

**Silane Safety Improvement Project
S71 Final Report**

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Silane Safety Improvement Project S71 Final Report

Technology Transfer # 94062405A-ENG

SEMATECH

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Abstract: This document is the appendix to the final S71: Silane Safety Improvement Report, Technology Transfer #94062405A-ENG. It contains the results of an Equipment and Risk Assessment Questionnaire developed by AT&T Bell Laboratories under contract to SEMATECH. The survey report was sent to approximately 270 participants including semiconductor manufacturing and research and development companies, solar cell manufacturers, flat panel display manufacturers, and universities. A compilation of silane incidents and associated estimated costs is also included.

Keywords: Furnaces, Epitaxial Silicon Deposition, Polysilicon, Employee Safety, Hazardous Materials, Silane

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1 EXECUTIVE SUMMARY

This document presents the results of the Silane Safety Improvement project (S71). The objectives of the study were to 1) identify and disseminate engineering control practices considered to be effective by those who work with silane, 2) quantitatively evaluate the risks of using silane, and 3) identify the most promising alternative to silane in compressed gas cylinders. Recommendations for future SEMATECH silane safety efforts are presented.

The engineering controls and risk information was gathered by survey questionnaires and site visits. Silane users from the semiconductor, photovoltaic, flat-panel display, and xerography industries were included. Universities, research laboratories, and silane producers and distributors also provided data for the study. Engineering control practices were described. The detailed data from this survey is found in the companion document, *Appendix to the Silane Safety Improvement Project Report*, SEMATECH Technology Transfer #94062406A-XFR.

The average reported cost of a silane installation was approximately \$306,000. The median value was approximately \$101,000. Silane-related accidents cause about \$500,000 in financial losses from damage and business interruption each year in the United States. During the past 13 years, one serious (burn) and two minor (burn and temporary hearing loss) injuries were reported to researchers for this study. The majority (45%) of silane incidents occur during processing, with smaller amounts occurring during maintenance (21%) and cylinder changes (21%).

Past and current research efforts to develop silane alternatives were evaluated. No further work on developing organosilanes to replace silane for polysilicon deposition processes is appropriate. Up to 20 atomic-percent of carbon is incorporated into the polysilicon because of the affinity of hydrocarbon fragments for silicon. Organosilanes and chlorosilanes have been successfully substituted for silane in silicon dioxide and epitaxial silicon deposition.

Point-of-use generation and purification of silane offer potential transportation safety and process-control advantages. Point-of-use generation is also attractive to small users and to those with facilities where storing hazardous materials is difficult or prohibited. A practical chemical mechanism for point-of-use silane generation is not known. Therefore, it is not possible to assess the probability of successful development of this technology. Development of this technology is expected to take three to five years and cost in excess of \$5,000,000. Given the relatively low financial losses related to silane accidents and the low injury rate, there is little motivation to begin such an uncertain undertaking.

Interest in bulk distribution systems continues to grow, with six installations either in existence or in the planning stages in the United States.

Professionals interested in silane safety were invited to a workshop sponsored by SEMATECH. The information gathered in this study was reviewed. The group developed the following recommendations for future efforts by SEMATECH:

- Form a silane users group to evaluate safety practices and disseminate information. The group would prioritize needs and provide help in project planning and execution. Assist in the development of codes, standards, and guidelines.

- Perform hazard analysis. Evaluate bulk silane distribution systems. Conduct experiments to test the effectiveness of limiting-flow orifices (LFOs) in preventing silane explosions. Compare silane hazards to other industrial materials. Compare the performance and hazards of different abatement systems.
- Evaluate the feasibility of point-of-use generation of silane. Find a practical chemical pathway for silane generation. Evaluate economic feasibility. Conduct a process hazard analysis of the whole reaction system.

2 INTRODUCTION AND PROJECT DESCRIPTION

Silane is a critical chemical reagent used in the manufacture of a wide range of silicon-based thin films for the microelectronics industry. Silane is also used in producing amorphous silicon and polycrystalline silicon films for solar cells, xerography, and advanced active-matrix displays. Because of its pyrophoric nature, serious safety issues have been raised concerning the use, transportation, and storage of compressed gas cylinders of silane.

There has been a persistent interest in finding less hazardous materials with which to replace silane. Alternatives have been found for some semiconductor applications, including silicon dioxide and epitaxial silicon deposition. However, deposition of high-purity polysilicon from any starting material other than silane has not been demonstrated. Several critical process performance challenges have been identified that have yet to be overcome.

Replacing silane is not the only activity that can be undertaken to improve worker and community safety. The SEMATECH Environmental, Safety, and Health (ESH) Focus Technical Advisory Board (FTAB) and the Materials and Bulk Processes FTAB appointed a Project Technical Advisory Board (PTAB) to assess current silane use risks and to recommend actions that SEMATECH should take to reduce the hazards associated with silane use. A contract was established with AT&T Bell Laboratories to

1. Survey silane users, producers, and distributors to benchmark common engineering control practices and identify effective practices.
2. Survey silane users, producers, and distributors to assess the risks associated with silane use and to document silane incidents, including costs and injuries.
3. Identify a silane replacement strategy that shows the highest probability of successful development.
4. Determine if replacing silane for silicon deposition is necessary and if there is a viable path toward replacement.

The information gathered during this study was presented at a Silane Safety Workshop, convened on June 1, 1994. The workshop was attended by professionals interested in silane safety, use, production, and distribution. The workshop participants reached conclusions based upon the information presented and developed three recommendations. These were ratified by the PTAB members and are documented in this report.

These recommendations are the consensus of a wide range of professionals concerned about silane safety. They provide objectives and data-driven direction for future SEMATECH projects aimed at improving silane safety.

The Silane Safety Improvement Project was designated project S71. The project objectives were defined after consulting with people from the industry with experience in safety, use, production, and distribution of silane. This input was obtained in a Silane Safety Workshop conducted on November 2, 1993, at SEMATECH. The minutes of that meeting were published in SEMATECH Technology Transfer #93112071-MIN. The project was further defined in a statement of work (SOW) in SEMATECH Technology Transfer #93112098A-SOW.

3 BENCHMARKING AND RISK ASSESSMENT DATA COLLECTION

Data concerning engineering control practices and risks was collected using surveys and making site visits. Silane users, producers, and distributors were included in the survey. In addition, insurance companies that serve facilities using silane provided information on silane incidents that resulted in large losses.

The benchmarking survey (included in Appendix I, SEMATECH Technology Transfer #94062406A-XFR) was developed to collect data in three general areas:

- Facility/Protocols Facility design and management procedures
- Equipment Cylinder, gas cabinet, and process tool features
- Incidents Description of silane incidents

Surveys were generated and results were tabulated using the software package *Survey Power*, published by WISCO Computing, Wisconsin Rapids, WI. Approximately 270 surveys were sent to silane users, manufacturers, and cylinder-filling facilities. Silane users included facilities involved in semiconductor manufacturing and research and development (R&D), solar cell manufacturing, and flat panel display manufacturing and R&D. These facilities also included universities. From the 270 surveys sent out, the following number of surveys were completed and returned:

- 45 Facility/Protocols Sections
- 67 Equipment Sections
- 55 Incident Sections

The tabulated results from these returned surveys are contained in Appendix II, SEMATECH Technology Transfer #94062406A-XFR. Approximately 25% of the surveys were returned.

3.1 Facility/Protocols—Facility Design and Management Procedures

The following is a summary of the results and open-ended responses from the survey questions on facilities and procedures protocols. For more detailed information, see Appendix II, SEMATECH Technology Transfer #94062406A-XFR, for the responses to individual questions.

3.1.1 Facility Description

Eighty-two percent of the responses came from semiconductor manufacturing/R&D facilities. The number of employees working at these facilities ranged from 25 to 5,000. The majority of the respondents consider their silane systems' integrity to be "very good," with a low probability/potential for injuries. Personnel/operators are considered to be highly competent. Facility walls, floors, and roofs are constructed out of concrete and/or metal and about one-half of the facilities contain a fire-resistive coating that has been applied to some part of the building. Many facilities have more than one floor, but most silane cylinders and (chemical vapor deposition [CVD] equipment) processes are located on the ground or first floor. Five facilities locate their cylinders on the roof in metal-mesh cabinets. One-half of the systems surveyed were installed before 1989. One system installed in 1972 was still operating.

Silane facility costs vary widely depending upon the type of installation. The median cost reported for a silane installation was **\$101,000**. The average reported cost was **\$306,000**. This study included very small research installations and very large silane cylinder-filling installations (more detailed cost information can be seen in the responses to questions 16 through 21, Appendix II, SEMATECH Technology Transfer #94062406A-XFR).

3.1.2 Cylinder Change Management

Silane cylinders are most often delivered during work hours or "as convenient." Only 12% of the respondents deliver cylinders out-of-hours. One large silane user does not allow cylinder changes or deliveries between of 12:00 a.m. and 5:00 a.m. Most silane handlers receive special training and require special qualifications (see questions #23 and 24 in Appendix II, SEMATECH Technology Transfer #94062406A-XFR); however, three facilities do not provide any training and eight facilities do not require any special qualifications. Because respondents represent manufacturing as well as R&D (industrial and academic), the frequency of cylinder changes ranged from daily for cylinder-filling facilities to years for small R&D operations. Just-in-time cylinder delivery is being used at about 50% of the reporting facilities.

3.1.3 Delivery System Preventative Maintenance

Twenty-five percent of the respondents indicated that they perform regular preventative maintenance on process vacuum pumps and gas monitors. Other equipment (e.g., regulators and delivery manifold/delivery line components) received about 10% of the responses. About one-half of the respondents said that no preventative maintenance was performed on delivery manifolds, and 70% said none was performed on delivery lines.

3.1.4 Codes and Guidelines

Permits from local authorities to operate silane systems and hazardous materials management plans are required in about one-half of the reporting facilities. Eighty-nine percent of the respondents reported that strict adherence to codes would not be adequate to prevent silane incidents. Compliance to much stricter industry or company guidelines is required for silane safety. Only two respondents said that their silane system/facility was not constructed to some sort of model code or company guideline.

3.1.5 Monitoring

Fire protection and gas monitoring systems most often have back-up power supplies when compared to equipment such as process controllers/computers, vacuum pumps, and exhaust fans. Temperature/heat detectors are the most common types of fire detectors used, followed by smoke and flame detectors. Seventeen percent of the respondents reported no fire detectors. Water is almost universally used in fire suppression systems. Gas monitors are being used in about 75% of reported facilities and of these, 64% use paper tape/chemcassette type systems. Formal process safety reviews have been conducted at 64% of the reporting facilities.

3.1.6 Risk Reduction Actions

The majority of respondents report that no alternative materials for silane have been considered; however, about one-half said that process/equipment changes were considered to reduce silane flow rates and/or concentrations.

Close to 70% of the respondents report that their silane supplier offers them assistance through a Product Stewardship Program.

3.2 Equipment – Cylinder, Gas Cabinet, and Tool Features

The following is a summary of the results and open-ended responses from the survey questions on silane handling equipment. For more detailed information, see Appendix II, SEMATECH Technology Transfer #94062406A-XFR, for the responses to individual questions.

3.2.1 Cylinders

Silane cylinders in use are most often 9-inches (diameter) x 51-inches (height), are made of steel, and contain 5,000 grams of silane at 790 psig. The 6-inches (diameter) by 19-inches (height) cylinder accounted for 20% of the responses as did aluminum cylinders of all sizes. Larger silane users purchase 10,000, 12,000, and 16,000 gram cylinders at pressures ranging from 1,200 to 1,650 psig. Tube trailers and cylinder clusters or bundles represented about 5% of the responses, but these were from silane manufacturers or cylinder-filling facilities only. When cylinder diluent gases are used to reduce silane concentrations, nitrogen is most often used.

Most cylinder valves are stainless steel (12% of respondents use brass valves) and have manual diaphragm types designed for the Compressed Gas Association (CGA) 350 connection. A trend does exist that favors pneumatically operated cylinder valves and the CGA 632 connection. Nine percent of the respondents do not use LFOs in the cylinder valve. Others use 6, 10, or 14 mil orifices (10 mil being the most common).

Eighty percent of the responses show that one or two silane cylinders are allowed in a single gas cabinet. Seventy-one percent have restrictions on the amount of silane allowed indoors; however, these restrictions do not affect the ability to process since 65% of the respondents stage silane cylinders indoors.

3.2.2 Personal Protective Equipment

Personal protective equipment for changing silane cylinders most often includes flame retardant suits, self-contained breathing apparatus (SCBA), face shield and goggles or safety glasses, heat-resistant gloves, and safety shoes. Large silane users and manufacturers do not use SCBAs. Ear plugs are usually part of their standard equipment. One large silane user prefers leather jackets over standard turn-out gear based upon experimental results that showed leather's superior flame resistance.

3.2.3 Gas Cabinets/Pads

Despite the industry's emphasis on open-air installations, 74% of the responses show use of exhausted gas cabinets for staging silane cylinders. The cabinet or its surroundings are electrically classified according to the National Electrical Code Hazardous Locations or are considered to be intrinsically safe in 63% of the responses. The "not classified" response was chosen by 32% of the respondents. Gas cabinets are normally not locked.

3.2.4 Manifolds

All delivery manifolds are constructed out of stainless steel; one-half of them are manually (versus automatically) operated. Cylinder nitrogen is the purge gas of choice. Helium/nitrogen mixes are also being used because the helium component can also be used for leak checking. One purge cylinder is dedicated to one silane cylinder in about 50% of the responses and is usually (61%) not located in the same cabinet with the silane cylinder. House nitrogen is being used to purge 15% of the respondents' systems. Pressure/vacuum cycle purging is used, with the number of cycles ranging between 7 and 100. Only 6% of the respondents do not have an automatic shut-off valve at the cylinder, and 18% have no excess flow protection. Regulators are single or two stage and most often of the tied diaphragm design. All regulator diaphragms are stainless steel. Fifty percent of the responses show that valves on the low-pressure side of the delivery manifold are rated for high-pressure service (2,000 psig or greater). Manifold valves are diaphragm (63%) or bellows (18%); some packed valves are being used (6%). Welded manifolds with VCR fittings are preferred. Delivery manifold sensors/interlocks most often chosen include exhaust failure, overpressure, gas monitor, and sprinkler flow. Ninety-one percent of the responses confirmed the use of remote emergency shut-offs to the delivery manifold, but only one-half of these have emergency shut-offs for the entire silane staging area.

3.2.5 Delivery Lines

Delivery lines are stainless steel, 1/4 inch or 3/8 inch, with 0.035-inch wall thickness. Delivery lines are most often totally welded and are always leak-checked/pressure tested to company, SEMI, or ASTM specifications. Fifty percent of the delivery lines are monitored coaxial systems. Delivery pressures range between 15 and 30 psig, with flows controlled through process regulators (53%) and mass flow controllers. Check valves are present 45% of the time at the process equipment (CVD manifold). Silane flow to process equipment can be shut off for 16 different reasons (Appendix II, question #67, SEMATECH Technology Transfer #94062406A-XFR). All respondents chose the emergency-off button response. Multiple delivery lines are being installed from two or more cylinder cabinets with auto switch-over capabilities that feed multiple processes.

3.2.6 Vacuum Pumps

Some vacuum pumps on CVD systems are using hydrocarbon oils (17%). Most facilities are using perfluoropolyether type oils, but the trend is toward dry pumps. Only 8% of the respondents said that their vacuum pumps did not have a purge/ballast. Fifty-five percent said that their vacuum pump purge was not interlocked to process gas flows. Vacuum pump oil changes ranged from every two days to annually and also included “never” (8%) and “topped off” (10%) responses. Personal protective equipment for oil changes includes face shields, gloves, safety glasses/goggles, and safety shoes. In a few cases, SCBA or air-purifying respirators, flame-retardant suits, and ear plugs are also being used.

3.2.7 Exhaust Ducts

Exhaust ducts are dedicated to silane processes 50% of the time. They are made out of steel or flame-retardant polymer. Twenty-five percent of the respondents said that duct fire protection systems were not part of their silane systems. Burn boxes and wet scrubbers are most popular for emission control.

3.3 Description of Silane Incidents

The following is a summary of the results and open-ended responses from the survey questions on silane incidents. For more detailed information, see Appendix II, SEMATECH Technology Transfer #94062406A-XFR, for the responses to individual questions. A silane incident was defined as any unplanned release of silane.

3.3.1 Number of Events and Location

Out of the 55 incident surveys returned, 38 (69%) of the respondents reported that an incident had occurred during the last five years. A brief description of the 38 reported incidents and measures to prevent similar incidents is given in Incident Benchmark Survey questions #8 and #10 of Appendix II, SEMATECH Technology Transfer #94062406A-XFR. The majority of the incidents occurred in service corridors and gas rooms and involved different parts of the silane system from cylinder staging to emission control.

3.3.2 Additional Silane Incidents Reports

In addition to the 38 incidents, one survey respondent provided silane incident history data from 1985 through 1993 (this report is included at the end of Appendix II, SEMATECH Technology Transfer #94062406A-XFR). Of the 53 incidents included in this additional report, 46 of the cases resulted in no equipment damage. Equipment was damaged in seven of the incidents. There was no cost data included in the report.

The incident surveys also noted that there were two incidents involving personnel injuries. One person was severely burned during one of these incidents. In another incident one person received minor burns.

3.3.3 Activity Prior to Incident

Question #14 of the Incident Benchmark Survey (Appendix II, SEMATECH Technology Transfer #94062406A-XFR) shows that processing was the operation being conducted most often when silane was released (45% of responses). Twenty-one percent of the responses said that incidents occurred during cylinder change/delivery, and another 21% said that maintenance/repair was involved.

3.3.4 Consequences of Incident

Fire was most often the consequence of the silane release that was detected by human observation or gas monitoring.

Combustible vacuum pump oil and poor emergency response added to the consequences of the silane release, but in most cases (81%), nothing made the consequences worse. Only three respondents said that a sprinkler head activated: two inside gas plumbing enclosures and one inside an exhaust duct. Company emergency response teams responded to the releases most often along with engineers/technicians and ESH personnel.

Process tool downtime ranged from two days (most often) to one month. Nineteen percent of the incidents did not result in any downtime. Various costs for the parts of the silane systems were reported (questions #28–#33, Appendix II, SEMATECH Technology Transfer #94062406A-XFR) as a result of the incidents. The survey questionnaire respondents included financial loss data for 15 of the safety incidents they reported. These occurred between 1989 and 1993 and the total-loss value reported was \$238,000.

3.3.5 Analysis of Incidents

Root causes were poor design, human error, procedures, and inadequate construction as well as lack of training and improper maintenance.

When a particular component/part of the system caused the silane release, the CGA connection and inadequate purge were most often responsible.

In 92% of the reported incidents, no violations to codes, acceptable industry practices, or company guidelines were found. Process safety reviews had been conducted in 64% of the cases.

3.4 Site Visit Report

Benchmarking site visits were made to:

Semiconductor Manufacturers	–	9 Facilities
Semiconductor Research & Development	–	4 Facilities
Universities	–	4 Facilities
Silane Cylinder-Filling Facilities	–	4 Facilities
Silane Manufacturers	–	2 Facilities
Solar Cell Manufacturers	–	2 Facilities
Flat-Panel Display Manufacturers/Research and Development	–	3 Facilities

During these visits, the data gathered focused primarily on silane use, handling, and control details to supplement data gathered on the survey questionnaire. This data was gathered by conducting interviews, reviewing engineering drawings and incident investigation reports, and taking facility tours. The data contained here complements the survey data with additional details.

3.4.1 Management Structure

Facilities that maintain ESH departments (regardless of size) and are separated from technical and facilities management organizations exhibit programs with the most comprehensive silane controls. Facilities that delegate safety responsibilities as a part-time function to a facility or process engineer generally have less extensive safety programs. Facilities reflecting minimal controls often do not conduct process safety reviews and do not have personnel dedicated to critical functions (e.g., silane cylinder changes).

When a “technical safety champion” (e.g., process engineer/scientist or fab manager) existed who worked with a site safety committee, safety programs were as extensive as those found where separate ESH organizations existed.

3.4.2 Cylinders and Valves

The most common silane cylinder materials are carbon steel, aluminum alloy, and stainless steel. An electropolished stainless steel cylinder represents the highest purity container; however, its cost (\$2,000–\$4,000, depending on size) is prohibitive to many users. Purity between carbon steel and aluminum does not appear to be an issue, based upon extensive cylinder preparation and tight gas supplier specifications. Aluminum and steel cylinders are equally suitable as high-pressure containers, as concluded from U.S. Department of Transportation (DOT) cylinder abuse tests. However, because of the low temperatures used for tempering cylinder aluminum alloys, an aluminum cylinder involved in a fire could lose strength. Aluminum cylinders with fiber wrapping offer added strength and a tell-tale sign to the gas supplier when a cylinder is involved in a fire. Common cylinder quantities are 5,000g, 10,000g, 12,000g, and 16,000g.

Just-in-time (JIT) delivery of silane cylinders minimizes storage concerns. However, JIT delivery is not always possible. Locked, chain-link fence enclosures that are weather protected and located according to the Uniform Fire Code (UFC) separation distances are used. Many of the benchmarked storage areas are electrically classified according to the National Electrical Code as Class I, Division 2 hazardous locations. This UFC requirement may be removed from the 1994 re-write of Article 80. In many cases, stored cylinders are placed inside gas cabinets next to the “staged” cylinder.

Cylinder valves commonly include brass and stainless steel Superior valves and stainless steel Ceodeux manual and pneumatic valves. With dedicated, knowledgeable personnel, brass valves used with stainless steel delivery manifold connections offer leak-tight connections. Stainless steel valves with stainless steel CGA 350 connections have resulted in silane leaks. Tied-diaphragm cylinder valves (e.g., Ceodeux stainless steel) is one method to improve leak protection, because this design includes a dual seal. Ceodeux pneumatic cylinder valves were the only pneumatic cylinder valves noted in use.

CGA fittings include the left-hand thread 350 and the right-hand thread, diameter index safety system (DISS) 632. Overuse of the CGA 350 has resulted in nipple galling and silane leaks. Some benchmarked systems include a “stabilizer” block welded into the pigtail just downstream of the CGA nipple. This block is used to prevent the nipple from spinning when making the connection. Many older systems use National Pipe Thread (NPT) connectors with Teflon tape between the delivery manifold and the CGA nipple.

The DISS/CGA 632 connection for silane cylinders experienced some problems when it was first introduced. Some of these problems can be traced to the connection’s design, while others are due to the user’s lack of knowledge about the connection. Early in its introduction, silane leaks resulted from the lack of sealing gasket retaining clips, using the wrong gasket/part number, and using 316L stainless steel gaskets instead of the currently used nickel gaskets (some cylinders are still being supplied to users with stainless steel gaskets).

Past problems with making the connection also resulted in silane leaks. Some of the causes of these leaks still have the potential to cause leaks today. The first is failure to use a torque wrench when making the connection or replacing the dust cap. This can result in leaks from applying less than the recommended 35 ft-lbs (for connections with nickel gaskets) and not having tight connections. It can also result in leaks from applying more than the required torque and causing damage to the cylinder valve toroids. Too much torque can also work-harden a nickel gasket and cause toroid damage. A second cause of failure in making a good seal is by reusing gaskets.

Some cylinder-filling facilities are using KEL-F gaskets because they can be reused. KEL-F gaskets, as well as silver-coated stainless steel gaskets, are not affected by the Joule-Thomson effect when silane is released at high pressures. Cylinder-filling facilities have experienced silane leaks from this effect with nickel and stainless steel gaskets when pressure transitions go from 1,600 psig to atmospheric pressure. One silane cylinder-filling facility has experienced leaks when applying the recommended 12 ft-lbs torque to the CGA 632 connection using KEL-F gaskets. This supplier recommends a 20 ft-lbs torque to eliminate leaks. Some suppliers are considering supplying KEL-F gaskets with their CGA 632 connections to reduce the number of damaged valves received on returned cylinders as a result of too much torque being applied to the connection and/or dust cap. Pre-grooved nickel gaskets are also being considered to allow for re-use. Other concerns over the CGA 632 connection are the following:

- Backpurging through the nipple during cylinder change can result in dislodging the gasket.
- If a newly made connection leaks, it should not be tightened further. Proper procedure calls for remaking the connection.
- Approximately 10 ft-lbs is needed to loosen the connection. This could be a mechanism for leaks.

Many potential problems with the CGA 632 can be solved through education. Because the connection is a more sophisticated sealing mechanism than other, more common connections, guidelines have been recommended by the CGA for making the connection. Failure to follow their guidelines will adversely affect the sealing of the connection and its useful life. These guidelines can be found in CGA Technical bulletin TB-9--1993 “Guidelines for the Proper Handling and Use of the CGA 630/710 Series Ultra High-Integrity Service” Connections.”

3.4.3 Limiting-Flow Orifices (LFOs)

Since the publication of the IBM/Hazards Research Corporation report “Discharge of Silane in Open Air and in Toxic Gas Cabinets (1983),” the LFO’s importance in preventing silane explosions has gained wide acceptance. Some silane users, however, refuse to purchase cylinders with LFOs because they believe purging is inadequate behind the LFO and could lead to contamination problems. Little evidence exists that supports this theory. In fact, theoretical calculations predict adequate purging. There are, however, legitimate concerns over LFOs. For example, little data exists on the engineering design rationale of LFOs and the commonly used sizes of 0.006, 0.010, and 0.014 inches. From a practical standpoint, sizing of the LFO must consider flowrate in relation to the ventilation rate present where the silane cylinder is staged. This, after all, is one of the driving safety reasons for using LFOs in the first place. LFOs should be sized according to SEMI S5-93 “Safety Guideline for Limiting-Flow Devices.” Specifications on LFOs are not required by some of the largest silane cylinder suppliers. LFOs also create a problem in cylinder auto switch-over systems supplying gas to multiple processes. Because of the high flowrates demanded by such systems, autoswitch-over occurs prematurely because the LFO pressure-dependent flowrate cannot provide the demand. This results in larger than normal unusable quantities of silane left in cylinders to be returned to the supplier.

3.4.4 Gas Cabinets and Manifolds

The NFPA 318 “Standard for Protection of Cleanrooms” guideline states that when gas cabinets are used for pyrophoric gases, only single cylinder cabinets are allowed. In most of the benchmarked facilities using gas cabinets, this was not the case. Various configurations in use are listed below.

- Three-cylinder cabinets contain one on-line cylinder, one spare, and one purge cylinder. Some three-cylinder configurations also use auto switch-over with two delivery panels while others used auto switch-over with one delivery panel. In some cases, switch-over is conducted manually when a pressure signal is received at the process equipment. Still others manually switch-over only after visual checks of the cylinder regulator indicate it is time to do so.
- Walk-in cabinet designs contain many cylinders of different process gases.
- Cabinets contain three process gases, each with its own delivery manifold.

All benchmarked cabinet configurations appeared to be exhausted adequately; however, exhausted cabinets were found inside and outside buildings without exhaust failure/automatic shutdown, sprinkler protection, or scrubbers. Older installations manifolded different gases to the same piece of process equipment and were constructed with socket welds and lacked emergency shut-off valves. These systems have operated for approximately ten years with no incidents of any consequence. These systems were found in smaller facilities with highly-educated and job-dedicated personnel. Many of the cabinet enclosures in these facilities are homemade with unique design features (i.e., cabinet floor grates to allow for better exhaust air distribution and explosion-proof lighting). Some cabinets in use do not have windows.

Cabinets were found to be located in many different areas of facilities:

- In concrete block gas rooms in basements, penthouses, and outdoors.
- In “cut-off” room extensions to process buildings and laboratories.
- In chain link weather-protected (roofed) enclosures.
- In areas adjacent to process equipment.
- In service corridors and mechanical equipment rooms.

In all of these areas, fire-suppression systems existed but usually no fire detection. One facility doubles make-up air volumes to its silane cylinder bunker before personnel entry. Exhaust duct materials are usually metal or specified metal duct lengths that hook into FRP ducts that included sprinkler systems. No plastic duct such as PVC or polypropylene was observed; however, wet scrubbers used for emission control are made of PVC.

Design features observed on newer delivery manifolds/gas cabinets are listed below:

- Helium leak-check ports.
- Three-way valves (reduces tees and welds).
- Flame detection.
- Wire glass window on top of cabinet for light.
- Spring-loaded ramp for installing cylinder.
- Scales flush with cabinet floor for liquid gases.
- Two excess-flow switches—one on the high-pressure side and one on the low-pressure side (the trend is moving toward switches versus excess-flow valves because of the switches’ higher reliability).
- Valve position indicators.
- Pressure “step-down” valve between cylinder and regulator to protect against regulator diaphragm failure.

There is a trend to move gas cabinets currently located indoors to the outdoors. Many of the systems that are about 10 years old are being upgraded. As these systems are moved outdoors, an increase in single-cylinder manifolds feeding multiple processes will be required. Along with this move, more valve manifold boxes inside facilities will be required to direct gas flows to different pieces of equipment.

Delivery manifold purging is accomplished through different methods (i.e., pressure/vacuum cycles using inert gases, venturis, process vacuum pumps and dedicated vacuum pumps, or inert gas pressure sweeps only). At many facilities, the trend is to remove the human element from “hands-on” purging. Some facilities use cameras and conduct purging remotely. Purge gases are contained, most often, in dedicated cylinders; however, house systems are being used in some cases. Check valves are important in such designs. Most process engineers prefer to completely isolate silane systems to prevent cross-contamination of other gas supplies.

However, check valves have experienced failures. In 1992, two graduate students died in a silane explosion at Osaka University in Japan. The explosion was caused in part by a failed check

valve. Also, many people feel that check valves are particle generators. Check valves are being used on silane vent lines to prevent air contamination of delivery manifolds.

Vacuum venturis were observed being connected to house inert-gas systems. One facility uses a dedicated house nitrogen supply for gas pad pneumatics and vacuum venturis only. Some small research and development facilities/laboratories use cylinder nitrogen for purging as well as for running the vacuum venturi. This configuration requires a full nitrogen cylinder for every silane cylinder change; however, because cylinder changes are infrequent, the configuration is acceptable. Many silane users purge with inert gas mixes such as helium in nitrogen or argon, which double for leak checking the delivery manifold. Some users prefer to use a helium leak-check port for conducting leak checks after each cylinder change. Continuous purging of various delivery/purge components varies. In many cases, a vent header from a number of gas cabinets is continuously purged and monitored with a flow switch. If this header purge fails, interlocks prevent cabinet manifold purging. In some older installations, one purge cylinder is manifolded to a number of delivery manifolds.

In limited instances, preventative maintenance programs did not include periodic test and calibration of interlocks, automatic shutdowns, alarms, sensors, and switches.

The survey results show data on regulator use. Two unique configurations were observed. In one case, a two-stage regulator was being used that included two bonnet vents—one for each stage. In another case, a two-stage regulator included a pressure transducer between stages to monitor for out-of-spec pressure delivery conditions.

3.4.5 Delivery Lines

The delivery lines of all facilities visited during the study are stainless steel. Many installations are single wall (non-coaxial). There is some debate about single wall versus coaxial that centers around potential problems with silane accumulation in a coaxial space when the inner delivery line leaks. Silane manufacturers, cylinder-filling facilities, and high-volume users prefer single wall, totally welded delivery lines. When fittings become necessary, exhausted enclosures are used in about 50% of the facilities visited.

3.4.6 Gas Monitoring and Fire Detection/Suppression Systems

Gas monitoring for silane is a leak-detection practice, even though there is a belief that the pyrophoric nature of the gas causes leaks to go undetected. Many gas monitoring systems operate, however, without calibration or response checks. System readouts were also noted in locations that would be considered hazardous if a leak occurred. Modification to off-the-shelf systems (with manufacturer's consultation) for unique environments was observed at two installations. Calibration gases are being used in concentrations of 2 ppm silane in air and 1,000 ppm silane in nitrogen in two of the facilities visited. Alarm levels are usually set for high/low warnings and are based upon different multiples of the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) of 5 ppm.

Fire detection/suppression systems are, in most cases, standard water sprinkler systems with smoke and/or flame detectors. Some deluge systems have been installed in bunkers, gas pads, and cylinder storage areas. Some of these systems activate from a manual switch only; others operate automatically in conjunction with a fire-detection system. One benchmarked deluge

system, in a large cylinder storage area, is tested semi-annually. Sprinkler heads in cabinets were always located in the top of the cabinet. There is a question over this placement because of the potential consequences of extinguishing a silane flame at a leaking cylinder without stopping the leak. Since the primary purpose of an activated cabinet sprinkler is for cooling, the sprinkler placement may need further evaluation. Some silane gas cabinets were observed with sprinkler piping shut-off valves just above the cabinets.

Two unique fire detection systems were observed. One included a “protector wire” that followed the delivery line to the process equipment and was interlocked to silane flow. This wire was also present at manifolds and valve boxes. Whenever a leak occurs, the generated heat causes a change in the wire’s resistance, which triggers an alarm and shutdown. The other unique fire detection system included a pressure-monitored nitrogen flow through plastic tubing present at key locations of the silane delivery system. If a leak occurs, the plastic tubing burns, creating a change in the nitrogen flow pressure. This change is detected by a pressure switch that triggers an alarm and shutdown.

3.4.7 Process Equipment

Because of silane’s high purity, low-temperature decomposition, and familiar chemistry, alternatives chemicals have process limitations. Tetraethyl ortho silicate (TEOS) is used for oxide films, but no viable substitute exists for polysilicon processing. Process equipment efficiencies are improving, resulting in smaller on-site silane quantities. Deposition processes such as atmospheric CVD use lower silane flows than older conventional low pressure chemical vapor deposition (LPCVD) systems. Microwave plasma-enhanced chemical vapor deposition (PECVD) systems are experiencing efficiencies six times higher than RF/PECVD. Older process equipment at small facilities did not have exhaust enclosures around mass flow controllers/equipment manifolds and few had safety interlocks of any kind.

Some silane users operate process equipment vacuum pumps with combustible, hydrocarbon oil without nitrogen purging. When nitrogen purging was present, Tygon tubing was sometimes used. Very often, vacuum pump exhausts are manifolded, leading to a common scrubber. The trend in the industry is toward dry pumps with electronic monitoring packages for nitrogen purging, back pressure, temperature, etc.

Disilane is being used in some R&D facilities; however, because of its highly unstable nature, its use in production is practically non-existent at the facilities visited during the study.

3.4.8 Scrubbers

The most common scrubber observed during the benchmarking visits was the PVC wet scrubber using potassium hydroxide (KOH). Nitrogen purging (not monitored) was usually part of the design. Interlocked oxygen sensors were also being used. In some cases, no scrubbing was used. The wet scrubber was most common because it was also being used to abate other emissions. Flame or burn systems were also common silane emission controls. Silane manufacturers and cylinder-filling facilities have developed an expertise in silane treatment systems using commercially available systems. Also many company proprietary silane treatment systems have accumulated a long track record of reliable and safe operation. The outstanding feature of these systems is that no fuel gas is required. Some plasma “post-reaction” systems are also being used.

These systems can prolong vacuum pump life; also, fewer oil changes are required by eliminating silicon oxide before it reaches the pump.

3.4.9 Noteworthy Practices

The following is a list of unique systems and programs noted during the site visits:

- Site management systems combine computer hardware/software and data gathering sensors (including gas monitors) to provide around-the-clock system monitoring. These systems are commercially available. Other systems have been developed by the silane users. Some of these systems allow limited control functions in addition to full-time monitoring.
- Silane suppliers offer on-site technicians to maintain and operate silane distribution systems. This provides highly-trained, job-dedicated personnel for silane management. Supplier technicians are also part of emergency response teams and maintain incident logs. Supplier service contracts can enhance safety and decrease equipment downtime.
- Multiple gas cabinet delivery manifold purge vents tied into a nitrogen-purged, monitored, and interlocked header that goes to emission control equipment. This is to ensure system shutdown if the purge gas is lost.
- Some facilities use a “bang arrestor” intended to prevent the small silane explosions that can occur when the cap is removed from the silane cylinder. The bang arrestor is a stainless steel, perforated, 1/4-inch length of tubing that is shaped into a rectangle; this piece is placed around a cylinder valve when opening the dust cap. Nitrogen flows out of the perforations, reducing available oxygen to react with silane that may have leaked behind the dust cap.
- Heat wrapping all lines downstream of CVD equipment helps prevent silane condensation and/or particle formation in vacuum lines.
- Double blocking, blanking, or disconnecting all silane lines during lockout/tagout procedures helps prevent accidental releases of silane during maintenance. Design features in the silane control system allow for controllers on automatic gas cabinets as well as for entire gas pad controller power components to be locked and tagged out.
- Exhaust systems utilize emission control systems on any process equipment using silane concentrations greater than 6% to help prevent silane accumulation.
- Two excess flow switches on the gas cabinet delivery manifold help to detect excess silane flows. One switch is as close to the cylinder valve as possible, which protects the high-pressure side of the manifold. The other switch is just downstream of the regulator and protects the low-pressure side of the manifold as well as the delivery line.
- Rotameter/flowmeters with contacts for alarms are used to detect excess silane flows where electronic flow switches may not be practical.
- Bellows valves equipped with pressure gauges are used for leak detection past the primary seal.
- Bellows valves fitted with a nitrogen sweep above the valve seat are used to aid in leak detection. The nitrogen “carries” any silane that may have leaked past the seat to a thermal conductivity detector that is interlocked to alarms and shutdowns.
- Helium release/tracer studies were conducted on custom made gas cabinets to characterize containment efficiency.

3.4.10 Concerns Noted During Site Visits

Discussions with visitor hosts, process engineers, and technicians identified removal of cylinder dust caps as one of the primary concerns when working with silane. Manufacturers and cylinder-filling/gas suppliers agree that during shipment, vibration, and cylinder movement can cause tiny amounts of silane to leak past the cylinder valve. Tie wraps, shrink wraps, wires, etc., are being used to ensure that the valve handle does not turn during shipment. Pneumatic cylinder valves (i.e., Ceodeux valves) feature a locking mechanism to prevent valve movement during shipping. These efforts appear to be successful in preventing valve movement; however, tiny amounts of silane are still occasionally being found behind dust caps. This appears to be a difficult condition to prevent. The bang arrestor, described previously, is a device being used to deal with this problem. Other concerns expressed at some of the facilities included

- Low education level and high turnover among technicians requires diligent attention to training programs.
- Some were concerned with the reliability of software-interlocked shutdowns as compared to hard-wire interlocks.
- Automatic purging manifolds are easier to operate than manual pressure/vacuum purge cycles.
- Change-out of particle filters on PECVD vacuum systems can pose a fire hazard.
- If air movement is desired for outdoor gas pad applications, high air-volume blowers are preferred.
- Care must be taken to prevent the formation of the amorphous silicon powder that can react with acids or bases to form hydrogen gas. In the absence of oxygen, reacted silane produces amorphous silicon powder. Acids and bases are found in scrubbers.
- Silane cylinders are sometimes shipped without LFOs.

3.4.11 Silane Manufacturers and Cylinder-Filling Facilities

Because of the knowledge and expertise of silane manufacturers and personnel at cylinder-filling facilities in handling silane, this section has been devoted to the features of systems found at these facilities. Silane manufacturers are also large silane users because of their on-site polysilicon manufacturing processes. Cylinder-filling facilities are also considered to be silane users from the standpoint of using bulk supplies (ton quantities) for filling hundreds of cylinders as well as for analyzing the gas to ensure compliance with their purity specifications.

Evidence of this expertise can be found by looking at accident statistics for the facilities, which reveal the millions of staff hours worked without a lost-time injury. New installations, as well as facility modifications, require rigorous process safety reviews. Extensive risk analyses have been conducted on all bulk supply trailers including demographic modeling for overland transportation. Bulk supply trailers never sit overnight between shipping/receiving points. Manufacturers visit their customer facilities to conduct training, process safety reviews, and safety audits. All non-compliance issues must be resolved before silane is sold to any customer. Periodic reviews also take place. Cylinder-filling companies also offer services, equipment, and training on handling silane.

The manufacture and shipment of ton quantities of silane require the highest level of attention to safety. Cubic feet per minute silane flow rates are common at these facilities. Specific features of these facilities' silane systems include the following:

- All system valves are sealed and inspected monthly.
- Cylinder fill manifolds are of all welded stainless steel construction. VCR fittings are used only on a limited basis. There are no exhaust enclosures around fittings.
- All delivery lines are single wall (no-coaxial lines).
- Indoor cylinder-filling facilities are electrically classified (NEC Hazardous Locations) Class I, Division 2.
- Outdoor cylinder-filling facilities are not classified.
- Rooms with any potential for silane leaks during filling operations are exhausted with high air-volume blowers.
- Venturi vacuum generators are not used. Dedicated vacuum pumps are used for line evacuation.
- All vent lines are continuously purged.
- Electrically classified hazardous locations use nitrogen Z-purges on electronics enclosures.
- Cylinder-filling facilities require evacuation upon exhaust failure.
- Vacuum pump enclosures are nitrogen purged according to NFPA 496/ISA code S124.
- Bellows valves are used.
- Dry pipe water deluge fire protection systems, activated by flame detectors, are used in cylinder storage areas.
- Extensive emission control equipment is well maintained.

3.5 Insurance Company Reports

In addition to site visits and survey questionnaires, insurance companies specializing in industrial risks supplied reports for silane-related losses. This information is thought to capture most of the insured losses in the United States for the time period reported. These losses were incurred by a variety of silane users. The part of the data attributed to semiconductor manufacturers is not available. The detailed information is found in Appendix III, SEMATECH Technology Transfer #94062406A-XFR. Forty-eight incidents (in addition to the 108 reported in the survey questionnaire) are reported between 1978 and 1994. In eight of these cases, little or no damage was reported.

Twenty-six of the incidents recorded between 1981 and 1988 (eight years) reported losses due to damage and business interruption. The total reported losses for this period amounted to \$38,000,000.

However, during the last five years, the rates have dropped significantly. From 1989 to 1993, seven incidents including loss data were reported, with losses totaling \$1,660,000.

No injuries were reported for any of the 48 incidents reported by insurance companies.

4 DISCUSSION OF SURVEY AND SITE VISIT RESULTS

4.1 Statistical Evaluation of Survey Results Inconclusive

To objectively establish relationships between silane handling practices and silane safety results, an attempt was made to statistically correlate the engineering control system descriptions with the number and types of silane safety incidents. Forty-five completely filled survey forms were returned. Seventeen of these reported no incidents within the past five years. Twenty-eight systems reported on 31 separate incidents. All but three of the reported incidents had the potential for creating injuries or property damage.

The data from these 31 incident questionnaires was matched with data from the corresponding equipment and facilities questionnaires, providing information on more than 100 variables. Data types included variables data, such as cylinder quantity, process flow, population density, attributes data (like cylinder construction material), and process operation and equipment involved in the incident. Multivariate analysis of the information was performed using the SPSS statistical package.

4.1.1 Factor Analysis

Using principal component factor analysis, the more than 100 variables were reduced to a smaller number of factors. Factors bring together variables that appear to be measures of a single underlying global concept. Factor analysis reduced 23 of the variables into seven factors, but these did not show any clear pattern or meaning. A summary of the factor analysis is found in Appendix IV, SEMATECH Technology Transfer #94062406A-XFR.

4.1.2 Incident Frequency and Severity

Chi-squared analysis was used to find statistical relationships among variables, incident frequency, and severity. No significant relationships were seen between levels of any variables and whether or not the reporting facility had a silane incident within the past five years. The chi-squared analysis tables can be found in Appendix IV, SEMATECH Technology Transfer #94062406A-XFR.

4.1.3 Conclusion

The system design factors that can predict the probability of a silane incident are too many and complex for the sample of 31 incidents. Subjective evaluation of the other data collected in the study must be used to develop conclusions.

4.2 Key Observations

- **Moderate Incident Severity**

Most of the silane incidents included in this report did not result in fires large enough or hot enough to activate sprinklers. System designs include gas and fire detection, excess flow, LFOs, and flow and pressure sensors that cause automatic shutdown of silane flow. While these protective measures did not always prevent silane releases, they did limit the consequences of the releases. Human control was an important part of the control system.

Sixty-seven percent of all silane releases reported in the incident survey were detected by human observation.

Between 1981 and 1993, 156 silane incidents were reported in the U.S. from various sources in this study. Only one serious burn injury and two minor injuries (minor burns and temporary hearing loss) were reported during that time period.

Between 1989 and 1993, incidents serious enough to result in property damage and/or business interruption occurred at a rate of about 5.2 events per year, with an average loss of \$86,000 per incident. During the last five years, the average reported total loss by the study participants was less than \$500,000 per year.

The loss rate for the last five years is substantially lower than the eight years between 1981 and 1988. While the data is not complete enough to give an average number of incidents per year, the average cost per reported incident was \$1,300,000. The average cost for reported incidents was \$4,900,000 per year.

- **Lack of Consensus About Practices**

Some of the survey responses showed differences in silane handling practices. For example, are coaxial delivery lines safer than single wall delivery lines? Another question is, “How many purge cycles are required before opening a line?” Are two stage regulators better than single stage regulators? Another issue is whether or not to use high-pressure rated components downstream of the delivery manifold regulator.

- **Codes Need to Be Updated**

Various code requirements dictate allowable silane quantities depending upon storage configurations and locations. The code requirements are complicated and sometimes contradict each other. The Uniform Fire Code (UFC) Articles 51 and 80, various building codes (e.g., Uniform Building Code, Chapter 9) and NFPA 318 “Standard for the Protection of Cleanrooms” deal specifically with pyrophoric gas storage and controls. Changes are being proposed to UFC Article 80 for 1994 that will include requirements for silane (2% or greater) storage, dispensing, and use. Because of the many different caveats included in the codes, each user must apply them carefully to the particular configuration under consideration.

Table 1 shows some examples of code-allowable quantities and the number of cylinders required to reach these quantities. Table 1 is for illustration purposes only; specific allowable quantities must be determined for each individual case. Table 1 does illustrate, however, how quickly code-allowable quantities can be reached, especially with larger cylinders. Large cylinders are preferred because change-out is less frequent, which enhances safety by reducing the potential for cylinder change-related incidents. Table 1 shows the need for codes that address bulk silane delivery systems, which are being considered by some silane users.

Many facilities stage silane cylinders indoors inside cabinets that contain more than one cylinder. NFPA 318 guidelines call for single-cylinder cabinets, but this is not always an optimum storage solution. One delivery manifold with auto-switchover for multiple cylinders is common. The NFPA 318 guideline also calls for exterior storage and dispensing, which is becoming more common.

Table 1 Cylinder Size and Code Allowable Quantities

Cylinder Size		Allowable Number of Cylinders per Code Requirement		
grams	ft ³⁽¹⁾	2,000 ft ^{3 (2)}	6,000 ft ^{3 (3)}	9,000 ft ^{3 (4)}
16,000	423	4	14	21
12,000	317	6	19	28
10,000	264	7	22	34
5,000	132	15	45	68
1 ton bulk	24,000	—	—	—

(1) Volume in cubic feet determined from quantity x 12.0 ft³/lb. (silane specific volume at NTP).

(2) Maximum allowable quantity for one control area inside a building according to Uniform Building Code, H occupancies.

(3) Proposed maximum exterior storage per nest, not detached (Uniform Fire Code, Article 80).

(4) Maximum quantity of flammable gases allowed in a single fab area (Uniform Fire Code, Article 51).

- **Maintenance and Hazard Management Systems are Important**

The extensiveness of preventative maintenance programs, hazardous materials management plans, and formal process safety reviews varied among those surveyed.

Incidents involving cylinder changes appear to be decreasing as remote and automatic purge systems become more common, showing the effectiveness of good fault analysis followed by corrective actions. Regular preventative maintenance is important in preventing equipment failures, such as silicon dioxide blockage of exhaust and purge gas flows. Strict lockout/tagout procedures are important in preventing incidents during maintenance and repair activities. Scheduling preventative maintenance plans must take production schedules into account when equipment utilization is high.

Process safety reviews can help prevent incidents occurring during processing. Many of the root causes reported for incidents may be corrected through such programs.

4.3 Engineering Control Practices

During the survey and site visits, the following engineering control practices were often recommended by study participants.

4.3.1 Facility/Protocols

- Limit the number of silane cylinders on site by developing a JIT delivery system in cooperation with the silane supplier.
- Change-out and deliver silane cylinders during time periods when emergency response personnel are most available.
- Purchase the largest available cylinder quantities to reduce the frequency of cylinder change-out (providing the silane delivery system complies with all code requirements).
- Request assistance/advice from the silane supplier through a Product Stewardship Program.

- Develop a hazardous materials management plan that addresses silane emergencies. Share the plan with the local bureau of fire prevention or fire department.
- Establish a strict lockout/tagout program for all silane gas cabinets/delivery manifolds and gas pad and staging areas. Use double block/blank/disconnect when performing maintenance on silane systems.
- Provide back-up power to critical silane protection system components (i.e., gas monitors, fire protection, and exhaust).
- Conduct formal process safety reviews (e.g., What-if Analysis or Hazards and Operability [HAZOP] studies) on new silane installations or those undergoing significant modifications. Update the reviews every year.
- Conduct periodic response checks and ensure proper point-sampling of gas monitors. Gas monitors are effective silane leak detectors.
- Use water for fire suppression systems.
- Use UV/IR flame detectors in cylinder staging areas.

4.3.2 Equipment

- Install equipment and systems according to SEMI “Facility Standards and Safety Guidelines.”
- Use steel- or fiber-wrapped aluminum cylinders.
- Stage on-line cylinders outdoors in open-air configurations with weather protection.
- Use flame retardant suits, leather jackets and gloves, face shields and safety glasses or goggles, safety shoes, and hearing protection when changing cylinders.
- Outdoor silane cylinder gas pads do not need to be classified as hazardous locations according to NEC provisions.
- Use cylinders with manual or pneumatic, stainless steel, tied-diaphragm valves designed for the diameter index safety system (DISS) CGA 632 connection.
- Follow “Guidelines for the Proper Handling and Use of the CGA 630/710 Series Ultra High-Integrity Service Connections” (Technical Bulletin TB-9-1993).
- Use cylinders equipped with LFOs (0.010 inch).
- Construct delivery manifolds out of 316L stainless steel.
- Use automatic/processor-controlled gas cabinets. Manual systems are acceptable if job dedicated, highly trained (low turnover) personnel change cylinders.
- Use one dedicated inert gas cylinder for purging one silane cylinder.
- Use helium/inert gas mixes for purging as well as for leak checking.
- Include a helium leak check port on delivery manifolds.
- Purge delivery manifolds into a continuously purged and monitored vent header. Purging operations cannot begin or are aborted if header purge is lost.
- Use a dedicated house nitrogen system to the gas pads for running vacuum venturis and valve pneumatics.
- Use pressure/vacuum-cycle purging.

- Install two excess-flow switches on delivery manifolds—one for the high-pressure side and one for the low-pressure side.
- Use remote and local manual emergency shut-offs that shutdown all silane cylinders on the gas pad or staging area. The shut-off valves are activated manually and automatically when sensors detect a fault condition.
- Use single-stage, stainless steel, tied-diaphragm regulators.
- Use diaphragm or bellows valves.
- Ensure that delivery lines are welded whenever possible (316L stainless steel). Fittings should be VCR.
- Ensure that delivery lines have wall thicknesses not less than 0.035 inches, coaxial monitored or single wall.
- Leak check/pressure test all delivery lines according to SEMI standards.
- Monitor fittings with a gas detector.
- Use sensors and interlocks on delivery manifolds that shut down silane flow. Consider the following sensor functions:
 - overtemperature
 - smoke/fire
 - exhaust failure
 - sprinkler flow alarm
 - gas monitor
 - pressure leak during purging
 - vacuum loss during purging
 - loss of purge gas during purging
 - overpressure
- Include all sensors and interlocks in the preventative maintenance program for periodic testing.
- Do not rely on check valves for primary protection.
- Consider using the following interlocks on process equipment for silane flow shutdown:
 - emergency off button
 - overpressure
 - overtemperature
 - high flow
 - runaway reaction
 - low pressure
 - low temperature
 - low flow
 - silane sensed by gas monitor
 - fire detection
 - loss of vacuum pump purge
 - loss of tool/vacuum pump exhaust

- Use dry vacuum pumps wherever possible. Always use perfluoropolyether vacuum pump oils in oil-sealed pumps.
- Purge vacuum pumps with N₂ and interlock the pump to process gas flows.
- Dedicate exhaust ducts to silane processes.
- Use non-combustible ducts.
- Install burn boxes or other emission control equipment outdoors whenever possible.
- Construct emission control equipment of non-combustible materials.
- Consider equipment designs that do not require fuel gas for burning.

5 ALTERNATIVES TO SILANE IN COMPRESSED GAS CYLINDERS

5.1 Introduction

Several alternative technologies could replace silane delivered in compressed gas cylinders: liquid source reagents, point-of-use generation of silane or related precursor, and bulk transportation and storage of silane (tube trailers). An assessment of each of these technologies was conducted on the basis of system performance (e.g., purity of reagent, flux, and delivery capacity), materials and device performance, and safety.

Silane is one of the most technologically important chemical reagents in the electronics industry because of its utility in producing a broad range of materials (e.g., silicon dioxide, silicon nitride and oxynitride, epitaxial and polycrystalline silicon) at low processing temperatures. To date, no other single silicon precursor reagent has proven to match this kind of diverse system and device performance. From an industrial perspective, the most readily accepted alternative technology will likely be the one affording versatility in materials fabrication and cost effectiveness, while providing increased margins of safety over the use of cylinders of compressed silane.

5.2 Liquid Source Replacements for Silane

Replacing silane with a liquid source reagent has received considerable attention by the research community over the last few years. It is clear that the advantages of a liquid source replacement for silane are that such materials can be relatively easy to use (via conventional bubbler delivery systems), sufficiently volatile for large scale production, and have the potential for being cost effective. Liquid source reagents used for depositing silicon by chemical vapor deposition (CVD) processes fall into two major categories: the inorganic silanes (most commonly the chlorosilanes such as SiCl₄, SiCl₃H (TCS), and SiCl₂H₂ (DCS)), and the organosilanes. Organosilanes are generally non-pyrophoric and non-corrosive and hence less hazardous than silane. Unlike the majority of inorganic silanes that are oxidized spontaneously on contact with oxygen and air, the organosilanes are stable in air and are not reactive with moisture [1]. Chlorosilanes have been used extensively in CVD systems to deposit high quality epitaxial silicon films but at the expense of considerably higher processing temperatures (1000°–1100°C). Although current work in this area is focused on reducing processing temperatures by understanding the reactions of chlorosilanes, little kinetics data is available for reactions of molecules [2].

5.2.1 Deposition of Polycrystalline Silicon

One of the earliest and most detailed studies on the application of liquid sources for the replacement of silane considered a variety of organosilanes for CVD growth of polycrystalline silicon and silicon dioxide [3, 4]. Experiments using intracavity laser spectroscopy (ILS) were conducted to monitor, in situ, the gas phase concentration of reactive silylene species (SiH_2) during the pyrolysis of several organosilanes including ethylsilane (ES), diethylsilane (DES), tertiarybutylsilane (TBS), and ditertiarybutylsilane (DTBS). Molecules were selected on the basis that a beta-elimination mechanism would lead to efficient decomposition of the precursor into stable hydrocarbons and reactive silicon containing molecular fragments. The results of this work have shown that although deposited silicon films appear to be physically the same as those produced using silane, the incorporation of carbon is totally unacceptable for practical applications and can be as high as 20 atomic percent. The carbon content of these films was not believed to be associated with the purity of the starting precursor reagent since similar results were obtained with varying purity samples of 99.995% TBS. However, the fact that lower processing temperatures leads to reduced carbon incorporation suggests that secondary heterogeneous chemical reactions may play as important a role as the primary dissociation process (via beta-elimination).

In another study on the growth of polycrystalline silicon from liquid sources, it was also found that the use of DES in a LPCVD reactor produced silicon films with carbon incorporation as high as 19 atomic percent [5]. Similar results were found with respect to the carbon content of silicon films deposited from a unique disilane precursor reagent named disylabutane (DSB, $\text{SiH}_3\text{CH}_2\text{CH}_2\text{SiH}_3$) [6].

In a very interesting and enlightening piece of work, Coon and co-workers studied the adsorption and decomposition kinetics of DES on silicon $\langle 111 \rangle$ surface using laser-induced thermal desorption (LITD) and temperature programmed desorption (TPD) techniques [7]. They found that ethylene and hydrogen are the only stable desorption species following the adsorption of DES on silicon. The presence of ethylene in the desorption yield suggests that the ethyl groups on the silicon surface decompose via a beta-hydride elimination reaction. Although ethylene has been monitored during the gas-phase pyrolysis of ethylsilanes [8], this is the first observation of beta-hydride elimination from a silicon atom on a silicon surface. In effect, these results also provide the first independent corroboration of the mechanism that was originally proposed for the decomposition of DES and TBS in the study contracted by IBM.

A fundamental question remains as to why there has been no record thus far of any organosilane reagent that is capable of producing low carbon content polycrystalline films. The answer to this question is sure to require continued research and probably a breakthrough in the understanding of the complex reaction pathways involved in organosilicon gas-phase and surface chemistry. As a point of reference, it is interesting to note that at least 27 elementary reaction steps (see Table 2) are used to describe the apparently simple process of depositing polycrystalline silicon films from silane and hydrogen. Nonetheless, it is plausible to suggest that the success of any organosilane for producing ultra-purity silicon will necessarily require two system performance components:

1. The ability to efficiently remove organic moiety from the silicon atom
2. Totally preclude the redeposition of hydrocarbon by-products

Table 2 Reaction Mechanisms for Silicon Deposition

Reaction	A ^a	β ^a	E ^a
R1 SiH ₄ ↔ SiH ₂ + H ₂	9.81 × 10 ³⁷	-7.79	61.29
R2 SiH ₄ ↔ SiH ₃ + H	3.69 × 10 ¹⁵	0	93
R3 SiH ₄ + SiH ₂ ↔ Si ₂ H ₆	5.01 × 10 ¹²	0	1.29
R4 SiH ₄ + H ↔ SiH ₃ + H ₂	1.04 × 10 ¹⁴	0	2.5
R5 SiH ₄ + SiH ₃ ↔ Si ₂ H ₅ + H ₂	1.77 × 10 ¹²	0	4.4
R6 SiH ₄ + SiH ↔ Si ₂ H ₃ + H ₂	1.45 × 10 ¹²	0	2
R7 SiH ₄ + SiH ↔ Si ₂ H ₅	1.43 × 10 ¹³	0	2
R8 SiH ₄ + Si ↔ SiH ₂ + SiH ₂	9.31 × 10 ¹²	0	2
R9 Si + H ₂ ↔ SiH ₂	1.15 × 10 ¹⁴	0	2
R10 H ₂ SiSiH ₂ ↔ SiH ₂ + SiH ₂	1.00 × 10 ¹⁶	0	59
R11 SiH ₂ + H ↔ SiH + H ₂	1.39 × 10 ¹³	0	2
R12 SiH ₂ + H ↔ SiH ₃	3.81 × 10 ¹³	0	2
R13 SiH ₂ + Si ₂ H ₅ ↔ Si ₂ H ₅	6.58 × 10 ¹²	0	2
R14 SiH ₂ + Si ₂ ↔ Si ₃ + H ₂	3.55 × 10 ¹¹	0	2
R15 SiH ₂ + Si ₃ ↔ Si ₂ H ₂ + Si ₂	1.43 × 10 ¹¹	0	18.8
R16 H ₂ SiSiH ₂ ↔ Si ₂ H ₂ + H ₂	3.16 × 10 ¹⁴	0	53
R17 Si ₂ H ₆ ↔ H ₂ SiSiH ₂ + H ₂	2.51 × 10 ¹⁴	0	52.2
R18 H ₂ + SiH ↔ SiH ₃	3.45 × 10 ¹³	0	2
R19 H ₂ + Si ₂ ↔ Si ₂ H ₂	1.54 × 10 ¹³	0	2
R20 H ₂ + Si ₂ ↔ SiH + SiH	1.54 × 10 ¹³	0	40
R21 H ₂ + Si ₃ ↔ Si + Si ₂ H ₂	9.79 × 10 ¹²	0	42.6
R22 Si ₂ H ₅ ↔ Si ₂ H ₃ + H ₂	3.16 × 10 ¹⁴	0	53
R23 Si ₂ H ₂ ↔ Si ₂ H ₃	8.63 × 10 ¹⁴	0	2
R24 H + Si ₂ ↔ SiH + Si	5.15 × 10 ¹³	0	5.3
R25 Si ₃ H ₈ ↔ Si ₂ H ₆ + SiH ₂	4.90 × 10 ¹⁵	0	52.99
R26 Si ₃ H ₈ ↔ H ₃ SiSiH + SiH ₄	4.79 × 10 ¹⁴	0	49.24
R27 H ₃ SiSiH ↔ H ₂ SiSiH ₂	6.31 × 10 ¹²	0	29.2

Although the first requirement appears to be feasible in view of the results discussed earlier, achieving the second may be difficult if not nearly impossible. For example, there is a considerable body of experimental evidence on the chemisorption of hydrocarbons onto “clean” silicon surfaces. The carbon reacts on the surface to form silicon carbide with the amount of carbon incorporation increasing with increasing temperature. In studies on the adsorption of ethylene and propylene on Si <100> [9, 10, 11], it was found that C₃H₆ decomposes on the surface even at room temperature conditions. This notion of hydrocarbon re-deposition could in fact turn out to be an inherent fundamental limitation in the use of organosilanes for producing high-purity grade polycrystalline silicon.

As a footnote, it is worthwhile to emphasize that the purity of silanes continues to dominate as one of the most important factors governing the production of high-quality, high-resistivity polycrystalline silicon films. The highest purity grades of silane now have total impurities of less than 100 parts per million (ppm). Critical impurities such as water, oxygen, and carbon-containing molecules often have specifications at 1 ppm or below [12]. The purity standards for silane set by the Semiconductor Equipment and Materials Institute (SEMI) are shown in Table 3. Future studies on the use of organosilanes as liquid-source replacements for silane might include a methodology that is based upon direct investigation of the deposition of hydrocarbon by-product(s) rather than on the original precursor. In this manner, an organosilane molecule may be designed that has a *priori* higher probability for success than would otherwise be the case.

Table 3 SEMI Standards for Silane Purity

	C3.STD.10 Silicon Nitride Grade	C3.STD.9 Polysilicon and/or Silicon Dioxide Grade	C3.STD.8 Epitaxial Grade
Purity	99.9417%	98.8937%	98.8897%
Impurities	Maximum Acceptable Levels (ppm) *		
Argon and Helium	40		
Carbon monoxide and carbon dioxide (CO + CO ₂)	10	10	10
Chlorosilane (Ionizable chlorides including HCl reported as chloride)	10	1,000	1,000
Heavy Metals	**	**	**
Hydrocarbons C ₂ -C ₃	10	40	40
Hydrogen (H ₂)	500	10,000	10,000
Nitrogen (N ₂)			40
Oxygen (O ₂)	10	10	10
Particulates	**	**	**
Water (H ₂ O)	3	3	3
Total Impurities	583	11,063	11,103

* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

**To be determined between supplier and user.

5.2.2 Deposition of Silicon Dioxide (SiO₂)

Silicon dioxide is perhaps as important a material as polycrystalline silicon for the manufacture of microelectronic devices. It is perceived that new CVD sources for silicon oxide films will be needed to meet the ever-increasing demands of advanced VLSI circuit designs. The use of silane and oxygen has been the conventional method for producing oxide films at relatively low temperatures (350–450°C) and in both atmospheric and low pressure CVD reactors. However, this process tends to produce non-conformal deposition of oxide films and is known to provide a source of particulate generation within the reactor. In the last few years, tetraethylorthosilicate (TEOS) has been used to deposit highly conformal (70–95%) films of oxide with good step

coverage relative to silane [13]. Although TEOS is flammable, it is non-pyrophoric and non-corrosive and is far less hazardous than silane [14]. With respect to system performance, TEOS has several disadvantages when compared to silane: 1) higher processing temperatures (650°–750°C), 2) difficulty in doping with phosphorus, and 3) low vapor pressure. However, oxide films deposited from TEOS using LPCVD are highly conformal and carbon-free down to the detection limit for secondary ion mass spectrometry (SIMS).

In the search for low temperature oxide precursors, two other classes of compounds have been studied: the organosilanes (primarily DES), and cyclic siloxanes (e.g., 1,3,5,7 tetramethylcyclotetrasiloxane [TMCTS]). TMCTS is a non-pyrophoric, non-corrosive, flammable liquid source. It can be used to deposit oxide at lower temperatures (525°–650°C) when compared to TEOS, but only with the introduction of molecular oxygen. Although oxide films deposited with TMCTS show high conformality (80–90%), the deposition rate, film density, and film stress are all strongly influenced by the partial pressure of oxygen in the system as well as to the usual parameters of temperature, pressure, and wafer spacing. In this regard, deposition with TMCTS is a more variable process and, therefore, is expected to be commensurably more difficult to control on a large scale.

It is known that by reducing the number of alkyl and/or alkoxy groups bonded to silicon or alternatively by replacing the organic moiety with hydrogen affords the potential for lower deposition temperatures. The use of DES as a liquid source for oxide growth at relatively low temperatures (350°–475°C) has been shown to be effective for deposition onto aluminum or as a top layer passivation glass [15]. As with many other organosilanes, DES is also a non-pyrophoric, non-corrosive (yet flammable) liquid source. DES has performance advantages over silane including highly conformal films without the need for post-deposition annealing as well as good step coverage. When compared to silane, however, DES affords lower deposition rates at comparable temperatures. In effect, DES is considered to be a relatively safe, easily deliverable (high vapor pressure) liquid source reagent for the deposition of low temperature LPCVD silicon dioxide films [16]. Further studies, however, are required to assess the applicability of DES for atmospheric and PECVD systems. A general process and performance comparison of thermal silicon dioxides and silicon dioxides deposited from organosilanes is shown in Table 4.

Table 4 Silicon Dioxide Film Properties

Comparison of Thermal Silicon Dioxide and Silicon Dioxides Deposited from Organosilanes				
	TEOS*	TMCTS**	DES***	Thermal
Process temperature: range (°C)	650–750	525–650	340–475	N/A
Vapor pressure (Torr at 20°C)	1.5	6	200	N/A
Conformality (S/T)	70%–95%	80%–98%	80%–90%	N/A
1% HF wet etch rate (Å/sec at 21°C)	2.5	3.0	2.3	~ 1
Refractive index (±0.002 @ 632.8 nm)	1.444 @ 700°C dep	1.455 @ 590°C dep	1.460 @ 410°C dep	1.462
Dielectric breakdown (MV/cm)	3–8	4–7	> 4	8–10
Film stress at 28°C (10 ⁹ dynes/cm ²)	0.5T (no oxygen)	0.2C to < 0.5T	< 0.8T	3.1C
Applications	Interlayer over poly	Interlayer over refractory metals and silicides	Over aluminum	Field oxide
	Trench fill where high temperature is not of concern	Trench fill	Thick oxide	Gate oxide
	BPSG	BPSG	All applications in which SiH ₄ /O ₂ is now used	Isolation
	Thick oxides	Single wafer, PECVD, or where high dep rate needed	PSG	
		Thick oxide		
		Any TEOS application		

* Tetraethylorthosilicate

** 1, 3, 5, 7 Tetramethylcyclotetrasiloxane

*** Diethylsilane

The utility of a given precursor reagent for the growth of a given film or device often depends on the energetics of the material system under question. For example, it is clear that no single organosilane thus far has proven to be an effective replacement for silane in the growth of high-purity polycrystalline silicon films. In sharp contrast, the ability of DES, TEOS, and TMCTS to produce virtually carbon-free silicon dioxide can be explained, at least partially, on the basis of the binding energies for Si, C, and O in these different compounds [17, 18] (see Table 5). For instance, it is reasonable to expect that high-purity oxide can be formed without any carbon contamination because the binding energy of Si in either SiO or SiO₂ is almost 200 eV less than the binding energy of C in SiC. On the other hand, the growth of high-purity polycrystalline silicon is not favorable from a thermodynamic perspective because of the binding energy of carbon in SiC is commensurate to that of carbon in a saturated alkyl chain ((CH₂)_n).

Table 5 Binding Energies for Si, C, and O

Species	Binding Energy (eV)
Si	99.2
Si in SiC	100.4
Si in SiO	101.4
Si in SiO ₂	103.5
C in SiC	282.6
C in Graphite	284.1
C in (CH ₂)	284.6
O in Al ₂ O ₃	531.6
O in SiO ₂	533.0

5.2.3 Deposition of Epitaxial Silicon and Silicon Nitride (Si₃N₄)

The deposition of epitaxial silicon layers on silicon wafers is the first CVD step towards the fabrication of an integrated microelectronics device. Epitaxial layers are used in all bipolar devices, most discrete devices, and approximately 10% of all MOS devices. Although the silicon epitaxy process has grown substantially over the years, there is an industry trend for using chlorosilanes rather than silane in semiconductor processing. Among the reasons for this shift in process technology are economics and the ease of handling liquid-source reagents. In addition, it is also believed that the use of chlorosilanes has a synergistic effect on the growth of high-quality silicon epilayers. During the high-temperature deposition process, the HCl formed as a by-product of the overall reaction appears to have a gettering effect, thereby actually improving the overall quality of the deposited silicon film.

Although the chlorosilanes are generally corrosive and not very volatile, they can be used effectively to deposit silicon dioxide and silicon nitride by LPCVD processes. However, these reagents are not suitable for producing polycrystalline films on devices because the process runs at exceedingly high temperatures. The typical deposition process for epitaxial silicon usually involves hydrogen reduction of trichlorosilane at fairly elevated temperatures (in the range of 1000–1100°C) Research in the area of chlorosilanes is focused on improving the volatility of the

reagents while lowering the deposition temperature sufficiently to yield a potentially viable alternative for the growth of polycrystalline silicon films. For the general class of halogenated monosilanes, higher vapor pressures with concomitantly higher deposition temperatures are afforded by the series. For a given halogenated monosilane, however, the corresponding disilane is found to have a lower deposition temperature. However, disilanes and other members of the binary series are much less stable than their counterpart monosilane. In a recent study, hexachlorodisilane (HCDS) was used in an LPCVD system for deposition of polycrystalline silicon at 600°C and 650°C [19]. Although reasonable deposition rates were found for HCDS, the film exhibited contamination of up to 2 atomic percent chlorine or 9×10^{20} atoms/cm³. In addition, HCDS is a highly corrosive liquid with a relatively low vapor pressure (boiling point 145°C). While substitution of two chlorines by hydrogen atoms should improve volatility, the synthetic progression toward the fully hydrogenated disilane should also lead to serious disadvantages of increased reactivity and pyrophoricity.

Thin films of silicon nitride are used widely as diffusion masks, oxidation barriers, and dielectric in MNOS (metal-nitride-oxide-silicon) device structures. The preferred method of growth is using DCS and ammonia in an LPCVD system at 800°C. In a recent study, it was found that DES could be used to replace DCS for the growth of silicon nitride and silicon oxynitride [20]. The advantages are lower deposition temperatures and the elimination of condensation and particle formation associated with the use of DCS. It was found that the use of DES and NH₃ lead to carbon incorporation with a magnitude proportional to the partial pressure of DES used in the reactor. The addition of N₂O to a mixture of DES and NH₃ led to carbon-free films of silicon oxynitride rather than Si₃N₄.

5.3 Point-of-Use Generation of Silane

Just-in-time production and real-time consumption of hydrides is a viable approach to improving the margins of safety associated with the use of hydride reagents. The elimination of storage and transportation of these materials, through on-demand production, is particularly attractive for the single investigator performing small-scale experiments in the laboratory where a reagent generator would replace the conventional and more hazardous compressed gas cylinder. Additionally, the development of large-scale, on-demand generators for hydride materials could potentially eliminate the need for commercial suppliers to transport and store large quantities of hydrides on the customer's premises in tube trailers.

On-demand chemical generators of precursor reagents like silane, arsine, and phosphine integrated with on-line purification and concentration monitoring constitute an approach for the future that may ensure consistent quality and quantity of reagents needed for semiconductor device manufacture. In this approach, commercially available low-toxicity reactants (preferably in the form of gases) are purified on-line before they are introduced into a reaction chamber where they are induced to react by the application of an appropriate non-contaminating source of energy (i.e., electrons, photons, radio frequency, or microwave fields, etc.) to produce the desired product, which may ordinarily be a highly toxic and/or potentially dangerous reagent. The concentration and flux of the on-demand generated precursor is then measured and controlled before it is introduced into the semiconductor growth chamber or process tool for device manufacture. This approach maximizes safety while reducing the costs of manufacturing by obviating, in large part, the need for the implementation of remote storage facilities. The

possibility of leveling out or improving device yields by preventing fluctuations in the reagent purity from one cylinder to the next is inherent in the in situ generation procedure.

AT&T has conducted extensive research and development efforts in the design and engineering of on-demand chemical generators for several gas phase reagents used in the electronics industry [21, 22]. On-demand chemical generators for arsine have been developed and used successfully at Bell Laboratories in several applications including hydride vapor phase epitaxy (H-VPE), metal organic CVD (MOCVD), gas source molecular beam epitaxy (MBE), and doping silicon epilayers. Materials and devices produced using the on-demand arsine generator system were found generally to have equal or superior electronic properties when compared to those made with commercially available cylinders of high-purity grade arsine. Recent chemical engineering advances made of system optimization have provided the basis for design of the next generation of high-performance generator systems with delivery capacities exceeding five pounds of arsine. Such high delivery capacity systems producing a consistently high-purity and high-output concentration of arsine (~94% (v/v)) offer a superior alternative to compressed gas cylinders.

Fundamental investigations of homogeneous and heterogeneous chemical reactions are required to devise new approaches for the on-demand generation of other strategic reagents used in semiconductor device manufacture.

5.3.1 Point-of-Use Technology Compared with Other Alternatives for Silane

Modification of the chemical structure of silane (SiH_4) to reduce its chemical reactivity (pyrophoricity) has long been employed through partial chlorination. As the number of H-atoms are replaced by chlorine, SiH_3Cl , SiH_2Cl_2 , SiHCl_3 , and SiCl_4 , the pyrophoricity of each reagent progressively decreases to the point where the fully chlorinated molecule, SiCl_4 , is deemed non-flammable. Increasing chlorination of SiH_4 decreases the volatility of the reagent to the extent that beyond SiH_2Cl_2 the reagents exist as quite stable liquids. Thus, in principle, the liquefied reagents resulting from substitution SiHCl_3 and SiCl_4 are substantially less hazardous than a cylinder of compressed gas SiH_4 (i.e., if a catastrophic failure of the cylinder were to occur). Unfortunately, the chlorinated precursors may require above room temperature distribution systems to generate the requisite high-mass fluxes and will necessarily require higher processing temperatures for the deposition of epitaxial and/or polycrystalline silicon. Additionally, the use of chlorine-substituted reagents also produces by-products such as hydrogen chloride (HCl , which is highly corrosive) and chlorine gas (Cl_2) that must be treated as end-of-pipe pollutants.

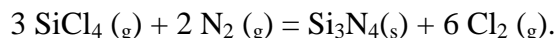
In contrast to epi- or poly-silicon deposition, the fabrication of SiO_2 dielectric layers can be accomplished with low toxicity, chemically safe (non-pyrophoric or non-explosive) alkoxy compounds such as $\text{Si}(\text{OCH}_3)_4$ (TMOS) or $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ (TEOS). However, oxygen impurities must be kept to a minimum during the deposition of solar cell amorphous silicon panels. Therefore, SiH_4 is widely used for this purpose, while the chemically safe, non-pyrophoric, liquid precursors, $\text{Si}(\text{OCH}_3)_4$ or SiCl_4 , are incompatible for this application. On the other hand, silicon tetrafluoride (SiF_4) rivals SiH_4 in reactivity, is also a gas, and when available in sufficiently pure form (free of oxygenated impurities) has been used for deposition of amorphous silicon.

More recently, alkyl silanes (HSiR_3) are being investigated as possible safer precursors for silicon deposition. Although these alternative reagents indeed increase safety by reducing pyrophoricity, direct reduction to the silicon requires higher temperatures compared to SiH_4 and

leads to the inevitable carbon incorporation in the film, particularly during plasma deposition processes. Additionally, many of the alkyl silanes now being considered as replacements for silane are also significantly higher in cost and, therefore, prohibitive to practical commercial application.

5.3.2 Plasma Generation of Reactive Silane Precursors

The introduction of PECVD processes has enabled the development of alternative reaction chemistries for the deposition of a wide range of high purity materials used in the semiconductor industry. Conceptually, plasma processing affords increased margins of safety by replacing the use of highly reactive and unstable gases with considerably less hazardous reagents that are then converted into the requisite highly reactive intermediates within the plasma itself. An example of this technology is the etching of silicon using an RF plasma containing carbon tetrafluoride (CF₄) [23]. Numerous other examples exist in the literature including the deposition of silicon dioxide by PECVD of TEOS and oxygen [24] and the preparation of high purity silicon nitride in a nitrogen microwave plasma according to the following reaction [25],



Without the nitrogen plasma, pyrophoric reagents like silane and DCS would be required to produce these materials. In essence, the use of plasma-induced chemistry with the appropriate precursor may afford safer processing and fabrication of devices in the future.

From a synthetic perspective, it is reasonable to assume that under certain conditions, silicon-containing reactive species for deposition of polycrystalline silicon or silicon dioxide films may be generated using a hydrogen microwave plasma and an appropriate source of silicon (e.g., high-purity grade solid silicon). Since plasma systems typically operate at sub-atmospheric pressures, a point-of-use generator employing this approach would likely produce low fluxes and therefore be able to supply reagent only to a single deposition process tool. Additional concerns involving the plasma-assisted approach include the formation of a multitude of silicon oligomers and the potential for generating contaminant particulates within the reactor confinement.

5.3.3 Basic Research Required to Develop Point-of-Use Generation

From the discussion above, it is clear that point-of-use generation of silane is desirable and that other materials have been generated in that manner. However, at this time, there is no chemical mechanism for point-of-use generation of silane. Basic research into possible chemical pathways is the first step toward this new technique.

5.4 Bulk Silane Delivery Systems

Currently six facilities in the U.S. are using or are designing for bulk silane delivery systems. These high-volume silane users are primarily in the xerography, photovoltaic and glass manufacturing industries. Some U.S. semiconductor facilities are also strongly considering bulk supplies; it is thought that their plans will materialize by 1995. In Europe, some semiconductor facilities are using bulk silane supplies, but the details on these sites were not obtained. This trend towards bulk supplies is gaining momentum with high-volume users as a means of reducing costs and providing consistency.

Different configurations of bulk silane delivery systems are available. Three- and six-ton tube trailers are being used by the silane supply industry as well as smaller (< 1 ton) modules or cylinder clusters. Silane manufacturers have conducted extensive process safety risk analyses on their bulk supply systems and have an excellent safety track record. Their concluding risk analyses require strict engineering control system designs that include many of the same features found in cylinder systems, such as

- DOT approved containers equipped with safety fusible plugs and burst discs
- All welded stainless steel manifolds
- LFOs
- Self-contained purge systems
- Safety venting of all purged silane
- Remote and automatic emergency isolation
- Excess flow protection
- Fire detection/suppression systems
- Open and unconfined installations

Many of these safety features are similar to those found on other bulk gas-supply systems, such as hydrogen.

The silane incident survey showed that 21% of the reported incidents occurred during cylinder delivery and cylinder changing. Bulk supply systems could reduce these incidents by reducing the required silane source changing frequency. Depending on use requirements and bulk supply quantities, change frequencies could be limited to one or two times per year. When changeout does occur, it would be conducted by the supplier's personnel, who have considerable expertise. Strict adherence to written procedures would take place and emergency response personnel would be present. When the "empty" bulk trailer or cluster is returned to its supplier, valves and critical manifold components can be tested and rebuilt. This also provides an advantage over cylinder supply systems that rarely have their component parts included in preventative maintenance programs.

5.5 Conclusion

Silane has already been replaced by safer chemicals for silicon dioxide and epitaxial silicon deposition process when the alternatives show superior performance. Organosilanes are being used for silicon dioxide deposition and chlorosilanes are used for epitaxial silicon deposition.

Organosilanes show little promise as silane replacements because of carbon incorporation into the deposited silicon film. There is no known way to prevent adsorption of the hydrocarbon fragments onto the silicon surface.

Bulk silane delivery systems offer an engineering solution for large silane users for reducing silane incidents associated with cylinders and their handling.

Point-of-use generation silane integrated with on-line purification and concentration monitoring equipment is a desirable long-term solution to some silane transportation and handling risks. Conceptually, less hazardous and lower toxicity reactants can be used, purified on-line, and then introduced into a reactor, whereupon application of a suitable energy source (electrons, photons,

RF, or microwave fields) produces the requisite precursor for deposition of materials in downstream process tools. This approach optimizes safety while having the potential for reducing manufacturing costs incurred by the need for remote storage facilities for silane and associated safeguards.

6 POINT-OF-USE GENERATION DEVELOPMENT PLAN

The previous discussion identified bulk delivery and storage as a means of reducing silane-handling risks for large users. These systems are already commercially available to silane users that want them. Point-of-use generation of silane was selected as a desirable alternative to silane in compressed gas cylinders. This section describes the steps necessary to develop point-of-use generation of silane to the point of commercial availability.

6.1 Research and Development Program

The research and development program for on-demand silane generation would consist of three phases. In Phase I of this program, the chemistry for the turnkey production of silane will be investigated and optimized to achieve the efficiency and yield required for meeting real-time flux demands for important silicon device applications. Model chemical reactions simulating the chemical dynamics of a silane generator, but devoid of the hazards of pyrophoricity and explosion, will be studied in detail. Alternative chemistries will be researched. The leading candidate chemistry (based on economics, ease of execution, scale-up, etc.), will be taken through chemical engineering simulation and modeling to optimize the design parameters for a laboratory-scale test reactor.

In Phase II of the program, a prototype reactor will be designed and constructed. Proper housing in an ESH-approved silane laboratory will occur prior to chemical engineering optimization experiments on the reactor. Silane monitors for real-time process control will be developed and integrated with the chemical generator. A commercial provider will be engaged as a partner during the prove-in of the generator design. Systems for on-site use at beta-test facilities will be produced. Various prove-ins of the reactor will be conducted by the principal technical task team with other industrial corporations.

Phase III of the program, the development of commercial-scale systems, will be pursued in partnership with a major U.S. supplier of gaseous chemical products. Of specific interest to this joint venture will be assessing the economics of developing the next generation technology for silane manufacture based on the on-demand chemical generator approach.

The successful development and commercialization of an on-demand silane generator depends upon having sufficient knowledge about the process gained at the laboratory bench and at the pilot-scale. In general, a critical amount of experimental data about the process will be required to accomplish the following goals: 1) choose the type and size of the reactor, 2) integrate the reactor with the overall CVD process, 3) predict the needs for satisfactory scale-up of the process, and 4) provide the necessary breadth of knowledge and understanding so that modifications may be made during the optimization stages of development.

For a silane generator system based upon known inorganic chemistry and predictable reaction products, the resultant thermodynamic and kinetic characteristics of the various reactions will

have to be optimized for compatibility, particularly with respect to its dynamic impact on the life-cycle and efficiency of the generator for producing silane. This kind of information will require the execution of a strategic set of carefully planned experiments. In addition, it will be necessary to validate all materials chemistry, first by a combination of fundamental and experimental studies within the laboratory, prior to the scrutiny and engagement of a larger pilot-scale process. Developing a pilot-scale generator also requires exploitation of various chemical engineering designs, modeling, and dynamic simulation studies for optimizing the process before constructing a prototype on-demand silane generator for process applications.

Conceptually, an analytical approach to designing and modeling an on-demand generator for silane must consider the following aspects: 1) a materials mass balance for all of the reactants and products, 2) a thermal balance of all the reactor compartments and components, and 3) evaluation of the performance of the system by the appropriate combination of phenomenological and first principles modeling and simulation studies.

6.2 Development Tasks

Phase 1: Define and Optimize Chemistry

- Develop the basic on-demand chemistry for the turnkey generation of silane:
 - Model promising chemical reactions
 - Evaluate reaction kinetics
 - Evaluate thermodynamics
 - Estimate reaction efficiency
 - Estimate delivery rate vs. operating parameters
 - Analyze chemistry of gases
 - Analyze chemistry of by-products
 - Ensure compatibility with silane
- Develop and optimize the critical reactor components:
 - Materials
 - Primary and supplemental reactions
 - Geometric configuration of the reactor
 - Ancillary components
 - Reactor life-cycle analysis
- Assemble a complete small-scale reactor system:
 - Optimize function
 - Test
- Assess commercial feasibility and economics

Phase 2: Develop and Test Pilot Scale Generator

- Design a pilot-scale system on the basis of the chemical engineering modeling and simulations:
 - Sensors and controls
 - Simulation of function
 - Safety systems
- Construct the pilot-scale system and test using the model chemistry
- Test of silane production:
 - Process optimization
 - Measure reaction efficiency
- Partner with a commercial supplier
- Evaluate polysilicon deposition at a semiconductor user beta-site.

Phase 3: Develop Commercial Scale Generator

- Select a commercial partner for commercialization
- Develop execution plan, schedule, and budget
- Develop and test commercial silane generator

Execution of this plan is estimated to require between three and five years and to cost more than \$5,000,000.

6.3 Probability of Success

It is impossible to estimate the probability of the successful development of a point-of-use silane generator, because a suitable reaction pathway is not known.

7 SILANE SAFETY IMPROVEMENT WORKSHOP

A workshop was held June 1, 1994, in Austin, Texas, to discuss the information gathered in this study. Forty-seven professionals with expertise in safety, use, production, and distribution of silane attended the workshop. The conclusions reached by the workshop participants are discussed in the next section. A summary of other points of discussion is as follows:

Further effort to find a chemical replacement for silane is not practical. The chemistry of hydrocarbons in the presence of a silicon surface was discussed. There is no known way to prevent carbon incorporation in polysilicon films that are grown using organosilanes as the silicon source. There is no reason to spend anymore effort on the development of organosilane silane replacements.

The codes, standards, and guidelines need enhancement. Various codes, standards, and regulations are not well coordinated. There are gaps and overlapping areas among the various documents. The existing codes and standards do not always apply directly to silane. There is variation in how these codes and standards are interpreted. The codes do not address some of the installation configurations expected to be used in the future. The issues related to bulk silane distribution systems are not addressed effectively by existing codes and regulations.

There is a lack of consensus about some silane safe-handling practices. Some participants questioned the effectiveness of LFOs. The optimum diameter for the hole in a LFO has not been established. There are questions about the best material for the construction of ductwork.

The justification for silane replacement is weak. This study counted the silane-related losses reported by those participating in the study. This measurement is intended to provide a reference point for future funding of silane safety improvement programs. The annual cost of silane incident losses due to facility damage and business interruption was found to be relatively small (about \$500,000 per year for all silane using industries).

The accuracy of the loss value measurement was challenged. There was some question as to whether business interruption losses were completely reported, if losses from smaller users outside the SEMATECH membership were comprehended and if losses from SEMATECH member companies were comprehensively reported.

The study included a wide variety of silane users. The losses reported during the survey process provided the only available data.

Bulk distribution systems are controversial. While silane producers and distributors and a few large silane users have or are planning for bulk distribution systems, many in the industry have questions about the need for (and the appropriate design of) the systems. The risks should be evaluated further. Community concerns must also be addressed.

One silane supplier is seeking a partner in a semiconductor manufacturing plant to design and install a model bulk silane distribution system. The elements of such a project were presented.

There is a need to continue the free exchange of silane-use information. During the course of this study, information about silane engineering control systems, equipment performance, and safety issues was shared freely with a few exceptions. There is a need to continue this free exchange of information. Forming a "Silane user group," modeled on the Chlorine Institute was suggested.

The purpose of a group devoted to silane issues would be to aid in the development of effective codes and standards. Another function would be to provide a forum for the evaluation of silane handling practices and training.

Limiting flow orifices may be proven to prevent silane explosions. If the speed of the silane molecules flowing from an opening in a silane container is less than the flame propagation rate, silane explosions may be prevented (LFOs control the rate of silane flow through an opening). A statement of work was presented describing experiments to test this hypothesis. The consensus of the group was that further testing of LFOs would help system designers and those working on codes and standards.

8 CONCLUSIONS

Silane is being used without major safety incidents in the U.S. semiconductor industry. Only one serious and two minor injuries were reported in the U.S. during the survey process (1981 to 1993). Industry-wide financial losses are now about \$500,000 per year (1989 to 1993).

Organosilanes and chlorosilanes have already been successfully substituted for silane in silicon dioxide and epitaxial silicon deposition processes. This is due to the superior safety and process performance of the alternatives.

Carbon incorporation into polysilicon films prevents the use of organosilanes for polysilicon deposition. There is no known way to alter the chemistry of organosilane decomposition to overcome process problems.

Point-of-use silane generation and purification offers potential distribution safety and process control advantages.

Automation of and increased attention to the cylinder delivery and change processes appears to be effective in reducing silane incidents. Only 21% silane incidents occur during cylinder changes today.

Data indicates that more attention with respect to silane safety should be given to the process tool and maintenance activities. Forty-five percent of the incidents occurs during processing. Twenty-one percent occurs during maintenance activities.

Bulk distribution systems for silane continue to be considered for use by large silane users. It is expected that more of these systems will be used increase in coming years. System design and regulatory issues and community concerns need to be addressed before systems are built to prevent safety problems, regulatory obstacles, and community relations challenges.

The survey respondents gave a number of practices that may improve silane safety. These are listed in Section 4.3.

The effort to statistically correlate engineering control practices to silane incident counts and severity was unsuccessful.

9 RECOMMENDATIONS

The recommendations developed by the workshop participants will be presented to the SEMATECH Environmental Safety and Health Focus Technical Advisory Board for consideration.

Form Silane Users Group

A silane users group should be formed. The priority of issues should be as follows:

- 1) Determine what organization will sponsor the users group.
- 2) Define the scope of the mission:
 - Include silane users, producers, and distributors
 - Include users from outside the semiconductor industry
 - Include process tool manufacturers
 - Include safety and regulatory people

- 3) Establish a means for information exchange and dissemination.
- 4) Prioritize needs based on incident data:
 - Process hazard review of process tools
 - Supplier participation in process tool safety system design
 - Evaluation of safety practices and recommendations for best practices

Perform Hazard Analysis

- 1) Bulk silane distribution system:
 - Process hazard review of entire system:
 - Production
 - Distribution and transportation
 - User facilities
 - Perform consequence analysis on user bulk storage system.
 - Benchmark installations outside the United States.
- 2) LFO performance:
 - Observe silane releases through LFOs
 - Experimentally evaluate explosion potential
- 3) Compare silane hazard to other industrial hazards:
 - Acetylene
 - Bulk hydrogen
- 4) Evaluate silane abatement system designs.

Identify Feasible Chemistry for Point-of-Use (POU) Generation of Silane

- 1) Execute Phase 1 of the POU development plan (see Section 7.2).
- 2) Deliverables

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