1) and flush with copious amount of water. For larger spills, refer also to Section 8.5
- Do not mix HF with other laboratory generated waste
- All containers used to store HF waste should be made of polyethylene, polypropylene, or polytetrafluoroethylene plastic
- Never store or use HF waste with glass materials/containers—HF is highly reactive with silica and will attack glass bottles and form toxic SiF_4

Figure 8.2: HF hazardous waste accumulation area underneath the acid bench in ECEE 271

- If HF waste also contains hydrogen peroxide (H_2O_2), please refer to Section 2.6.1 for appropriate methods for handling H_2O_2 waste and keep the HF/H_2O_2 waste in the HF waste storage bin shown in Figure 8.5.

9.0 DISCIPLINE

The above write-up is intended to provide information and guidelines necessary to keep the lab running smoothly. Many of these guidelines are simply common sense and require consideration of the other laboratory users. Others require specific knowledge of either proper equipment use or of chemical handling and safety. It is the user's responsibility and obligation to be trained on a particular piece of equipment or to be aware of correct chemical handling procedures. If a user does not have these skills, please request training from a FAB staff member before performing the task.

The guidelines are subject to revision dependent upon laboratory procedural changes. Be aware of new or changing lab guidelines.

Please encourage proper facility usage among other users and report any serious violations of the guidelines to lab staff.

The following procedure will be used to discipline offenders in the laboratory. For each offense by a particular individual which is deemed unique by the FAB safety officer, the following three step system will be used:

- **First Offense:** The individual will meet with the safety officer. If the offense was a rule the individual was unaware of, a warning will be given. If the offense was more severe, a memo will be sent to the advisor. This determination will be made by the safety officer and the offender.

- **Second Offense:** The individual will meet with safety officer, FAB director, and advisor. The corrective action will then be decided by this group. This action may include suspension of lab use, retraining, and/or charges billed to the user's account for clean-up/handling of the infraction by FAB staff.

- **Third Offense:** The individual will be suspended indefinitely from the laboratory and/or charges will be billed to the user's account for clean-up/handling of the infraction by FAB staff.