Safe Handling of Excimer Laser Gases

The past decade has seen a profound increase in excimer laser use. Processes using excimer laser-generated UV wavelengths are now becoming standard in semiconductor fabrication, materials processing and medical procedures. With the proliferation of these refillable gas lasers, the industry must not sidestep or ignore a critical issue in their successful utilization: that of safely storing and handling laser gases. It is in the best interests of the laser community to fully understand what precautions should be taken to avoid serious accidents involving the use of compressed laser gases.

Excimer lasers are currently found in many universities, corporate research facilities and government laboratories. The safety record from this pool of predominantly scientific researchers has been reasonably good to date. This positive record is more a function of luck than safety protocol, however. The typically well educated users of these lasers often neglect or disregard the basics in gas cylinder handling and storage.

Picture this scene when entering a university laser lab. There is an excimer laser in a small room, cramped in next to an optics bench. Gas cylinders seem to be everywhere, especially under foot. Tygon or copper tubing exiting from broken gas regulators to the laser ports look more like spaghetti than a gas delivery system. Sophisticated toxic gas monitors, otherwise known as graduate students, let the visitor know that there is a hint of fluorine in the air (as if one didn't smell it already!). Ventilation systems, if they exist, are not utilized properly.

Before we make specific safety recommendations to rectify the situation in this stereotypical lab, it would be helpful to discuss the hazards associated with excimer laser gases.

A multitude of hazards are associated with handling laser gases, including high pressure, asphyxiation, toxicity, and corrosivity. The gases typically used vary with laser type and manufacturer. However, all excimer lasers have fill gases comprised of halogens including either HCl, F_2 or sometimes NF_3; rare gases including Xe, Kr or Ar; and a buffer gas of He and/or Ne.

There are hazards common to all of the above gases, but the one most overlooked and underestimated is the high pressure itself. All cylinders used in the laser industry have pressures typically between 300psi and 3000psi. At these pressures, an accident causing the cylinder to fall could shear an unprotected valve, causing the cylinder to simulate the action of an unguided missile. A second hazard also underestimated by laser gas users is found in the seemingly benign gases such as He, Ne and Ar which can act as suffocants due to the displacement of oxygen.

The two hazards most often associated with the use of excimer gases are the corrosivity and toxicity of the halogen component. Fluorine and hydrogen chloride gases are by far the most common halogen donors in excimers. Extreme care should be taken when handling these products. Both gases, if not properly used and safely stored, can be devastating. They are irritants of the upper respiratory tract and can cause pulmonary edema. Exposure to high concentrations of either gas, even if only brief, is usually fatal. Mild, dilute exposures will result in coughing and choking and burning of the eyes and nose. Vapor contact with the skin will cause tissue irritation and necrosis. Although not usually present in the pure form for this application, liquid HC1 or F_2 can cause painful burns of the tissue and bone if they come in contact with the skin. These effects are real and are not overstated for effect.

In the event of an accident with pure HCl or F_2, follow the emergency steps shown in Table 1. In addition, special first aid preparations for F_2 burns should be used immediately. These include magnesium oxide & glycerin paste, as well as a 10% calcium gluconate solution for injection under the skin (after use of local anesthetic) to halt tissue decay.

Another problem these halogens pose is the corrosive attack on laboratory equipment. Of the two gases, HCl is the more destructive. If an HCl mix were to vent accidentally, every piece of electronic equipment including computers and telecommunications equipment would be ruined. Optical components and other specialized equipment in a laser lab would also be adversely affected.

In case of accident

If precautions are not heeded, accidents can and will occur. If a rapid or violent release of any gas occurs from a cylinder not secured, contained and vented, one must quickly ascertain what went wrong and what laser gas is escaping into the room. Then make sure the ventilation system is on and that all personnel are removed from the area. Don't try to be a hero and stop the leak of a toxic gas.

If anyone was exposed to toxic gases or shows evidence of suffocation due to the lack of oxygen, administer first aid (Table 1) and call a physician immediately.

First aid for inhalation of fluorine, hydrogen chloride and even carbon dioxide laser mix, if it was severe enough to cause loss of consciousness, is nearly identical. If breathing is labored, give 100% oxygen under positive inhalation pressure for half-hour periods every hour for six hours. If the patient is not breathing, give artificial respiration. The patient should be kept warm, not hot, and stay under the supervision of a physician until the danger has passed.

First aid for halogen mixes which ontact the skin and eyes is to subject the person immediately to a drenching shower with all clothing being removed as rapidly as possible. With fluorine exposure, the skin should be washed with 2-3% aqueous ammonia solution and then flushed with water again. Compresses that include saturated solution of Epsom salts or iced 70% alcohol should be applied for at least 30 minutes as well. Check with your specialty gas supplier for more details. For HC1 contact, flushing with water only is recommended. BE SURE TO RECEIVE THE ADVICE OF A QUALIFIED PHYSICIAN QUICKLY.

Make sure the gas has completely dissipated before re-entering the lab. After donning clean neoprene gloves, coat, boots, and a self-contained breathing apparatus, enter the lab and inspect the damage. If it was a halogen gas that vented, remove the cylinder and then systematically clean away the films of hydrofluoric or hydrochloric acid that will have formed on all the equipment.

Prevention of accidents

The two key ingredients of preventing accidents involving laser gases are (1) properly educated and trained personnel, and (2) suitable safety equipment.

The aforementioned hazards can be avoided if one adheres to the following rules for the safe handling of compressed gases. These rules are specifically applicable to the laser lab and include:

- When moving gas cylinders, use a hand truck designed for gas cylinders. Cylinders, especially those in halogen service, should never be rolled, dragged or dropped.
- Cylinders should be secured at all times, and protective caps should be attached over the cylinder valve when not in use.
- Always know what is in the bottle; don't ever assume.
- Use proper equipment and compatible CGA fittings and regulators. Dedicate equipment to a single service.
- Purge systems should be incorporated into most gas-delivery configurations. The purpose is twofold: (a) For toxic and corrosive gases, purge gas is to be used as an advance leak check; (b) Purge gas is also used to keep the gas system clean and free of atmospheric contaminants when installing the system and during subsequent cylinder changes.
- When connecting cylinder(s) to a gas-delivery system, make sure there are no leaks. If there is a leak, tighten the connection only after the purge gas is vented to lessen the pressure.
- Make sure all construction materials in your system are compatible with the gases being used — particularly important when handling fluorine, an oxidizer.
- Safety equipment such as toxic gas monitors, protective clothing and glasses, and breathing apparatus should be readily accessible, and all personnel should know how to use them.
- For any other assistance or questions, don't hesitate to call your specialty gas suppliers...they are the experts. They can and should supply you with Material Safety Data Sheets (MSDS). They will also familiarize you with what equipment is typically used with certain gases. Expect the best products and information from your supplier.

Since the issues of safety are most acute when dealing with halogens used in excimer lasers, we will now give particular emphasis to equipment for handling excimer gases safely. To rectify the unsafe lab conditions earlier described, the following cost-effective steps should be taken.

1. Secure all inert compressed-gas cylinders with brackets to stable benches or walls.

2. Secure the halogen gas mixtures in either a fume hood or vented safety enclosure which has sufficient

TABLE 1.
EMERGENCY FIRST AID GUIDE TO INJURY CAUSED BY EXCIMER LASER GASES

SYMPTOM/CAUSE	EMERGENCY FIRST AID STEPS
Suffocation due to lack of oxygen	
• Labored breathing	Administer 100% O_2 at half-hour intervals for 6 hours.
• Not breathing	Artificial respiration.
	In both cases keep warm, not hot. Keep under qualified physician's care until danger has passed.
Halogen contact with skin	This is first aid for a worst case situation... modify as needed.
• F_2 gas exposure	1. Drenching shower. Remove all clothing as soon as possible.
	2. Wash skin with 2%-3% aqueous ammonia solution.
	3. Flush skin with water again.
	4. Apply compress of saturated solution of Epsom salts or iced alcohol for at least 30 minutes.
• HCl gas exposure	1. Drenching shower. Remove all clothing as soon as possible. No other steps are recommended.
Halogen contact with with eyes	Call emergency vehicle. (Best medicine = prevention)

BE SURE TO RECEIVE THE ADVICE OF A QUALIFIED PHYSICIAN AS SOON AS POSSIBLE

Have emergency telephone numbers easily accessible.

Ambulance________ Fire Dept.________

Doctor________ Corporate Safety 2222

HALOGEN EXPERTS: SPECTRA GASES INC.
1-800-932-0624 (in NJ: 1-201-372-2060)

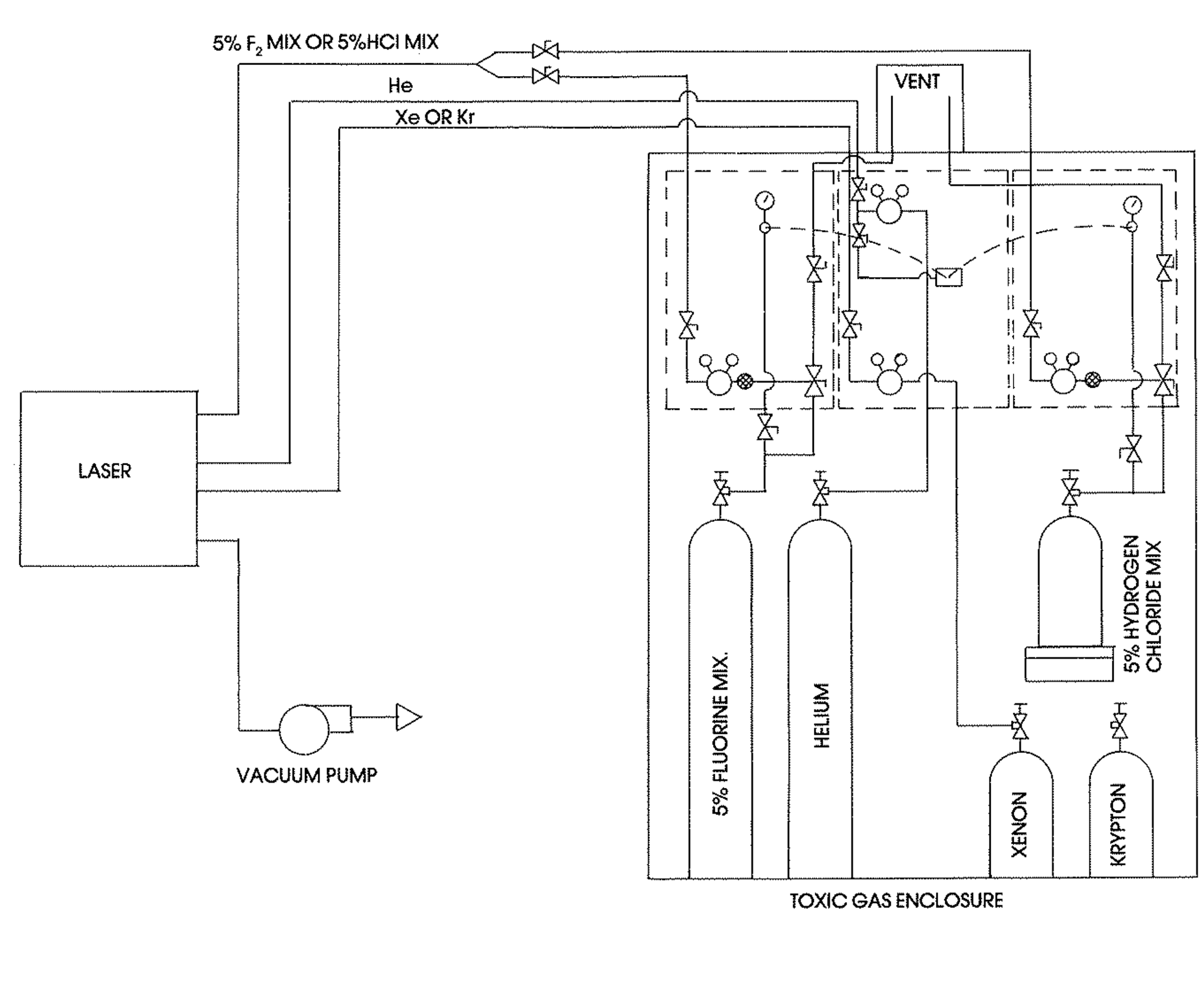

Figure 1.
Schematic of a safe high-purity gas delivery system.

exhaust flow to prevent diffusion of any leaked gas back into the room. A vented cabinet should be designed to allow the user to close a cylinder valve without allowing any gas to enter the room.

3. Replace hoses or tubing to meet the following recommendations: For F_2 or HCl mix (up to 10%), use high-finish, clean, stainless steel tubing (high-pressure copper tubing is acceptable for F_2 use, but is not preferred due to its softness). For inert gases, use high-pressure copper, brass, or stainless steel tubing.

4. Inspect your monel, stainless steel, or nickel-plated regulators that have been in corrosive gas service. If there is any evidence of a problem, arrange for repair by your supplier.

5. Incorporate the use of either a cross-purge or deep-purge (dual-pigtail) system for each halogen gas being used.

A complete excimer gas handling system

In addition to all the safety requirements listed above, a gas handling system for excimer laser gases must offer flexibility and ease of use. All these requirements are met by the three-panel system shown in Figure 1 (designed by Spectra Gases Inc.). This dual-halogen system (very often both HCl and F_2 spectral lines are used in research situations) has the unique safety feature of isolating the halogen panels from each other. The purge hose must be switched manually from one halogen panel to the other when a new spectral line is to be used. This offers the ultimate safety precaution: Even if valves fail, there is never an opportunity for fluorine to come in contact with hydrogen chloride.

The cabinet is the most important element of your gas handling system because it will safely vent any leak, minor or catastrophic. This system incorporates a ventilated safety cabinet (not shown) to hold two halogen mixes, helium as a buffer and purge gas, as well as Xe and Kr. Made of 11-gauge steel, the cabinet comes with locks, automatic door closures, sprinkler head and cylinder brackets. An air flow velocity of 75 ft/min. is maintained through the cabinet.

Experience has shown that a nickel-plated brass, 316 stainless steel, or monel regulator that incorporates a positive seal, often referred to as a tied diaphragm, works best for halogen service. The design prevents creep even when particles have accumulated on or around the seat. When being used as part of a cabinet system, regulators are mounted on a panel to avoid damage when moving cylinders in this confined area. An additional advantage

TABLE 2.
FACTORS DETERMINING DESIGN OF EXCIMER GAS DELIVERY

Applications	Work Environment	Projected Power & Duration	Gov't Safety Regulatory Bodies
Materials processing (i.e.: micro-machining of plastics & metals)	Production floor, Multiple excimer system	Varied — probably continuous (24 hr/day, 6-7 days/wk)	OSHA
Medical procedures (i.e.: laser angioplasty)	Hospital or outpatient clinic, Operating room	Varied — usually short duration (sec to hours)	FDA OSHA
Semiconductor processing (i.e.: photo-lithography)	Clean room	Varied — probably continuous	OSHA

is the ability to see and adjust panel-mounted regulators easily. Either a high-pressure flexible hose or a stainless steel pigtail (coiled tubing) connects the cylinder to the regulator.

A control panel has two major functions: the safe delivery of gases to the point of use and the prevention of system contamination during cylinder exchange. Safe delivery of the gases is assured by carefully selected components to reduce and control pressure, to control flow and to eliminate potential leaks.

The user gains several other important benefits by using a purge system:

- leak check new connections
- prevent air from contaminating the system during cylinder changes
- purge toxic gases from the lines before a cylinder is removed, or when the system is on extended shutdown.

Every panel should be clearly labeled and easy to use and maintain in working order.

Additional safety equipment may be required by state, local or corporate regulations. These options may include:

- toxic gas detector
- emergency shut-down system (electropneumatic controller)
- halogen scrubbers
- flow restrictors in the cylinder valve.

Systems can also be partially or fully automated, with local or remote controls. Automation is most often a corporate safety requirement in production situations. Table 2 lists additional factors to consider in designing a safe gas-handling system.

Summary

In conclusion, excimer-based systems are now realizing their potential. They may alter the need for eyeglasses and heart bypass surgery, improve IC manufacturing, and help make possible rapid strides in the manufacturing of thin-film substrates for superconductors. These are just a few of the new markets that are currently using excimer lasers. For excimer-based systems to be successful in these fields, the issues of gas safety must not be ignored.

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