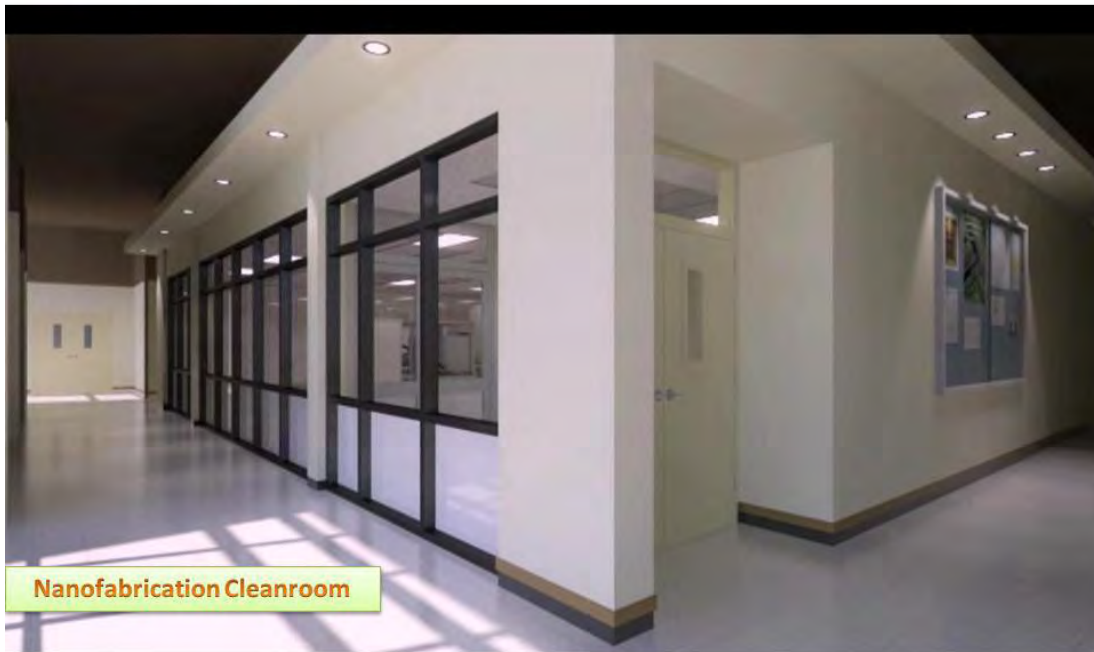


UNT CMEE Nanofabrication Cleanroom User's Manual



EMERGENCY CONTACTS

Primary Emergency Contact: 911
Poison Control Center: 800-222-1222
UNT Police: 940-565-3000

For Non-Emergency Chemical Situations:
Department of Risk Management
(DRM): 940-565-2123

If Time Permits, Contact the Cleanroom Staff:
Dr. Jianchao (J.C.) Li: 940-369-5318

Emergency Response Checklist

IF A TOXIC GAS LEAK OCCURS

1. Push a Yellow “Gas Off” button
2. Evacuate the building immediately
3. Alert others on the way out
4. Meet outside in parking lot 1 at Discovery Park

IF YOU HEAR THE FIRE ALARM

1. Evacuate the building immediately
2. Alert others on the way out
3. Meet outside in parking lot 1 at Discovery Park

IF YOU SEE SOMEONE UNDER THE EMERGENCY SHOWER OR EYE WASH

1. If the victim is by themselves, stay close to assist.
2. Call 911 and demand an ambulance.
3. If requested, assist the person in removing contaminated clothing being careful not to become contaminated.
4. Advise person to stay in shower 5 minutes for HF contamination, 15 minutes for all other chemicals.
5. If the chemical is Hydrofluoric Acid (HF) assist the victim in applying Calgonate (calcium gluconate) while wearing clean gloves.
6. Get the MSDS sheet (E151) and hand it to the Emergency Response Team or fire department.
7. Notify a staff member.

IF YOU GET CHEMICALS ON YOUR SKIN

1. Approach the nearest emergency shower or eye wash and pull the handle to activate.
2. Demand help but remain under the emergency shower or eye wash.

IF A FIRE STARTS

1. Pull fire alarm located at emergency exit doors.
2. Evacuate the building immediately.
3. Alert others on the way out.
4. Meet outside in parking lot 1 at Discovery Park

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Policies & Procedures

Highlights & specific issues:

- Hair net, gown, booties w/shoe covers, masks, gloves, and safety eyewear.
- Keep all hair and ears covered with hood or cap.
- Never open your gown in the cleanroom.
- Never touch your skin with your gloves. If you do, put on clean gloves immediately.
- Only authorized users may enter the cleanroom unescorted.
- The buddy system must ALWAYS be used in the cleanroom.
- Visitors must be escorted by a cleanroom qualified faculty/staff member.
- Visitors must sign in/out in the visitor log.
- No food or drink is permitted in the cleanroom.
- No corrugated cardboard, styrofoam, foam rubber or non-cleanroom paper is permitted in the cleanroom.
- No pencil, erasers or retractable pens are permitted in the cleanroom.
- Be considerate by cleaning up your own mess, not messing up someone else's work, letting the staff know when new supplies are needed, etc.
- Ask for permission before bringing anything in or taking anything out of the cleanroom.
- DO NOT modify equipment without the approval of the Cleanroom Staff.
- IF YOU AREN'T SURE HOW IT WORKS, ASK BEFORE YOU USE IT!
- Follow the Cleanroom Safety Guidelines.

1) Wafer Handling [2]

- A. NEVER sneeze, cough, or spit toward your wafers even with a mask. Resulting spots are non-removable.
- B. Never speak towards your wafer.
- C. Avoid passing anything over your wafer which may release particles
- D. Whenever possible, store wafers in covered containers.

2) Tools and Repairs

- A. Vacuum or blow clean all equipment followed by an Isopropyl alcohol wipe before taking it into the cleanroom. No equipment will be modified without prior approval of the Cleanroom Staff. No new equipment will be moved into the cleanroom without prior approval of the cleanroom manager.
- B. Keep parts and tools at the workstation as clean and orderly as possible. Use toolboxes where possible.
- C. Any work or tools dropped on the floor shall be considered contaminated, and must be cleaned.
- D. Never leave exposed critical parts on the workbench.

E. Work on a clean surface.

3) Good Manners and Good Sense

A. Obey signs on equipment or in specific areas.

B. Refill squirt bottles that you find empty.

C. Let empty solvent jugs evaporate dry. Rinse acid and solvent jugs three times with DI water.

D. When working with acids or solvents, wear chemical resistant nitrilite/neoprene gloves available in the storage room. Before using the gloves, be sure they are in good shape. Replace them if they are not.

F. When disposing of acid mixtures, **dilute with lots of water.**

G. Label all mixtures with Chemical Safety Warning Sheets available in a bucket in the hallway.

Cleanroom Gowning Procedure

The dirtiest thing in our cleanroom will be the people who use it. Consequently, all cleanroom users must wear cleanroom garments which trap and hold the particles emitted by their bodies and clothing [2].

A. Put on shoe covers located inside at the entrance of the gowning room. Only flat or very low-heeled shoes may be worn. No sandals or open-toed shoes.

B. Carefully put on a bouffant cap and face mask

C. Remove your cleanroom garment from the hanger and inspect.

Take care to keep the garment completely off of the floor at all times. Inspect your garment each time you wear it for tears or soiling.

D. Put on your cleanroom gown. First, step into the gown legs, taking care not to let the garment touch the ground at any time. Then pull on the upper half of the gown and zip it all of the way up.

E. To put on



shoe covers, sit on the gowning bench.



F. Put on Cleanroom Gloves. Carefully put on the first glove, touching the outside of this glove as little as possible. Put on the second glove using the previously gloved hand, taking care not to touch your skin with the gloved hand. Pull the cuff of the gloves over the sleeve of the jumpsuit so that any particles falling from your sleeves are trapped in the glove. Gloves should be worn at all times, no bare hands or fingers.

Cleanroom Etiquette [2]

I. Disposal of Damaged or Non-Functional Equipment

Whenever something quits working, please give it to a member of the cleanroom staff, who will then either repair it or decide if it needs to be disposed of. Lab equipment is inherently expensive, and eventually much of the cost is passed on to the users. Therefore it helps everybody when we can avoid buying new equipment needlessly.

II. Broken and Uncleanable Glassware, Broken Wafers, Razors, and Other Sharp Objects

With all the glassware used in the cleanroom, obviously breakage will occur, or things will get contaminated beyond the point of being cleanable. If you find glassware meeting this description, please be sure to throw it into the container marked “Sharp Objects Only”. This also applies to the following materials: wafers, razor blades, needles, microscope slides and cover slips, and anything else that is questionable.

III. How to Make the Laundry Guy Happy (N/A)

This one’s simple, but it really speeds up that painfully slow and boring job of doing the laundry. When you are finished with your gown, before you put it into the dirty clothes can, please zip it up and make sure it is not inside out. Also, please unfasten the booties from the gown and each other.

IV. Labeling Things When You Cannot Stick Around to Watch Them

Frequently, cleanroom users will need to leave things under the fume hoods overnight or for part of the day unattended. Our policy here is simple: Anything left unattended must be labeled with your NAME, PHONE NUMBER WHERE YOU CAN BE REACHED (not the number of any front office), WHAT IT IS THAT IS SITTING THERE, and the DATES AND TIME of when you left it AND when you will return to get it. All this can be filled out on the Chemical Label Forms provided inside the cleanroom. If you do not use this form, your chemical(s) will be disposed of immediately

Chemical Label Form

Name: _____ Phone number: _____ Chemical (s): _____ Start Date: / / month day year Start Time: _____ Remove Date: / / month day year Remove Time: _____		Dangers <small>(check all that apply)</small> <input type="checkbox"/> Poison <input type="checkbox"/> Flammable <input type="checkbox"/> Corrosive <input type="checkbox"/> Explosive <input type="checkbox"/> Handle with gloves <input type="checkbox"/> _____ <input type="checkbox"/> _____ <input type="checkbox"/> _____
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V. Disposal of Solvent-and Photoresist-Soaked Materials

We have several red trash cans in the cleanroom built specifically for the disposal of solvent-soaked materials, and require that they be used for the disposal of all such materials. While it may seem like a couple of TexWipes with photoresist on them is not that bad, just remember that the air in the cleanroom is constantly recirculated, so all those vapors will find their way back in eventually for everyone to breathe. The following materials should be put in the solvent cans:

Any alcohols (ethanol, methanol, isopropanol, etc.)
 Acetone
 TCE (Trichloroethylene)
 Chlorobenzene (this stuff is particularly dangerous)
 Photoresist and related products

VI. What If I Do not Know How to Use Something, or If It Malfunctions While I am Using It?

If you need to use a particular piece of equipment and you are not absolutely sure how to use it, first of all, **DO NOT TRY TO LEARN BY DOING IT!!!** The staff is here to help you, and they can point you to the right person to show you how to do it. If something breaks during a process, tell the staff and they will take care of it. Above all, please **DO NOT** try to fix something on your own!!

VII. What Are The Procedures For Cleaning Up?

All cleanroom users are responsible for cleaning up their own mess. You should put away all tools, throw away all wipers and disposable items, and thoroughly clean all glassware. Make it look as though you were never there, or better yet, make it look better than it was before you

were there. If you find a beaker that someone else left dirty, why not wash it while you are washing your own?

VIII. How Do I Store Things?

Make sure to bring your own toteboxes for sample storage and properly label them.

IX. What If I See Someone Else Doing Something Wrong?

From time to time, people will have other things on their mind and unintentionally do something they really shouldn't do. Most people don't mind a friendly reminder now and then. It's up to the users to keep the cleanroom operating smoothly, and as long as everyone cooperated then the chances of ruined projects, injuries, and problems in general are greatly reduced. If anyone has a problem with being politely told about something that may endanger somebody, tell the staff about it and we will take care of the problem.

Cleanroom Emergency Equipment & Locations

BASIC SAFETY EQUIPMENT



Safety Glasses Function: For eye protection. **Use:** Wear with gowning attire. **Location:** In room E151 inside the safety glasses compartments of cabinets.



Nitrile Gloves Function: For hand/skin contamination protection. **Use:** Wear with gowning attire. **Location:** In room E151 in the glove compartments.



Safety Showers Function: For chemical decontamination on a person or their clothing. **Use:** Pull lever for body wash. **Location:** E152 near the double door exit and Chase and Mechanic room.

Eye Wash Station Function: For a chemical splash in the eye. **Use:** Push the plate to activate water fountain. **Location:** In the push-plate under the safety shower.

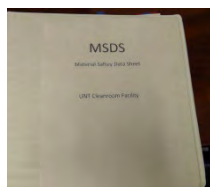


First Aid Kit Function: For minor injuries and minor burn pain relief. **Use:** Apply on minor burns (thermal burns only, not chemical) and minor injuries. **Location:** In room E151 and wet etch hallway.



Phone Function: For contacting help in case of an emergency and contact people inside the cleanroom. The number is 940-369-5318. **Use:** Dial 911 when calling for help during emergency situations. **Location:** In the E151 on the computer cart.

CHEMICAL SAFETY EQUIPMENT



MSDS Binders Function: For determining the hazards of chemicals and precautions to use while working with them. **Use:** Look up information on all chemicals in the cleanroom by finding them in the binders or online in the MSDS library. **Location:** In E151.



Chemical Aprons and Face Shields Function: For Personal protection against Chemical spills. The items are chemical resistant, NOT chemical proof. **Use:** Always wear when working with chemicals. **Location:** By the wet etch benches in the wet etch bay and in the lithography bay.



Chemical Gloves Function: For personal protection against Chemical spills. Do not immerse gloves in chemicals as they are only chemical resistant, NOT chemical proof. **Use:** Always wear when working with chemicals. **Location:** By the wet etch benches in the wet etch bay.



Calcium Gluconate “Calgonate” Function: For hydrofluoric acid (HF) burns. **Use:** see reference on p19 “Chemical Spill”. **Location:** In the wet etch bay on the table by the windowed wall.



FIRE AND HAZMAT



Fire Alarm Activation Station Function: To alert others of a fire in the case that the alarm does not sound on its own. **Use:** Lift cover and pull. Then evacuate the building immediately. **Location:** Pulls are located next to E151 and E152 emergency exit room door, in the chase by the emergency exits.



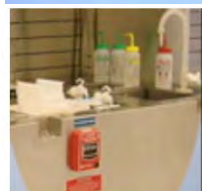
Fire Alarm Enunciator and Strobe Function: To alert building occupants of a fire or similar emergency requiring immediate evacuation. **Use:** Evacuate the building immediately if lights are flashing or the alarm is sounding. **Location:** next to E151 and E152 emergency exits and Chase exit door.



HAZMAT Alarm Activation Station Function: To alert others of a HAZMAT situation in the case that the alarm does not sound on its own. User need to evacuate the cleanroom. **Use:** Lift cover and push button. Then evacuate the building immediately. **Location:** Push buttons are located in E151, E152 and Chase exits.



HAZMAT Enunciator and Strobe Function: To alert Cleanroom and support area occupants of high and low level emergencies such as chemical release or exhaust failure. **Use:** Evacuate the building immediately if lights are flashing or alarm is sounding. **Location:** Speakers at E151 and E152 and Chase exists.

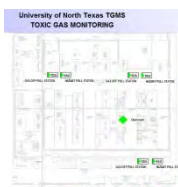


Carbon Dioxide Alarms Function: Puts out fires at benches by spraying large amounts of carbon dioxide. The Carbon Dioxide fire suppression system requires the user to vacate the area immediately after activation. **Use:** Activate in case of a fire in a wet bench or spinner hood if alarm does not start on own. Push down the lever. **Location:** On the solvent wet benches.



Fire Extinguishers Function: For fires smaller than a waste paper basket. **Use:** Follow instructions on side of extinguisher. Use only if trained. **Location:** multiple locations through E152 and E152 A&B. refer to the emergency layout of the cleanroom.

OTHER EMERGENCY EQUIPMENT



Toxic Gas Monitoring System (TGM) Function: To monitor the concentrations of certain gases and exhaust, oxygen concentrations in the Cleanroom and support areas in order to insure the safety of personnel. **Use:** Watch monitor for alarm indications. **Location:** in the manager's office.



Gas Off Activation Station Function: To shut off the toxic gas cabinets and gas cylinders in the case that the alarm does not sound on its own. User need to evacuate the cleanroom. **Use:** Lift cover and push button. Then evacuate the building immediately. **Location:** Push buttons are located in E151, E152 and Chase exits.



Air Showers: For emergency exit, push the **RED** EPO button to disable the interlock of the doors. Under normal condition, the shower will be on automatically when the front door is closed. During the showering, both doors are locked. To prevent contaminates from going through, only ONE door open at a time.



Personal Protective Equipment (PPE) [1]

Chemical **safety glasses** should be worn at all times when in the Cleanroom.

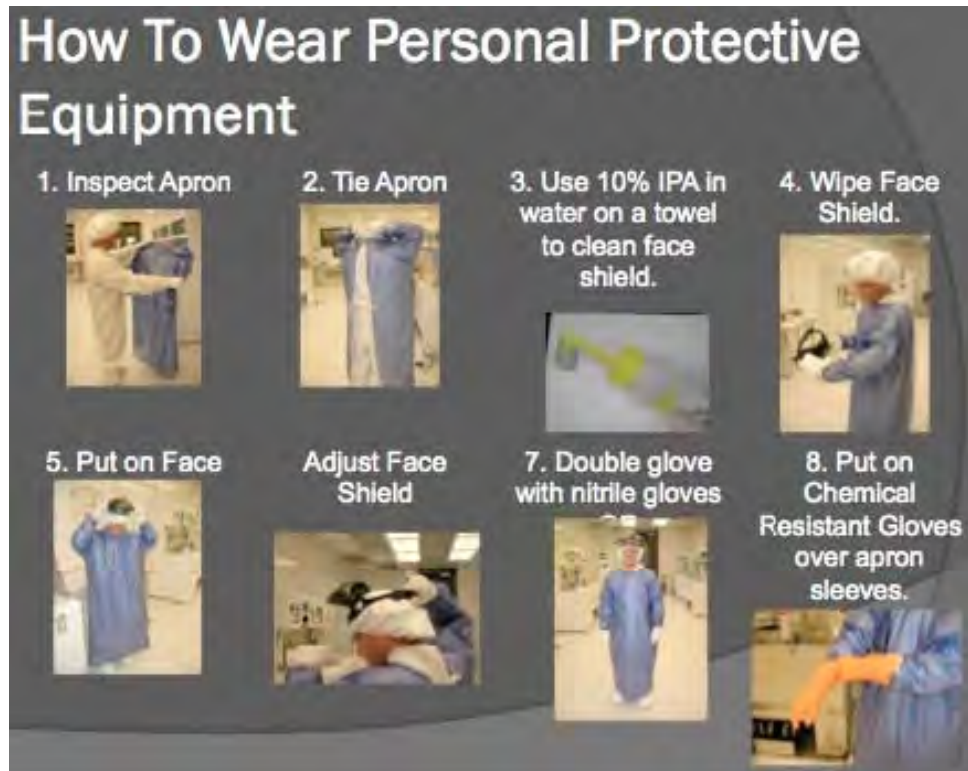
Full-sleeved aprons should be worn when working with chemicals or when working at a wet bench.

Face shields should be worn when working with chemicals. **Safety glasses** should still be worn even if wearing a face shield.

Gloves must be worn to enter the Cleanroom, however if dealing with chemicals, a second layer of gloves or heavy-duty triple gloves (orange gloves) must be worn. All gloves should be checked to make sure they are suitable for use (holes, stains and deterioration make gloves unsafe to use). Reusable gloves should be washed and dried frequently if used for an extended period of time. Wash and dry the outside of gloves before removing them.

How to Wear Personal Protective Equipment:

1. Inspect **Apron** to make sure no chemicals, holes or other deformities are present.
2. Slide **Apron** on and tie in back.
3. Use 10% IPA in water on a towel to clean **Face Shield**. Wipe face shield inside and out and place on head. Adjust if necessary using the plastic knob on the back.
4. Put on **Gloves** (orange chemical resistant or nitrile) over apron sleeves.



How to Remove Protective Equipment:

- 1 Wash and dry chemical resistant gloves using cleanroom wipers. Place in bin. If gloves are stained or otherwise unusable dispose of in trash. If using nitrile gloves dispose of them in the trash can and put on a new pair for use throughout the rest of the cleanroom..
- 2 Remove **Face Shield**.
- 3 Hang face shield.
- 4 Hang **Apron**.



PPE Rules & Restrictions: Personal Safety Equipment must be worn at all times while working with chemicals at the wet benches. Chemical apron, faceshield and chemical gloves must be removed after leaving the Wet Etch Bay area.

PPE found in the Wet Etch Bay must only be used in the Wet Etch Bay. PPE found in the Lithography Bay must only be used in the Lithography Bay. If no PPE is available at any of these two locations or they are being used by other clients, please contact cleanroom staff.

Chemical Use

- All chemicals must be handled in wet benches or in some exhausted enclosure.
- Chemicals are to be handled and mixed only by personnel who are authorized and are wearing the appropriate personal protective equipment.
- Open chemical containers cautiously. Point the top of the container away from your face and body. Pressure may have developed inside the containers during transport.
- When pouring chemicals, pour slowly in a controlled manner to avoid splashing.
- After pouring chemicals from bottles, wipe the neck of the bottle clean to prevent the chemical from dripping down the side of the bottle and damaging work surfaces or personnel.
- “Always Add Acid” (AAA) to water, never the reverse.
- Do not mix a solvent with an acid or mix an acid and a base. Solvents and oxidizers must never be stored or mixed. These chemical groups are incompatible and can react violently.
- Immediately clean up chemical residues on work surfaces. Clean up with wipes and place in appropriate waste debris cans located in the wet benches.
- When bottles are completed they must be properly cleaned and disposed of. Details will be provided during laboratory room orientation.
- To reduce possibility of fire or explosion chemicals can only be heated to less than 10 degrees of flash point of that chemical (Class I liquids-flashpoints below 73F can never be heated on hot plates---acetone, Isopropyl alcohol, MIBK/IPA etc)

Chemical Labware [3]

- Check glass labware before using for cracks.
- No hydrofluoric in glass/Pyrex/quartz containers. HF etches all these.
- Approved labware and fixtures only – check before bringing in your own.
- Used labware must be rinsed & dried before placing on dish cart.
- Puddles of liquid on surfaces is not safe.
- Labware used for metals (Au, Cu, etc) must be kept separate to avoid cross-contamination.

Best Practices for Manual Chemical Processing

- Move your processes in ~12" from the edge of the bench.
- Plan your work – know what you have to do step by step – have your supplies/materials ready.
- Only have what you need on the wet bench. Don't crowd! No clutter!
- Handle labware carefully, use boats and beakers properly.
- Be careful with nitrogen blowoff guns near chemistry.
- Need to pour chemicals in a bath – use a beaker with a handle.
- Can't reach – get assistance.
- Clean up when you are done
- Put your wafers/materials away.
- Dispose of chemistry properly.
- If leaving hot chemistry to cool – let us know what you are doing.
- Double contain chemicals (small beaker of chemistry in a larger pan).

Hotplates

Hotplates represent a higher level of risk and are therefore kept locked up and are released to users upon request and a brief explanation to staff what it is that you are heating.

- Approved mixtures on hotplates only, ask first.
- No plastic or aluminum foil on hotplates.
- Keep signage away from hotplate surfaces.
- Hotplates must be attended – do not leave the area.
- No heating of solvents with flashpoints <130°F.
 - Wafer baking hotplates are not for chemicals. – Vacuum grooves.

Wafer Cassettes & Boats

There several wafer cassette styles and materials in the cleanroom

1. Polypropylene Shipping and Machine Cassettes

- Used in wafer shipping containers and for moving wafers in & out of processing tools
- Do not use for wet chemistry



2. Metal Machine Cassettes

- Used in moving wafers in & out of processing tools
- Do not use for wet chemistry



3. Quartz Cassettes

- Used in moving wafers in & out of high temperature furnaces
- Do not touch with gloved hands – only use appropriate handling tools
- Do not use for wet chemistry



4. Teflon Cassettes

- Teflon has high resistance to chemicals and temperature, PFA and TFE varieties
- Much heavier than polypropylene cassettes
- Teflon can be colored – do not use colored Teflon for processing

Cassette Handles

There are two type of handles used to lower Teflon boats into the chemical baths.

1. Slingshot Style

- Fasten onto top of cassette through notch.
- Slide down cassette on track until handle stops– slide handle all the way to end of cassette middle.
- Handle is not stable in middle
- These handles are more appropriate for open baths with no covers.



2. Squeeze Style

- Fasten onto top of cassette in notches on end of cassette.
- Use right size handle for cassette–4” and 6” versions – do not mix
- Do not tilt handle & boat– hold straight up.
- This style is more appropriate for baths where a cover is used.



Spill Response Procedures [3]

I. Introduction

Many potentially dangerous chemicals are used in the cleanroom and the possibility of a major spill always exists. It is necessary to know how to react quickly and properly to any chemical spill to avoid injury, death or major equipment damage. A large acid spill, HF for instance, might cause serious injury or even death if handled improperly. These procedures are intended only to provide guidelines. Common sense should always be used when dealing with any chemical spill. Safe practices should be foremost on your mind whenever you are in the cleanroom. Be advised: you should never work alone in the cleanroom. Cleanroom policy dictates that you must have at least one other person in the cleanroom with you at all times.

II. Spill Response Cart Items

The cleanroom spill response buckets are near the wet processing area. When spill occurs, contact cleanroom staff immediately.

III. First Aid

1. Did the chemical spill on you?

- If the chemical is a strong acid or base, run the affected area under water for 10 to 20 minutes. This should relieve some pain and reduce the danger of severe burns.
- If the chemical is HF, run the affected area under water for 15 to 20 minutes and then apply a liberal amount of calcium gluconate gel following the directions on the package. Seek medical attention as soon as possible.
- If the chemical is a solvent, rinse the affected area for 10-15 minutes to reduce any irritation.

2. The chemical spilled on someone else:

- If the person is coherent, find out what chemical they were using.
- If they are unable to tell you, have someone place them under a safety shower and remove contaminated clothing while you attempt to identify the chemical:
 - * Look for clues to the chemical's identity: labels, tipped containers, etc.
 - * Wearing an acid glove, use the litmus paper to identify whether the chemical is an acid, base or solvent and its strength.
- If the chemical can be classified as an acid or base with the paper but not identified, assume it is HF or Sodium Hydroxide.
 - * Take necessary first aid action, including the use of HF ointment.
- Notify UNT police 940-565-3000

Special Chemical Hazards [3]

Hydrofluoric Acid & Fluorinated Acids

- Is used to etch silicon dioxide and other materials (glass, quartz, Pyrex).
- Comes in a variety of concentrations and solutions.
- BOE or Buffered Oxide Etch – HF with NH_4F – may be close to neutral pH.
 - 10:1, 5:1, 20:1 - X parts 40% NH_4F and 1 part 49% HF – 10:1 BOE is ~ 4% HF
 - Pad Etch – Ammonium Fluoride (NH_4F) solution for etching SiO_2 over Al.
- Freckle Etch contains fluoroboric acid (HBF_4) which has the same dangers as HF & NH_4F
- Is very dangerous
 - Solutions of less than 10% may take hours before symptoms appear.
 - Solutions of 14.5% immediately produce symptoms.
 - Solutions of 12% may take up to an hour to produce symptoms.

- Solutions of less than 7% may take several hours before onset of symptoms, resulting in delayed presentation, deeper penetration of the undissociated HF acid, and a more severe burn.
- The fluorine ion in the fluorinated acids readily penetrates human skin, allowing it to destroy soft tissues and decalcify bone.
 - Severe destruction of skin; may require amputation.
- Burns are extremely painful.
- Fluorine ions deplete calcium – body's electrochemistry altered – muscles need Ca.
- Death can and has occurred from fluorine exposure.
- An area the size of the hand (approx. 2.5% of the body surface area) is generally seen as the minimum for potential lethal action following contact with concentrated hydrofluoric acid.

HF / NH₄F / HBF₄ is dangerous because

- 1. It looks like water.**
- 2. It is not initially painful upon contact (For the weaker solutions typically used in the SMFL)**
- 3. It is absorbed through unbroken skin.**
- 4. It depletes calcium and destroys tissue.**
- 5. It is potentially lethal – treat as toxic.**

HF Case Studies

1) “Whilst sitting at a fume cupboard processing mineral samples a laboratory technician knocked approximately 100 mls of hydrofluoric acid (70%) onto his thighs. Immediate 10% body burns ensued. Despite rapid flushing with water and emergency hospitalisation he died 15 days later.”

· Department of Consumer and Employment Protection Government of Western Australia, 1994

2) “A drop of concentrated HF splashed on to the finger nail of a patient. The finger was insufficiently washed. The exposed point turned gradually to a white-yellowish colour, but no further visible changes were observed. Pain occurred 7hr later which continued for about 30 hr. Examination of the tissue under the nail then showed that a pea-sized area had already been destroyed by necrosis requiring surgical treatment.”

· “Symptoms and treatment of HF injuries” D. Peters and R. Miethchen J of Fluorine Chemistry Vol 79 pp 161-165 (1996)

3) IMMEDIATE SHOWERING AND APPLICATION OF CALCIUM GLUCONATE TO 22% BURNS RESULTED IN SURVIVAL

· “Case of a 50 year old worker who survived burns to 22% body surface area from 70% hydrofluoric acid. He showered immediately, had calcium gluconate gel applied to the wounds

and was taken to a nearby hospital where he was promptly treated with subcutaneous and intravenous calcium.

- It is evident that apart from the location of burns, the size of the burns and concentration of the acid, washing the affected area immediately and the application of calcium gluconate gel to reduce the uptake of fluoride ion may prevent a fatality.

- Greco, R.J., Hartford, C.E., Haith, L.R., and Patton, M.L., 1988, Systemic fluoride poisoning resulting from a fluoride skin burn: Journal of Occupational Medicine, v. 15, p. 39-41

These cases illustrate some of the outcomes of fluorine poisoning due to HF exposure

Case 1 – Death

- Did not have knowledge of the hazards
- Did not have proper PPE – no apron
- Did not have proper treatment available – working alone, no calcium gluconate

Case 2 – Amputation of finger tips

- Did not have knowledge of the hazards
- Did not have proper PPE – no gloves

Case 3 – Chemical burns but survived

- Had knowledge of the hazards
- Had proper treatment and response

Accidents can happen even with all of our safety precautions. It is important to do what we can to prevent them and be ready to deal with the situations when they happen.

Tetra Methyl Ammonium Hydroxide (TMAH)

TMAH is used in two main areas of semiconductor processing. In higher concentrations (25%) it is used as a crystallographic etch of silicon – similar to KOH etching. In lower concentrations (2.4%), it is used as a positive photoresist developer.

It has always been known that higher concentrations TMAH solutions pose a toxic threat.

- TMAH acts to interfere with the nervous system, often shutting down breathing.
- There is no antidote at this time.
- Death has occurred shortly (30 min) after exposure to quantities of higher concentration TMAH solutions (greater than 7% body surface area exposed).
- So far, there have been no reported deaths due to exposure of developer strengths (one case had the patient on a respirator in intensive care).

The key to TMAH poisoning appears to be strength of solutions and area exposed. Time to decontamination does not appear to be important – absorption through skin may be very rapid.

Symptoms of TMAH poisoning

- Muscle weakness
- Salivation
- 2nd or 3rd degree burns
- Irregular breathing and heartbeat
- Progressing to coma, shock and in most high concentration cases – death.

The UNT Cleanroom does not have high concentration THAM solutions. We do have developers (CD-26) that are at the 2.4% strength. A small amount of developer on your skin will most likely result in a chemical burn. A large amount of developer splashed onto your body is a matter of serious concern that would require immediate hospitalization.

The key – as always – is our procedures for protecting yourself from chemical exposure

- 1) Know the hazards of the chemistry you are working with
- 2) All Chemical operations are done at a wet bench / fume hood
- 3) All protective gear must be worn when working with or around chemistry.

Piranha Etch

Piranha Etch refers to a solution for removing photoresist / organic residues from surfaces. It is a mixture of sulfuric acid and hydrogen peroxide.

We use solutions of 3:1 or 4:1 ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$) with 30% H_2O_2

- Piranha solutions are very exothermic when mixed, rapidly heating to over 100°C in a short period.
 - Safety Reminders For Use of Sulfuric Acid/Hydrogen Peroxide Mixtures
 - o It is difficult to dispose of piranha because the waste continues to react and decompose for a long period of time. This builds up pressure in the waste bottles, causing them to burst.
 - o Commercially stabilized versions of Piranha are available such as Nanostrip (<http://www.cyantek.com/htm/nano-strip.htm>).
 - o Personal protective equipment is always required when working with piranha solutions.
 - o Whenever handling Piranha, only use glass containers, preferably Pyrex.
 - In preparing a Piranha solution, add hydrogen peroxide to the sulfuric acid - slowly!
 - o Piranha solution is very energetic and potentially explosive. When being made it is very likely to become hot, more than 100 degrees C. Handle with care.
 - o Substrates should be rinsed and dried before placing them in a piranha bath.
- Piranhas are used to remove residues of photoresist and acetone, not the compounds themselves.
- o Adding any acids or bases to piranha or spraying it with water will accelerate the reaction. This includes some photoresist developers, some of which are strong bases.

o Leave the hot piranha solution in an open container until cool on one of the SMFL wetbenches.

o Do not store piranha. Mix only enough fresh solution for each use. Excess solutions should be disposed via the drain (once cool), followed by flushing with copious amounts of water.

o Mixing hot piranha with organic compounds may cause a very violent reaction. This includes materials such as acetone, photoresist, isopropyl alcohol, and nylon.

Nitric Acid

Nitric acid poses special hazards due to the fact that it is a strong oxidizer. As such, it should always be kept away from flammables, solvents and metals.

The nitric acid at the SMFL is secured and must be requested by the lab users.

Peroxides

Peroxides are by their nature oxidizing materials. They are therefore stored separately from flammables and solvents. Hydrogen peroxide can form explosive mixtures with some organic substances.

Another hazard of peroxides is oxygen pressure buildup from decomposition. Once peroxide is taken from its original container, it should never be put back. Used peroxide should be stored in vented cap containers or open containers until decomposition is complete.

The hydrogen peroxide that is found in the SMFL is a 30% solution. It should not be confused with the 3% hydrogen peroxide found in stores for treating skin abrasions/cuts/infections.

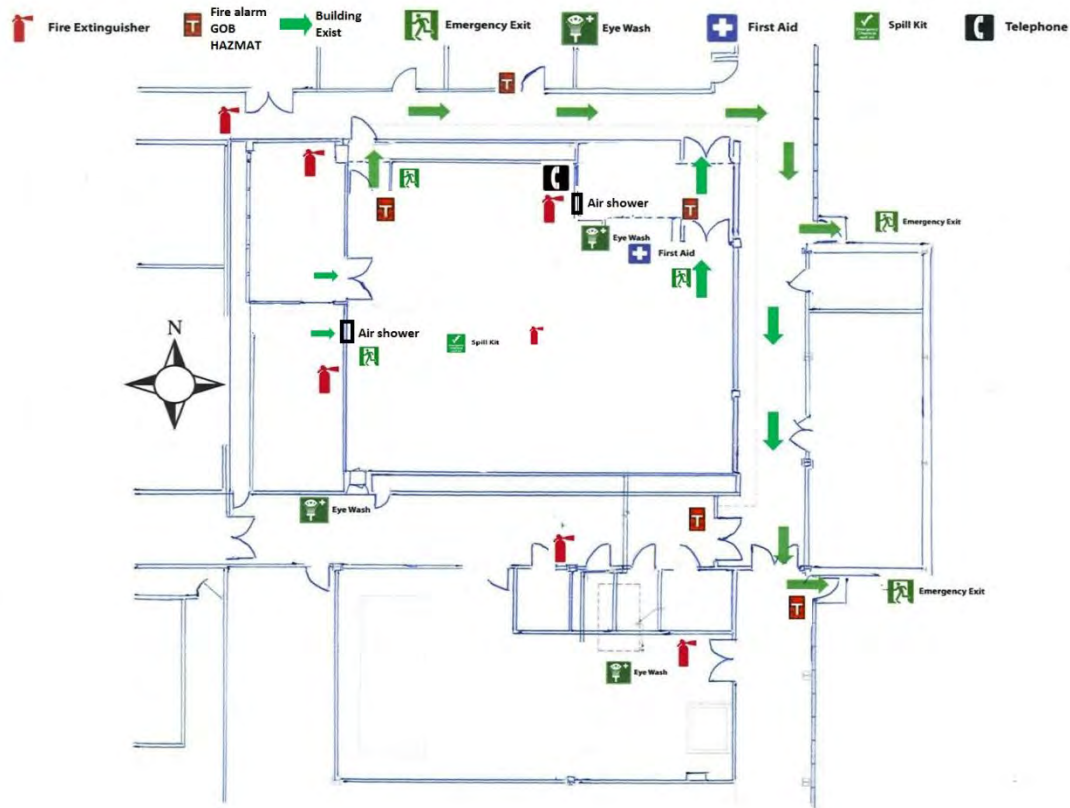
Hazardous Gases

Below is a brief summary of the more hazardous gases. These gases are delivered to the tools via high pressure cylinders. All are stored in exhausted cabinets and are monitored by the toxic gas monitoring systems. Users are protected by multiple interlocks and safety systems but should still be familiar with their hazards.

- Boron Trichloride BCl₃: Used in the LPCVD/RIE. A toxic colorless, fuming liquid or gas with a pungent odor. Reacts rapidly with water forming boric and hydrochloric acids. Used for dry etching of aluminum.
- Chlorine- Cl₂- Corrosive, toxic greenish-yellow gas with strong irritating odor. Highly irritating to skin, eyes, lungs. Very high concentrations cause fluid in lungs, death. Strong oxidizer. TLV = 0.5 ppm. Used for dry etching of Al and other metals.

- Dichlorosilane SiH_2Cl_2 : Used in the LPCVD - A colorless, flammable, toxic gas which has an irritating odor and fumes in moist air. TLV = 5 ppm. Will form corrosive hydrogen chloride upon exposure to moisture. Used to form silicon nitride.
- Phosphine - PH_3 - Used in the LPCVD - A toxic/flammable gas with an odor of decaying fish that ignites at very low temperatures upon exposure to air. A source of phosphorous for doping silicon. TLV = 0.3 ppm
- Silane - SiH_4 - Used in the LPCVD and PECVD- A gas with an unpleasant odor. Used in the chemical vapor deposition of epitaxial silicon, polycrystalline silicon and silicon nitride. TLV = 5 ppm Ignites in air with concentrations down to 1%, extremely flammable.

Nanofabrication Cleanroom Emergency Exits



References:

- [1] University of Louisville cleanroom safety manual
- [2] Georgia Tech cleanroom manual
- [3] RIT standard operating procedures