SILANE SAFETY IN AMORPHOUS SILICON AND SILICON NITRIDE OPERATIONS

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ABSTRACT: The PV industry is one of the fastest growing industries in Europe, the United States, and Japan. As PV manufacturing is scaled-up to meet a growing demand, preserving the safe, environmentally friendly nature of the industry becomes even more important. Silane is one of the inherently dangerous materials used in the deposition of silicon nitride (SiN_3) and amorphous silicon (a-Si). In this paper, we review established methods for using this gas safely; they include risk-prevention strategies, passive and active protection systems, outdoor storage, and adequate buffer zones for bulk-silane installations.

Keywords: silane, hazards, safety, photovoltaics, risks

1 INTRODUCTION

The semiconductor industry has used silane for years but during the rapid growth of that industry in the 80s and the 90s, it remained a challenge due to its potential for delayed ignition and explosion. Although pyrophoric, silane does not always auto-ignite when released to the atmosphere, and it entails the potential for severe damage due to its fast deflagration or detonation. Accidental releases of silane present potentially serious consequences, since the gas can ignite spontaneously and, under certain conditions, explode when released into the air. Silane- related risks are illustrated by the number of incidents recorded in the semiconductor industry. A survey of twelve U.S. semiconductor manufacturers showed that there were 36 incidents between 1982 and 1997 [1]; they included 15 fires in ducts and process tools, 6 fires from silane leaks in cabinets or gas supply systems, 5 explosions in ducts, and 3 explosions in cabinets or gas-supply systems. These accidents involved different parts of the silane system, from changing cylinders to emission control. One serious injury (burn) and two minor ones (burn and temporary hearing loss) were reported. The majority (45%) of silane incidents occurred during processing, with fewer during maintenance (21%) and cylinder changes (21%). Together, they caused about $500,000/yr in financial losses from damage and business interruptions [1]. During the same period, two accidents resulting in three fatalities were reported in Japan, both in silane chemical-vapor- deposition systems (Hirano, 2002); the first was an explosion in a gas cabinet (December 1989), and the second an explosion in a laboratory in Osaka University (October 1991). Recently (Nov 2005), a fatal accident was reported during a SiN_3-deposition process (Moltech, Taiwan).

The silane-gas manufacturers and crystalline-silicon producers handle silane in quantities larger than those encountered in manufacturing semiconductors and solar cells. The U.S. EPA Risk Management Program's (RMP's) national database includes six accidents that were associated with silane use in the producers' facilities from 1994 to 1999. Among them, four involved silane only, while the other two were dichlorosilane- or trichlorosilane-leakages. None of these accidents resulted in deaths or severe damages, but two injuries and $686K in economic losses were reported. No accidents with silane were reported in the database during the most recent submission period, 1999-2004.

In response to these hazards, national fire codes and industry standards were designed and developed to prevent further incidents and totally protect silane-handling facilities. The PV industry has benefited from the experience gained by using silane in semiconductor applications, which is distilled in these codes and standards. This paper summarizes the characteristics of such hazard and the protection guidelines applicable to the PV industry.

2 EXPERIMENTAL IGNITION STUDIES

Experimental studies, conducted in the 1980s by the Hazard Research Company (HRC), and the Southwest Research Institute, illuminated several aspects of the conditions under which silane explodes. They were discussed in a previous paper [2]; the major highlights are summarized below:

1) Slow discharges of 100% silane into ducts containing air self-ignited only when the silane concentration reached about 3 to 4%;
2) Small leaks (i.e., 40 lpm) of 100% SiH_4 in gas-storage cabinets purged with 500 cfm of air burned smoothly, without exploding;
3) A larger leak of SiH_4 at 500 psi through a 1-mm (0.06") orifice (flow rate of ~330 lpm) into a storage cabinet caused a sudden explosion, even though the cabinet was continuously purged with 500 cfm air flow;
4) A leak in the upper part of the same cabinet where purging was more effective produced neither an explosion nor a flame;
5) Discharges of mixtures of silane in nitrogen at concentrations of 5-, 7.5-, 10-, and 15-% in a ventilated gas cabinet revealed that a 15% silane mixture explodes even when released

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from a 50 psi source through a 1 mm flow restricting orifice; and,

6) The unconfined outdoor discharge of 100% silane through 0.15 mm (0.006") flow-restricting valves burnt smoothly without generating high temperatures, whereas releases through an open valve without an orifice generated long flames and high temperatures (e.g., >1000°C).

Experiments conducted by Union Carbide [3] show that releases of 100% silane auto-ignite if the exit velocity is below a critical value, in the range of 10-50 m/s, depending on ambient temperature and the orifice's diameter. More recently, Factory Mutual Research (FMR) [4-6] reported auto-ignition starting at exit velocities greater than these values. This contradiction points out the need to account for the different types of ignition that are possible in ventilated enclosures with different geometries and ventilation patterns, in addition to the release conditions. FMR identified five possible ignition-scenarios: prompt ignition; ignition during flow decay; ignition at shutoff; piloted ignition; and, bulk auto-ignition. They found that the reactivity of silane depends on the volumetric concentration of the silane/air mixture (X_f) created from a release, as follows [4-6]:

$X_f < 1.4\%$	Non-flammable mixtures
$1.4\% < X_f < \sim 4.1\%$	Flammable and stable mixtures
$X_f < \sim 4.5\%$	Metastable mixtures

The identification of a lower explosive limit (LEL) of about 1.4% confirms what we knew from previous studies (about 2% LEL). However, the other two sets of conditions represent new knowledge that can be used in guidelines for preventing explosions. At concentrations equal to or greater than 4.5%, the mixtures were metastable and ignited after a certain delay. In an accident, such an event could be extremely destructive and the protection provided by venting would be totally ineffective.

3 GUIDELINES FOR CYLINDER-BASED INSTALLATIONS

Previous studies showed that storing silane in an open space reduces the risk of an explosion, and that if silane is stored indoors in adequately ventilated cabinets, the ventilation effectively prevents the explosion of small releases through 1 mm orifices. Articles 51 and 80 of the UFC list the requirements for ventilation inside an enclosure.

The different results obtained in HRC's experiments with constant silane and ventilation flows, but at a different location of release in the cabinet, shows that pockets of explosive concentrations of silane can be formed even in cabinets with a high ventilation rate. The FRR studies empirically determined that to prevent pockets of metastable 4% silane concentrations accumulating in gas cabinets or other enclosures, the silane inventory must be limited to 1% of the enclosure's volume. However, this determination assumes an instantaneous inventory release; if the release is a function of time, then less restrictive limits can apply. FMR also determined that the ventilation system must be sized so that the maximum concentration of silane inside the cabinet does not exceed 0.4 vol%.

1) The recent FMR studies demonstrate the need for design requirements, which include, but are not limited to, the following: 1) To prevent bulk auto-ignition, limit to 1% the maximum concentration of silane that would result from a release in an enclosure. The silane inventory used in these calculations is the volume of silane contained in the piping between the restricted flow orifices (RFOs) or between an RFO and the end of the point of use. If the net volume of the cabinet (or enclosure) is too small for the silane inventory, then additional RFOs should be installed to segment the supply lines and reduce the inventory to the desired value of 1% of the cabinet enclosure's net volume.
2) Size the ventilation system in gas cabinets and other enclosures to limit the maximum concentration of silane inside the cabinet to 0.4 percent by volume. Base the maximum concentration of silane inside the gas cabinet on the continuous release of SiH_4 at a standard volumetric flow-rate given by the size of the RFO in the discharge line and the maximum storage pressure in the SiH_4 gas cylinder. .
3) Ensure explosion-venting for gas cabinets and enclosures to limit the build-up of overpressure inside gas cabinets and enclosures to 0.25 psig (1.7 kPag). Venting can be provided by door panels, windows, louvers, or exhaust-duct openings.

4 GUIDELINES FOR BULK SILANE STORAGE INSTALLATIONS

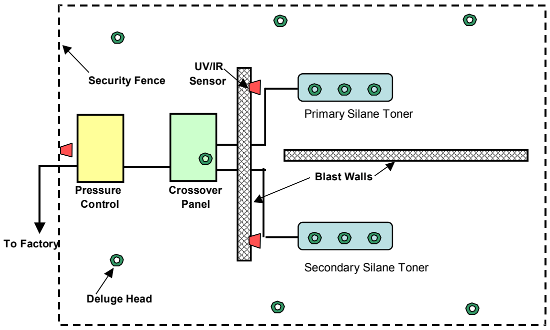

Figure 1. Mini-Bulk and Bulk Silane Storage Installations

A large fraction of the previously reported incidents occurred when changing cylinders. Because of this, and the increased volume requirements for silane, the industry is oriented towards mini-bulk or bulk silane-installations. The former comprise a "toner", a large cylinder with capacity of about 100 kg, whereas bulk systems consist of a tube trailer. Though fewer incidents would be expected with bulk silane installations, any incidents that do occur would be more severe.

The NFPA 318 Committee dedicated an entire chapter to addressing this hazard. The maximum release flow rates in these installations are reduced by flow restrictors, pressure transducers for cylinder- and delivery-pressures, excess flow switch, shut off valve close to pigtail connection, silane system alarm tie-in to central control room for monitoring purpose, and the potential for loss is reduced by blast walls, spacing the tanks with 2 hours fire wall separation, having a deluge system, and secure fencing separation zones. UV/IR detectors are used in the gas installations, with hydride sensors downstream in the tools for using silane gas.

As in standard cylinder installations, the operators' training and safety procedures with buddy system for changing a cylinder are extremely important. Procedures for operators include but are not limited to: 1) Conducting several pre-purge cycles; 2) ensuring that at the end of the pre-purge cycle, the system maintains a triple purge (approx. 1-3 psi) through a pigtail connection to prevent any air or moisture getting into a manifold via an opening; 3) Don Nomex suit, gloves, ear plugs 4) disconnecting the pigtail connection; 5) removing and inspecting used Ni gaskets; 6) checking the torroids' sealing surface and inserting a new gasket.; 7) connecting the pigtail by using a specific torque wrench; 8) checking the system for gross leakages; 9) conducting helium leak checks (outboard leak check), the pigtail connections, and all connections at the manifold; 10) conducting static leak checks; 11) ensuring the system runs several post-purge cycles; 12) refilling the manifold with process gas. 13) Record tonner and delivery pressure and other anomaly if any. Also, operator does daily walkthrough for system check.

In addition, operators inspect the safety features with a preventive maintenance schedule: They include but are not limited to: Testing the emergency gas-off button; valve testing checks by pressure-decay methodology; calibration of pressure transducers; and, checking of process regulators.

5 HAZARD ANALYSIS TO PROTECT FACILITIES

Facilities that handle highly hazardous chemicals above certain threshold quantities are required to comply with the Occupational Safety and Health Administration’s (OSHA’s) Process Safety Management (PSM) Rule, and the Environmental Protection Agency’s (EPA’s) Risk Management Program (RMP). The former focuses on accident prevention, whereas the latter expands beyond prevention to the mitigation of the consequences of an accident. About 180 materials presently are listed in these rules, some of which are used in PV manufacturing. Most of today's PV facilities are not required to comply with these rules because they handle quantities smaller than the threshold quantities. Nevertheless, a pro-active approach on minimizing risks is to the utmost advantage of the PV industry, and the OSHA and EPA provisions should taken as guidance for all PV facilities that handle highly hazardous materials. Perhaps the most important item in a PSM is the process-hazard analysis (PHA). These focus on equipment, instrumentation, utilities, human actions, and external factors that might impact the process and cause an accident- initiating event.

Due to their potential for catastrophic events, bulk-silane installations particularly need to be evaluated via a comprehensive hazard analysis. Several methods of hazard evaluation are available to the industry. They include hazard and operability analysis (HazOp), failure modes and effects analysis (FEMA), event-tree analysis, fault-tree analyses (FTA), layers of protection analysis (LOPA), safety analysis reviews (SAR), and Security Risk Analysis. We discussed the strengths and weaknesses of each method, and presented sample applications in PV manufacturing elsewhere [7]. The costs of conducting hazard analyses and implementing the corrective actions were moderate; the expected benefits by far surpass the costs. Furthermore, such analyses, while enhancing the safety of a facility, also can lead to improvements in reliability and productivity.

6 CONCLUSION

The PV industry has an excellent record in complying with existing safety codes and regulations. Prevention options, adherence to safety codes and standards, and continuous vigilance can maintain the safe, environmentally friendly nature of the PV facilities during their current expansion.

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