

Photovoltaic Specialty Materials Safety

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Abstract — The PV industry uses an assortment of specialty gases and liquids many of which are reactive, pyrophoric or highly toxic, requiring care in handling and special training for emergencies. In addition, some of the PV facilities are being located in countries or regions which have not yet developed the supply or EHS support infrastructure for these materials. Regional expertise is limited, even in the US where facilities are sometimes located in rural areas. The dominant PV technology is crystalline which typically uses silane, phosphine, trimethylboron and ammonia in the process. These gases have a wide variety of hazard characteristics that must be controlled. The dominant specialty gas used is silane, which many users assume will always ignite during an intentional or accidental release. Unfortunately this is not always the case. Tragically, the PV industry suffered two fatal silane accidents in 2005 and 2007 and there have also been numerous fires and explosions. The Integrated Circuit (IC) industry experienced similar problems in the 1970's and 1980's. From 1985 through the 1995, a series of silane technical and safety seminars were conducted in the United States and Europe. These created awareness of potential problems and helped to drastically reduce the number of incidents and/or their severity by establishing industry safe practices and regulations throughout the industry. The PV industry is relearning these lessons learned.

This presentation will be a review of the hazard characteristics of the key metal hydride gases used in PV manufacturing. It will also summarize significant incidents involving silane.

Index Terms — arsine, diborane, germane, hydrogen selenide, metal hydride gas, phosphine, photovoltaic cells, silane

I. INTRODUCTION

The metal hydride gases key raw materials used in various PV manufacturing processes:

Gas	PV Process
Arsine (AsH ₃)	III-V thin film
Diborane (B ₂ H ₆)	Crystalline silicon, thin film amorphous silicon
Germane (GeH ₄)	Thin film amorphous silicon, Tandem Junction
Hydrogen Selenide (H ₂ Se)	CIGS thin film
Phosphine (PH ₃)	Crystalline thin film, III-V thin film
Silane (SiH ₄)	Crystalline silicon, thin film amorphous silicon, III-V thin film

Table 1. Metal hydride gases usage in PV

Metal hydride gases did not find wide commercial use until the late 1960's. During the first 30 years (1965 – 1995) they were used primarily in the fabrication of silicon

semiconductor integrated circuits. During this time, there were numerous releases during manufacturing, handling, transportation or use. Lessons learned from these incidents led to better packaging, systems and controls.

They are used as pure gases or mixtures. Many are also used in low concentrations (100-200 ppm) as dopants.

II. PROPERTIES

With the exception of silane, the metal hydride gases are liquefied gases at ambient temperatures of 70°F (21°C). They are all flammable and with the exception of silane are toxic. These gases have unique chemical and physical properties that the user must be aware of and consider for safe use.

A. Flammability

All of the metal hydride gases have extremely wide flammable ranges >60%, considerably wider than the hydrocarbon gases such as propane (2.15-9.60%) or butane (1.6-8.4%), which many consider to be extremely flammable have ranges much less than 10%. [1]

Diborane has the widest range 0.8% to 98%; in addition an unignited release will rapidly hydrolyze with the moisture in air to form up to 6 moles of hydrogen.

Gas	Flammable Range
Arsine (AsH ₃)	4.5 – 78%
Diborane (B ₂ H ₆)	0.8 – 98%
Germane (GeH ₄)	2.8 – 98%
Hydrogen Selenide (H ₂ Se)	4.5 – 68%
Phosphine (PH ₃)	1.6 – 98%
Silane (SiH ₄)	1.4 – 96%

Table 2. Metal hydride gas flammable range

Silane, phosphine, and diborane are also pyrophoric, with autoignition temperatures <130°F (54.4°C). Silane has been reported to be as low as -148°F (-100°C). [3]

Diborane will spontaneously ignite at temperatures below its reported autoignition of 104°F (40°C) due to impurities (pentaborane).[2] Many consider germane to also be pyrophoric since it can auto ignite in the presence of air and high pressure (500 psig, 3.45 mPa) at temperatures as low as 68°F (20°C). The autoignition temperature in air at 1 atm is has been measured at 194°F (90°C). [4]

Many users forget that hydrogen is formed during chemical scrubbing of the metal hydride gases. In one case a gas supplier ER team disposing of arsine from a leaking cylinder turned down the dilution air into the ER scrubber. This

allowed the byproduct hydrogen to exceed the lower flammable limit. The hydrogen ignited blowing up the scrubber.

B. Toxicity

In the US the transportation (DOT), worker safety (OSHA) and fire codes (IFC, NFPA) compressed gases are classified as toxic based on their LC₅₀ values. The test population for gases is white albino rats.

Gases with a one hour LC₅₀ <5000 ppm are classified as toxic and highly toxic if <200 ppm. The Globally Harmonized System (GHS) has also standardized on the use of LC₅₀ values that are 4 hr. These are is 2 times the 1 hr.

Internationally the reference standard that summarizes the accepted LC₅₀ values for pure gases is ISO10298 "Determination of toxicity of a gas or gas mixture". The standard also contains a simple method of estimating gas mixture toxicity. Table 3 is a summary of the LC₅₀ values for the metal hydride gases and recent changes. This standard underwent a major revision in 2008 with the addition.

Arsine, phosphine, hydrogen selenide and diborane are classified as highly toxic gases, while germane is toxic and silane is not toxic.

Gas	LC ₅₀
Arsine (AsH ₃)	178 ppm updated in 2008 based on better study, (formerly 20 ppm)
Diborane (B ₂ H ₆)	80 ppm
Germane (GeH ₄)	622 ppm
Hydrogen Selenide (H ₂ Se)	51 ppm updated in 2008 based on better study, (formerly 2 ppm)
Phosphine (PH ₃)	20 ppm, mouse data
Silane (SiH ₄)	19,600 ppm

Table 3. Metal hydride gas LC₅₀ values

C. Medical Treatment

The primary route of entry for the metal hydride gases is inhalation. None have a dermal route of entry. In the case of hydrogen selenide, moisture on the skin will hydrolyze it forming selenious acid, a severe irritant. Users of the metal hydride gases should be familiar with the symptoms of exposure.

The major toxic affect of the metal hydride gases are

Gas	Acute Exposure Affect
Arsine (AsH ₃)	Hemolysis (blood, kidney)
Diborane (B ₂ H ₆)	Irritant (respiratory system), byproducts can affect central nervous system
Germane (GeH ₄)	Hemolysis (blood, kidney)
Hydrogen Selenide (H ₂ Se)	Irritant (respiratory system)
Phosphine (PH ₃)	Irritant (respiratory system)

Silane (SiH ₄)	Not toxic, solid combustion products (SiO ₂) are irritants
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Table 4. Metal hydride gas toxic affect

Proper medical treatment of the local health and ER services is absolutely critical. The metal hydride gases differ in exposure symptoms and treatment. Most medical doctors are not familiar with diagnosis or treatment. As part of the user emergency response plan a copy of a medical treatment guideline should be available for the metal hydride gases.

The US Health Dept Medical Management Guidelines are excellent sources of exposure and treatment information. There are guidelines for arsine, diborane and phosphine. These can be found on the website, <http://www.atsdr.cdc.gov> under Medical Management Guidelines (MMGs) for Acute Chemical Exposures. These are comprehensive medical treatment guidelines developed primarily for EMTs, paramedics and medical doctors to diagnose and treat acute chemical exposures.

The image shows an ATSDR (Agency for Toxic Substances and Disease Registry) sheet for arsine (AsH₃). The sheet includes the following information:

- Chemical Name:** Arsine (AsH₃)
- CAS Number:** 7784-42-1; UN 2188
- Synonyms:** include arsenic hydride, arsenic trihydride, arseniuretted hydrogen, arsenious hydride, and hydrogen arsenide.
- Key Points:**
 - Persons exposed to arsine pose no serious risks of secondary contamination to personnel outside the Hot Zone.
 - Arsine is a flammable and highly toxic gas with a garlic-like or fishy odor that does not provide adequate warning of hazardous levels.
 - Inhalation is the major route of arsine exposure. There is little information about absorption through the skin or toxic effects on the skin or eyes. However, contact with liquid arsine may result in frostbite injury.
- Description:** Arsine is a colorless, flammable, and highly toxic gas. It has a garlic-like or fishy odor that can be detected at concentrations of 0.5 ppm and above. Because arsine is nonirritating and produces no immediate symptoms, persons exposed to hazardous levels may be unaware of its presence. Arsine is water soluble. It is generally shipped in cylinders as a liquefied compressed gas. Exposure frequently occurs when arsine gas is generated while metals or crude ores containing arsenic impurities are treated with acid and this is a common source of exposure.

Figure 1. ATSDR Sheet for arsine

As a best practice, a copy should accompany anyone suspected of being exposed. These should be translated into the local language and provided to the local medical facility to minimize delay in treatment.

Byproducts of diborane decomposition have caused numerous dermal exposures. Workers have reported mental confusion and memory loss, in one case temporary paralysis.[5]

D. Thermal Stability

The metal hydride gases all have positive free energies of formation, which means they can decompose into the metal and hydrogen, exothermically. As a result these gases have the potential to decompose violently with only a small energy input (heat, compression, and spark). The free heat of decomposition for the metal hydride gases are:

Gas	Decomposition Heat
Arsine (AsH ₃)	-69 kJ/mole
Diborane (B ₂ H ₆)	-87 kJ/mole
Germane (GeH ₄)	-113 kJ/mole
Hydrogen Selenide (H ₂ Se)	-16 kJ/mole
Phosphine (PH ₃)	-13 kJ/mole
Silane (SiH ₄)	-57 kJ/mole

These values, however, may not be an accurate predictor of whether the gas will sustain decomposition. Silane for example has been tested by numerous researchers over the last 40 years and proven to be very stable. [3]

Diborane is known to be thermally unstable. At room temperature it slowly decomposes forming higher boranes primarily Pentaborane (B₅H₉) and Decaborane (B₁₀H₁₄). Testing however has shown that it requires a significant input of energy to cause it to decompose.[6]

Germane was involved in a significant event on November 26, 1984 in Kawasaki, Kanagawa, Japan. A 44 liter carbon steel cylinder that was being unloaded by the truck driver suddenly ruptured. Subsequent testing demonstrated that germane is unstable, a little energy it will cause it to decompose. The decomposition reaction is exothermic. This heat will cause more germane molecules to decompose and the reaction is self sustaining. In this incident it was estimated that the cylinder was suddenly (100 milliseconds) pressurized to over 9000 psig of Hydrogen pressure. [6][7]

A second incident was reported by a Japanese germane manufacturing company in the late 1980's in a process vessel. After these events, stability studies confirmed that pure germane can easily be caused to deflagrate in the cylinder.

One mole of germane will produce 2 moles of superheated hydrogen and germanium. Since the reaction happens so quickly (adiabatic) will heat the byproduct hydrogen to 1719°F (937°C). As a best practice, gas suppliers in early 1984 reduced the fill density of the cylinders to accommodate the sudden pressure increase assuming a full decomposition in the cylinder. This practice was summarized in a report to the UN Transportation of Dangerous Goods Subcommittee and adopted in Dec 2006. (United Nation ST/SG/AC.10/C.3/34)

Testing by Horiguchi and others has shown that dilution of germane with other gases is effective in suppressing the decomposition reaction. Mixtures in helium containing up to 30% germane and mixtures in hydrogen containing up to 40% germane will not deflagrate in the presence of a source of ignition. The rate of the decomposition reaction energy is too low to sustain the reaction. [7]

As noted earlier, testing by Hazards Research Inc in 1985 showed that the presence of a small amount of air in the gas supply when suddenly pressurized with germane at a pressure of 500 psig (3.45 mPa) will auto ignite due to adiabatic compression heat. This will initiate the decomposition reaction back into the cylinder. [5]

The Compressed Gas Association sponsored similar testing in 1988 for arsine, phosphine, hydrogen selenide and 10% diborane. It was found that they do not sustain a decomposition reaction when heated or given a spark.[8] The Japanese High Pressure Gas Institute conducted similar studies in 1991, reaching the same conclusions

II. PACKAGE

Metal hydride gases are typically packaged in seamless high pressure alloy carbon steel cylinders that have been polished, cleaned and passivated to maintain high purity. Aluminum cylinders are also used.

The transportation regulations in the US and Europe mandate additional safeguards for packages containing highly toxic gases (i.e. 49CFR173.40).

Cylinders containing highly toxic gases also cannot be larger than 50 liters. Mixtures of these gases which have a mixture LC₅₀ > 200 ppm such as a 1% PH₃ balance hydrogen mixture can be packaged in larger cylinders.

A. Cylinder Fill

By definition the metal hydride gases are liquefied compressed gases however at normal ambient temperatures of 70°F (21°C), silane and diborane cannot exist as a liquefied gas. The metal hydride gases are also mixed with gases such as nitrogen or hydrogen in concentrations from ppm levels to 20%. Mixtures are supplied at pressures of up to 2000 psig.

The metal hydride gases have the following vapor pressures at 70°F (21°C)

Gas	Vapor Pressure
Arsine (AsH ₃)	217 psig (1.496 mPa)
Diborane (B ₂ H ₆)	Compressed gas
Germane (GeH ₄)	569 psig (3.923 mPa)
Hydrogen Selenide (H ₂ Se)	123 psig (0.848 mPa) 68°F (20°C)
Phosphine (PH ₃)	513 psig (3.537 mPa)
Silane (SiH ₄)	Compressed gas

Table 5. Metal hydride vapor pressure

Diborane (B₂H₆) has a vapor pressure of 522 psig (3.599 mPa) @ 60°F (15.6°C). Since it has a critical temperature of 62°F (16.7°C), it cannot exist as a liquefied gas at ambient temperature of 70°F (21°C). Because it slowly decomposes at room temperature, diborane is supplied as a pure gas under certain conditions. It is not shipped as a pure gas overseas. Diborane at ambient temperatures can fully decompose in the cylinder over time, forming 3 moles of hydrogen for every mole of diborane. This will increase the cylinder pressure. The transportation regulations require that this be considered when determining the maximum fill of a cylinder.

Silane (SiH_4) has a critical temperature of 20°F (-7°C) so it is a compressed gas under most conditions. During extremely cold weather the silane will liquefy if the cylinder is also at full pressure. The transportation regulations allow a 2400 psig (1.65 mPa) cylinder to be filled to a maximum fill density of 0.37 kg/l, a cylinder pressure of 2000 psig (1.379 mPa) at 70°F (21°C). At this fill density, the pressure in the cylinder can exceed 3000 psig (2.068 mPa) during extremely hot weather, 120°F (48.9°C). Most gas delivery systems are rated for a maximum working pressure of 3000 psig (2.068 mPa); therefore for safety reasons gas suppliers currently fill to 0.322 kg/l.

Because of Superfund Amendment and Reauthorization Act (SARA III), Process Safety Management (PSM), Risk Management Planning (RMP) or local regulations, metal hydride gas cylinders are sometimes filled to a level below the maximum allowed so as to not trigger the regulatory requirements. Arsine for example can be filled to 1.16 kg/liter which means a 44 liter cylinder can be filled to 112 lbs (51 kgs). The maximum most users will take is 50 lbs due to the SARA III and PSM threshold amounts. RMP is much higher at 1000 lbs.

With the liquefied gases the impurity levels increase dramatically as the liquid “heel” is vaporized. Many users of liquefied gases such as arsine will leave a small liquid heel in the cylinder. A 44 liter arsine cylinder will leave a “heel” of 10 lbs.

All of the metal hydride gases are filled by weight since they are liquefied gases. Silane under most conditions is a compressed gas, since it has a high thermal expansion and variable compressibility; it is filled by weight rather than by pressure.

B. Valve

As highly toxic or toxic gases, the cylinder valves must be a metal diaphragm type. To maintain high purity, polished stainless steel is used.

The valve outlet connection varies depending on country, CGA in US, DIN in Europe and JIS in Asia. For the metal hydride gases in the US the CGA 350 or 660 connections are used for older systems. For newer systems the face seal ultra high purity DISS 632 connection is used. For the metal hydride gases the best practice is to use a replaceable metal gasket. Some like the DIN 1, JIS -22 and CGA 660 use PTFE gaskets which can “cold flow” under high pressure conditions. A number of incidents involving silane and phosphine have occurred when an elastomer gasket was used.

To limit the flow from a cylinder, many users have a restrictive flow orifice (RFO) installed in the cylinder valve. The most common size is 0.010” dia.

As shown in figures 2 and 3, a 0.010” dia. RFO can dramatically reduce the silane flow rate from an open cylinder valve. The flow rate ranges from 333 cfm (9430 lpm) to 2.5

cfm (70.8 lpm). The resulting jet flame is 3 m versus 0.5 m. [13]



Figures 2 and 3: A silane release from a cylinder valve without (left) and one with a 0.010” RFO (right).

C. Product Migration

For some processes a continuous supply of the metal hydride gases is required. To provide this, a system that has one full cylinder on line and one full cylinder on standby is typically used. Many users for purity reasons will use the largest cylinder available with the highest weight.

As noted earlier, highly toxic gases cannot be shipped in cylinders larger than 50 liters in volume. Some users to supply multiple tools in a facility or to maintain an adequate flow rate, manifold 2 or more cylinders together. With a liquefied gas such as arsine or phosphine this can create conditions for product migration. An incident in 2003, two sets of arsine cylinders were returned to the gas supplier with widely different weights from the original fill of 50 lbs (22.7 kg). Of the two sets of 5 cylinders returned, one cylinder in each had over 100 lbs (45.4 kgs) of arsine (101 (45.8 kgs) and 113 lbs (51.3 kgs)) while others had considerably less than 50 lbs (22.7 kgs). Due to a quality problem only a small amount has been used before they were returned to the supplier for analysis. The investigation revealed that cylinders manifolded together and exposed to a slight temperature variance can cause the movement of vapor from one cylinder (hotter) into another (colder) where it will liquefy. This process can continue until one cylinder is completely liquid full, a very dangerous condition.

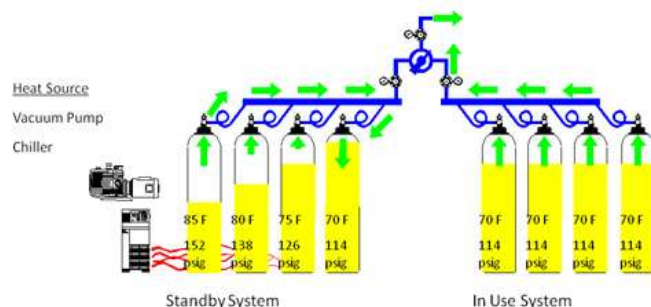


Figure 4. Example of product migration, ammonia

The gas supplier also found cylinders of ammonia from another customer returned with a similar variance.

To alert users of this problem the Product Migration safetygram #38 from Air Products and Chemicals Inc was developed. Users that manifold liquefied gas cylinders together must take this hazard into account and install appropriate safeguards

III. SILANE

Silane is the most commonly used metal hydride gas used to make PV cells in the crystalline or amorphous processes. It is a non toxic, pyrophoric compressed gas. Silane has been used in commercial quantities since the mid 1960's when the first Integrated Circuit (IC) manufacturers began operation. In those early days there was significant debate on how to handle silane safely. The manufacturers made it in small batch reactors and only filled a 49-litre cylinder to 1 kg. The fill weights are now approaching 18 kg. Knowledge of silane's physical and chemical properties was vague. There was significant debate as to its stability in a cylinder. Over the last 40 years considerable study has been conducted to better understand silane's properties and its behavior when it is released during an incident.

While Silane is a very pyrophoric gas with a wide flammable range, it can be released without immediate ignition. While most releases result in an immediate fire, silane under certain conditions has been released without immediate ignition. After a delay it suddenly ignites causing an explosion.



Figure 5. Gas cabinet silane explosion [11] [12] [14] [15]

It has been involved in more fatal accidents in use than the toxic metal hydride gases combined, 12 in the last 25 years.

In the IC industry during the 1970's and 1980's had numerous silane releases in gas cabinets. In a few cases there was a delayed ignition causing a detonations that destroyed the gas cabinet and a fatality. Similar events have occurred in the PV industry in Nov 2005 and March 2007 each causing a fatality.

Silane gas cabinet incidents which involved an explosion include

- Germany, 1976 – 1 fatality
- Japan, 1989, 1 fatality & 1 injury
- Japan, Dec. 13, 1989 – 2 fatality & 2 injuries
- US, Jan 1992 – 1 injury
- US, Feb 7, 1996 – no injuries
- Japan, Dec. 21, 1996 – 1 fatality
- US, Date Unknown – no injuries

- US, 2003 - no injuries
- US, Jan 16, 2005 - 2 injuries
- Taiwan, Nov 2005 – 1 fatality
- India - March 2007 – 1 fatality
- China - June 2009 - 1 injury
- China - 2010 - 1 injury

Numerous incidents involving a silane release and fire have also occurred. Emergency responses to these present a challenge to the user ER team or local fire department.



Figure 6. Gas supplier response to a silane fire.

Silane used at very high flow rates can liquefy due to Joules Thompson expansion cooling in improperly designed and installed systems. This cooling has been the cause of incidents due to regulator failures or leaks due to thermal contraction of mechanical connections. [13]

In 1988 and 1991 the backflow of nitrous oxide into a silane cylinder during use resulted in an explosive mixture (oxidizer and flammable gases). Both cylinders exploded causing 5 fatalities, many injuries and significant damage. After these incidents, the gas and semiconductor industries adopted a best practice to prohibit the sharing of purge gas cylinders with incompatible gases. Some companies use dedicated purge gas cylinders for each silane system.

IV. CONCLUSION

The metal hydride gases which are critical raw materials for the PV industry have the potential to cause incidents some of which can be severe. The user must aware of the hazards associated with them. For safe use the systems must be designed and installed appropriately and the cylinders handled properly.

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