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Prevention and Control of Accidental Releases of Hazardous Materials in PV Facilities

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This paper reviews the approaches to preventing and mitigating accidental releases of toxic and flammable gases in photovoltaic R&D and manufacturing facilities. The prevention options are related to safer technologies, processes and materials, safer use of material, preventing accident-initiating events, preventing or minimizing releases and preventing human exposures. The mitigation options include secondary confinement, emergency scrubbers and adsorption units. © 1998 John Wiley & Sons, Ltd.

OPTIONS FOR ACCIDENT PREVENTION AND MITIGATION

Accident prevention and mitigation in the process industries is based on the military concept of defense in depth;[1] if one line of defense fails, then others are available. Engineering and administrative options to prevent and control accidental releases and reduce their consequences can be considered sequentially in six steps (Figure 1), each one an additional layer of protection:[2]

(i) Inherently safer technologies, processes and materials.
(ii) Safer use of material (e.g. safer forms of a chemical, reduced on-site inventories, high material utilization and on-demand generation).
(iii) Options to prevent accident-initiating events (e.g. safer designs, safety analyses, operating and maintenance procedures and detection and monitoring systems).
(iv) Safety systems to prevent or minimize releases at the source (e.g. automatic shut-offs, flow-restricting valves and cooling and containment systems).
(v) Systems to capture accidental releases (e.g. secondary confinement, emergency-handling scrubbers and incinerators and adsorbers).
(vi) Options to prevent or minimize human exposures and their consequences (e.g. separation zones, physical barriers, emergency preparedness and response plans and evacuation plans).

Selection of technology/process/material

The most efficient strategy to reduce hazards is to choose technologies and processes that do not require the use of large quantities of hazardous gases. This is especially important for new technologies, where

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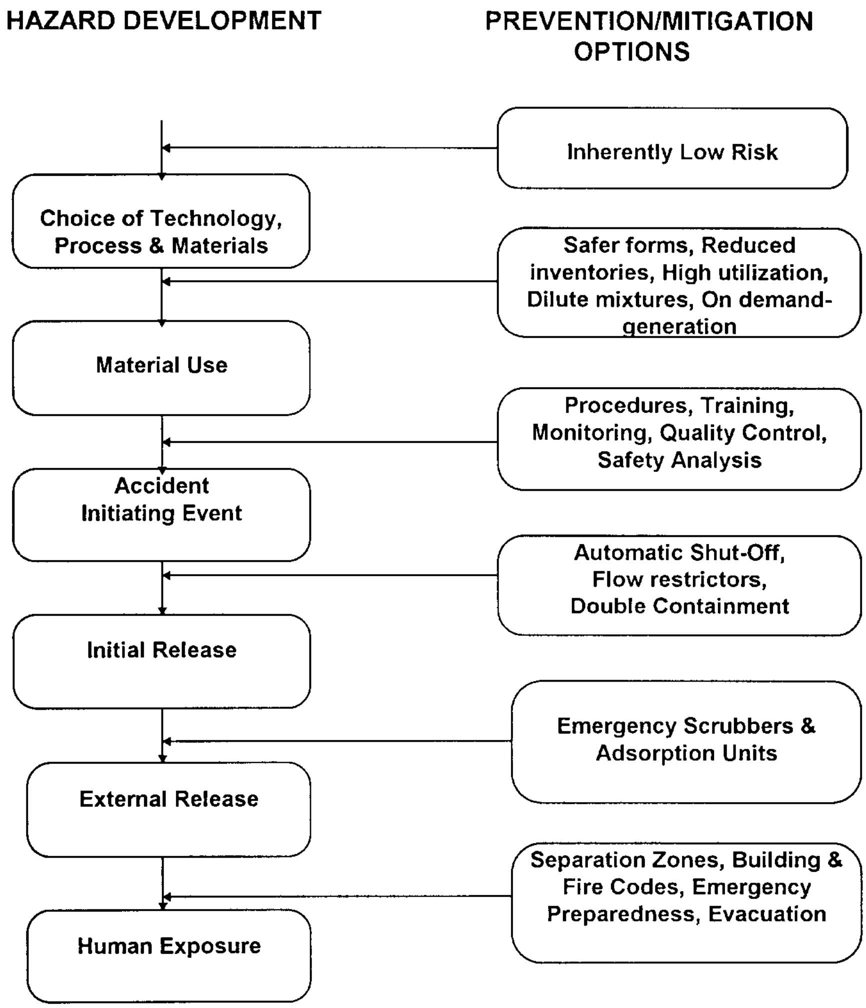

Figure 1. Prevention and mitigation of accidental releases of hazardous gases

this approach can be implemented early in development before large financial resources and efforts are committed to specific options. Life-cycle considerations are necessary in evaluating technology options and associated safety and environmental control costs, because some technologies present mainly occupational risks (e.g. a-Si) while others present mainly end-of-life concerns (e.g. CdTe).

Health and safety and environment (HS&E) criteria at the process level include the type and physical form of material used, the rate of use of the material, operation and maintenance requirements and potential electrical and electromagnetic hazards. Thin-film solar cells offer HS&E advantages because they use small quantities of materials and offer the potential for further material reductions via minimization of photovoltaic (PV) and metal layer thickness and increased material utilization.

Safer material utilization

This strategy can be implemented as: substitution (i.e. using safer material or environmentally more benign ones), use of a safer, less mobile form of a hazardous material; point-of-use generation; and reduction of the quantity or concentration of a hazardous material in process and storage. Alternatives need careful evaluation because there are frequently both advantages and disadvantages associated with every option. Examples are given of this strategy in the manufacture of amorphus silicon solar cells, where

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the alternatives are explored to silane (a pyrophoric and potentially explosive gas) and to phosphine and arsine (highly toxic gases).

Substitution

Silane replacement. Several inorganic and organic liquid sources of silicon have been investigated as silane alternatives in the semiconductor industry; namely organosilanes and chlorosilanes, which are delivered in modest pressure cylinders at liquid/vapor equilibrium. Organosilanes are generally non-pyrophoric and non-corrosive materials. Chlorosilanes are flammable but non-pyrophoric and because of their low vapor pressures are much less likely to leak than silane. These materials are not benign; they are hazardous but do not pose the potential for high explosion associated with silane. Also, they are delivered via a bubbler system, which is inherently safer than compressed-gas cylinders. Organosilanes have partially replaced silane in silicon dioxide deposition, and chlorosilanes are used for epitaxial silicon and silicon nitride deposition. However, the use of these compounds for deposition of either amorphous or polycrystalline Si is problematic; organosilanes cause hydrocarbon molecules to be incorporated in the film, and chlorosilanes require high processing temperatures that may damage the film's quality. A gas substitute for silane is disilane, which is pyrophoric at very low concentrations and burns smoothly, thereby minimizing hazards from explosion.

Arsine, phosphine and hydrogen selenide replacements. Potential replacements for arsine and phosphine include *tertiary*-butylarsine (TBA) and *tertiary*-butylphosphine (TBP). These metal–organic compounds combine a safer physical form (i.e. liquid versus gas) and lower toxicity (although potential for carcinogenicity exists) than the corresponding inorganic hydrides. Both compounds are strong reducing agents and may ignite if they are dispersed and exposed to oxidizers, but they are not explosively pyrophoric. American Cyanamid reports that these compounds are viable replacements to arsine and phosphine for growing semiconductor films, based on their high volatility, low thermal decomposition, purity and minimum carbon incorporation during film growth.

Solid sources of arsenic and phosphorus were developed in the early 1980s for semiconductor applications. Solid selenium is a potential alternative to hydrogen selenide for CIS and CIGS cells. Solid sources eliminate the risks associated with accidental release from storage, but not from processing. Solid sources are vaporized at 700–900°C and the vapors are transported into the deposition chambers; the potential therefore exists for accidental vapor releases from the vaporizers. The technical disadvantages of solid sources are the increased set-up time and maintenance, both of which can raise the manufacturing costs.

Safer forms

Sub-atmospheric pressure sources for dopant gases. The most recent development in the safe delivery of toxic gases is the sub-atmospheric pressure gas source (SDS^{TM}), developed by ATMI and Matheson,[3] to deliver dopants to vacuum processes (e.g. arsine, phosphine, boron trifluoride, germane and silicon tetrafluoride). The SDS comprises adsorbent media in a standard compressed-gas cylinder, which reversibly adsorbs the dopant gas. The cylinder is charged with the dopant gas to a pressure slightly less than 1 atm and uses pressure-swing (vacuum) desorption to deliver the dopant to the low-pressure process. This technique effectively changes the source from a high-pressure gas to essentially a solid and greatly reduces the risks related to leakage of these materials; it reduces both the probability of a leak and the associated consequences. Independent tests show that the worst-scenario releases of arsine, phosphine and boron trifluoride from SDS would cause concentrations below half of the corresponding Immediately Dangerous to Life or Health (IDLH) levels and, therefore, SDS eliminates the need for isolating the process and for catastrophic-release scrubbers.

Reduced concentrations. Inorganic hydrides (e.g. SiH_4, AsH_3, PH_3 and B_2H_6) frequently are diluted with hydrogen or an inert gas to reduce the consequences of accidental releases. In most cases, however, undiluted gases at high-pressure sources offer the highest productivity in PV manufacturing. Dilution requires more frequent replacement of cylinders and, sometimes, higher process pressures. For toxic gases

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with a very low concentration threshold there may be a trade-off between frequency of an incident's occurrence (e.g. a leak during a cylinder change) and the maximum consequences of such an event, which is proportional to the concentration and amount of material involved. However, for flammable and explosive gases' the benefit of dilution is less controversial because mixtures below a certain concentration do not present any explosion hazard. An example is silane, which is pyrophoric and potentially explosive. Dilution reduces both the probability for an explosion and the overpressure resulting from an explosion; mixtures of SiH_4 with Ar, N_2 or H_2 will burn down to $\sim$1 mol.%

Point-of-use generation
Point-of-use generation of hazardous materials reduces the hazards of both transportation and storage on-site. Bell Laboratories developed on-demand arsine generators with better purity than from compressed-gas cylinders. There has been no development of point-of-use generation of silane yet.

Reduced quantities
The potential maximum consequences of an accidental release are usually proportional to the quantities of the material on-site. Reduction of on-site quantities can be accomplished by increased rate of use of the material, thinner semiconductor and metal layers and strict control of inventories.

Material utilization rate. Some processes have much higher rates of material use than others (e.g. hot-wire deposition vs plasma-discharge deposition of silane, disilane and germane in a-Si deposition; electrodeposition vs spray pyrolysis in CdTe and CdS deposition). For hazardous chemicals, higher utilization rates offer safety advantages in addition to lower costs; the lower the amounts of chemicals used and stored in a facility, the lower the related potential risks. As PV reaches higher levels of commercialization, processes with low efficiency will have to be improved or unused materials will have to be captured, purified and reused.

Prevention of initiating events

Once specific materials and systems have been selected, strategies to prevent accident-initiating events need to be evaluated and implemented. In the USA, facilities that handle highly hazardous chemicals above certain threshold quantities are required to comply with the Occupational Safety and Health Administration (OSHA) Process Safety Management (PSM) rule and the Environmental Protection Agency (EPA) Risk Management Program (RMP). The OSHA PSM focuses on accident prevention, whereas the EPA RMP expands beyond prevention to the mitigation of the consequences of an accident. About 140 materials are presently listed in these rules; some of these materials are, or have been, used in PV manufacturing (Table I). As Table I shows, today's PV industry is not subject to compliance with these rules because the quantities used in such facilities generally are lower than the threshold quantities. Nevertheless, a pro-active approach on minimizing risks is to the utmost advantage of the PV industry and, therefore, the OSHA and EPA provisions should be of concern to PV facilities that handle highly hazardous materials.

A PSM program covers employee involvement in safety, training, process-hazard analysis, contractor work, mechanical integrity, temporary changes, incident investigation and emergency preparedness. Perhaps the most important item in a PSM is the process-hazard analysis, which has to be formal and rigorous. Hazard analyses focus on equipment, instrumentation, utilities, human actions and external factors that might impact the process and cause an accident-initiating event. An example of such analysis is the Safety Analysis Review (SAR), conducted pro-actively as a result of a self-appraisal by the National Renewable Energy Laboratory (NREL).[4] In this SAR, all the operations in a building underwent a rigorous assessment for accidents and associated risks. Thirty potential accident-initiating events were identified, the risk they may present was characterized and then administrative and engineering controls were implemented to ensure safe operation.[4] Examples of the control options include systems to avoid cross-contamination and cylinder suck-back, elimination of single-point failures that can create

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Table I. Compounds listed in OSHA-PSM and EPA-PMP of interest to the PV industry

Toxic substances			Flammable substances		
Substance	Threshold quantity (lb)		Substance	Threshold quantity (lb)	
	OSHA	EPA		OSHA	EPA
Arsine	150	1000	Dichlorosilane	2500	10000
Boron trichloride	2500	5000	Hydrogen	10000	10000
Boron trifluoride	250	5000	Silane		10000
Diborane	100	2500	Triclorosilane	5000	10000
Hydrofluoric acid (50%)	1000	1000			
Hydrogen fluoride	1000	1000			
Hydrogen selenide	150	500			
Hydrogen sulfide	10000	10000			
Phosphine	–	5000			

cross-connections, safeguards against process deviations and monitoring systems. An extensive list of such options can be found elsewhere.[5]

The importance of administrative options and procedures cannot be overemphasized. In the chemical industry, many accidents have happened not because safety engineering systems were lacking but because safe procedures and preventive strategies were not followed. Training of personnel is an extremely important item in all facilities. Written operating and maintenance procedures should always be in place, and people should follow them at all times. An operator who does not follow a standard written procedure and does not go through a checklist can become complacent. Also, periodic internal audits or third-party audits of operations are recommended.

Prevention and minimization of releases

The next step is to implement safety options to suppress a hazard when an accident-initiating event occurs (e.g. inherently safer design of process, gas distribution and storage systems, early detection, flow restricting and isolation valves, cooling systems, double-containment and adequate ventilation). Currently, most R&D and manufacturing facilities are using compressed-gas cylinders for toxic and flammable inorganic hydrides and other gases. Several incidents are known involving small accidental releases of such gases where there has been a gap in safety procedures or a fault in the design of a gas-handling system. Enhanced safety designs of process- and gas-handling systems is essential for the safe operation of today's PV facilities.

System integrity

Operational hazards are greatly reduced by certain system features, such as properly designed, constructed and vented enclosures for gas-handling systems, welded piping joints for all joints not enclosed in a vented cabinet, ventilation system back-up and alarms and interlocks for process chambers.

Gas cabinets

The introduction of commercial gas cabinet units in 1978–1979 increased safety by providing a containment for small leaks to be diverted away from the operators and controlled. Double stainless-steel cabinets are recommended for fire retardation.

Outside storage

Outside storage bunkers for toxic and pyrophoric gases, which are especially designed for passive ventilation, reduce the occupational risks associated with accidental releases.

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Explosion-proof bunker
Silane cylinders can be kept indoors in explosion-proof bunkers (with relief through the ceiling), but this is an expensive option with high capital costs.

Remotely operated cylinder valves
These valves enhance safety by separating workers from hazards and allowing for remote shutdown in an emergency; they can be integrated into a purge cycle.

Automated purging
Manual purging of a gas-manifold between cylinder changes and maintenance operations is demanding on the operator. Some types of excess-flow valves or check valves that need to be opened during purging do not have clear open positions. In some older facilities, the operator is expected to walk back and forth numerous times from the purging system to the process location during the purging operation. Where many such repetitive steps are involved in a task, there is a high probability for operator error. Automated purge systems radically reduce the number of operator functions needed to complete a purge procedure, thereby reducing potential human errors.

Toxic gas monitoring systems
These systems can give an early warning and allow for the process or source to be shut down before exposures occur. Hazardous-gas detection systems should be located in all areas where workers are potentially exposed. These systems should have both audible and visible alarms triggered at half-threshold limit value (half-TLV) to TLV levels. Today's gas monitors have much better reliability than early versions, offering the accuracy, sensitivity, and response time that are very useful in preventing a transient or a warning that it may occur. A new generation of commercial systems that integrate toxic-gas detection into gas-handling systems and process tools is expected to become available soon. In addition to toxic-gas monitoring and automatic cylinder shut-off, the new systems will probably include seismic monitoring, fire detection, manual pull-stations and autodials to the fire department.

Flow restrictors
Fail-safe equipment and valves, warning systems and safety controls can reduce and interrupt gas leakage. Flow-restricting orifices in cylinder valves have become a common option in pressurized cylinders with highly toxic gases and pyrophoric gases (e.g. AsH_3, PH_3, SiH_4). These orifices can reduce the flow out of an open cylinder-valve by up to two orders of magnitude; therefore, they provide superb passive-flow reduction.

Double containment
In the form of either double-walled storage tanks or double co-axial distribution lines and raceways, double containment is an important measure against leaks of toxic gases into occupational space. Many installations handling toxic gases incorporate some form of double containment, which provides an outer barrier to hold the toxic gas if the inner containment fails. Double piping is used extensively in the semiconductor and PV industry, where small-diameter tubes carrying highly toxic gases are enclosed in larger pipes under nitrogen pressure or are placed into air-purged raceways. Double-wall storage is practiced in many chemical industry applications. Secondary enclosures are used for processes, and pollution-control stations handling toxic vapors contain fugitive emissions and divert them to pollution-control equipment. In designing such enclosures, release and vaporization rates under worst conditions must be considered to determine the capacity and residence times of the scrubbing system or incineration system required to treat the contained gas or vapor. When flammable materials are handled in the plant, the containment must be designed to take into account the possibility of a vapor explosion in addition to the release of toxic materials.

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Redundancy of critical systems

If a hazard analysis identifies accidents that can be caused by the failure of a single component, redundant components may have to be installed. Such critical components may include, but are not limited to, flow regulators, valves, exhaust fans, pumps and compressors. For example, reactor rooms and hazardous-gas rooms and cabinets must be equipped with a dedicated exhaust ventilation system with redundant fans. Both fans should be connected to an emergency power supply and designed so that the auxiliary fan is automatically switched on if the primary fan fails.

Bulk deliveries vs cylinder deliveries

An option for gases that are used in large quantities (e.g. silane) is bulk delivery with tube trailers. Bulk gas delivery offers the PV manufacturer the advantages of better purity, due to less frequent change-outs, and of lower cost. However, the safety issue is controversial. The probability of a leak during a gas-source change is lower because the frequency of changing is lower. (Intel Corp. reports that 50–65% of all unplanned silane releases occurred when changing cylinders.) A counter-argument is that in an operation that takes place only once a year instead of once a week, the operator may become more complacent and the experience gained from this activity is reduced. But, alternatively, such a rare event may be treated in a precise, controlled manner and may become a special event that will have the attention of everyone (e.g. plant management, safety officials, gas supplier and local fire-department officials). The main disadvantage, however, of bulk delivery is the much greater consequences if an accident occurs on-site or during transportation.

Control and minimization of releases to the environment

If an accident occurs and the safety systems fail to contain a release of hazardous gas, then personal and engineering control systems must be relied upon to reduce or minimize environmental releases. Self-contained breathing apparatus (SCBA), spill control and other safety equipment should be available for quick use in all areas where there is the potential for an accidental release.

If the release is confined and can be diverted into the control equipment, chemical scrubbers, adsorption units and combustion chambers can be used. The highly transient nature of large, accidental gas releases demands special designs and configurations for these systems. Commercial wet scrubbers, using high liquid flow and fast-reacting reagents, can scrub up to 142 m^3 of a gas mixture within 5 min; they can be connected to process-equipment exhaust, fume-hood exhaust and gas-cabinets vents. Adsorption units called 'scrams' also can be used for accidental releases in confined spaces; they have been used for treating *dilute* mixtures of silane, chlorosilane, arsine phosphine, diborane, organometallics and acids. They can treat the entire contents of a slowly leaking cylinder (e.g., a 1-gallon 'scram' unit can treat approximately 2 kg of arsine flowing at 30 $l\ m^{-1}$.)

Prevention and minimization of human exposures

As a final defensive barrier, the prevention of human exposures is needed if a hazardous gas is released. This barrier includes storing the gas in a remote location, having exclusion zones adjacent to plant boundaries and having early warning systems, emergency preparedness, response and evacuation plans to prevent exposure to the public. It is essential that such plans are regularly rehearsed and practiced under simulated emergency conditions to test the response of personnel, increase their base of experience and evaluate the effectiveness of equipment. Quick response and medical preparedness is essential to reduce consequences if exposures occur.

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CONCLUSION

It is of the upmost importance to prevent and minimize accidental releases of hazardous gases through the choice of safer technologies, processes and materials, through better material utilization and process- and gas-handling-systems and by having employee training and safety procedures. During the last two decades, significant advancements have been made in the hardware, systems and procedures to reduce the risk of handling hazardous gases in the semiconductor and PV facilities. The most profound safety enhancements in hardware were probably the gas cabinets, flow restrictors and remote-controlled valves. Other very important safety improvements include auto-purge and detection/monitoring systems. Formalized safety analyses to identify potential accident-initiating events and single-component failures have seen increasing use in these facilities. However, the materials have, for the most part, remained the same: hazardous gases in compressed form. Lately, safer forms of toxic doping materials have been introduced, but further research is needed on safer materials and on higher material utilization.

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