SERI/STR-211-2575
(DE85008776)
Distribution Category UC-63

Monosilane and Disilane: 1984 Status Report

A Subcontract Report

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March 1985

Prepared under Subcontract No. CL-4-00371-01

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Prepared for the
U.S. Department of Energy
Contract No. DE-AC02-83CH10093

PREFACE

This report contains information on the improvements in the quality of monosilane and disilane now commercially available. Suppliers' analyses are tabulated along with capacity data. Suppliers currently have a higher purity grade of silane than previously, which yields a deposited silicon film with a resistivity of more than 1000 ohm-cm. Prices and grades are listed for the silane gases available in the United States and Japan. The silent electric discharge method of preparing disilane from silane is reviewed, with references. Properties and stability data for disilane are given. Handling and shipping of the silane gases are discussed, along with data on health hazards. Analytical procedures for determining impurities in silanes are listed; sensitivities are generally only to the 1-ppm level. Analyses at the parts-per-trillion level for boron, phosphorus, arsenic, and antimony in silane would be useful for photovoltaic work; suggestions are given for possible techniques that might be developed to achieve this.

SUMMARY

Objective

The objective of this report is to provide users and suppliers with a reference source of current data on silane and disilane in the United States and Japan.

Discussion

Since SERI published its contracted 1983 survey report on silanes, major improvements have been made in the quality of commercially available monosilane and disilane. The continued growth of the electronics market, the commercial production of amorphous silicon solar cells, and the potential demand for greater volumes of silanes to satisfy the requirements of several new uses caused silane suppliers to renew their interest in producing higher quality products.

Total world silane use will probably grow from the 64 metric tons used in 1983 to 98 to 120 tons by 1986. Semiconductor and related uses will account for most of this volume in 1986; photovoltaics will be using some 5 metric tons. The high end of the range will be reached if the use of silane for copy machines escalates, as the Japanese suppliers project that it will. Uses for and acceptance of disilanes will be in the development stages in 1985, with some 1000 kg probably allocated to photovoltaics by 1986.

Silane

In the United States, the volume of monosilane for electronic uses will grow about 20% in 1984 to 52 metric tons per year. This growth rate is expected to continue through 1990. Amorphous silicon solar cells were announced or first produced commercially in the United States in 1984 by ARCO Solar, Chronar Corporation, Energy Conversion Devices, Inc., and Solarex Corporation. Photovoltaic uses for silane will probably develop slowly over the next few years. Most of the seven domestic silane producers have improved the quality of their products, offering two to four grades. This has led to three-tier pricing: \$0.15 to \$0.32; \$0.50 to \$0.85; and \$1.30 to \$2.00 per gram, depending on the grade. The high-purity silanes generally have reported impurity levels below the 1-ppm detection limit of current analytical procedures. The small amounts of higher silanes found in silane are not considered impurities, as they have been found to not be detrimental in most uses. If the producers expand production to meet the demand, as they have stated, production should be adequate to meet users' needs for the near future.

In Japan, Komatsu continues to dominate 1984's 32-ton, domestic silane market with a 70% market share. Four more companies are now producing silane: Mitsui, Honjo, Teisan, and Showa Denko, and three more are ready to enter the market. Komatsu has expanded its capacity from 60 to 120 tons and should almost double this to 220 tons by 1986. This will provide adequate capacity

for the photovoltaics, electronic, and copy machine uses of silane; the copy machine market could potentially use 20 tons of silane per year. Mitsui, Honjo, and Shin-Etsu are considering selling their silanes outside of Japan. The quality of silane produced in Japan is generally good, and prices are competitive.

Disilane

In the United States, dramatic changes in the quality, stability, and pricing of disilane occurred in 1984. The two domestic producers, Chronar and Matheson, now have reported "below-detection-limit" pure disilane, at prices under $25 per gram. The silent electric discharge method of preparing disilane is discussed in this report, with references. Several suppliers expect to import high-quality disilane from Japan and sell it at prices under $10 per gram by 1985. Suppliers' data indicate that the purer disilane will exhibit at least 6 months' stability in cylinders. Thus, it is likely that there will be rapid development of new uses for disilane.

In Japan, three companies began producing disilane in 1984: Mitsui, Shin Etsu, and Showa Denko, and four other companies are researching production. The disilane's reported quality is good; prices in Japan range from $4.50 to $9 per gram. As in the United States, there is not yet a commercial market for disilane in Japan.

It is likely that disilane will continue to be sold in research quantities for the next few years, although prices have been greatly reduced from $60 to a projected $7 per gram, and the quality of the gas has been improved.

Safety and Handling

Handling and shipping procedures for the silane gases have not been standardized, but this should not hinder growth. Data on currently used procedures are discussed in this report. The threshold limit for day-to-day exposure to silane is now 5 ppm, as listed by the American Conference of Governmental Industrial Hygienists. Disilane limits of exposure have not been determined.

Analytical Methods

Analytical procedures for determining the impurities in silane gases are now generally limited to ppm sensitivity. The impurities in currently produced pure grades of monosilane are already below most detection limits by current analytical techniques. The sensitivity of solar cell performance to impurities in the silanes is still being studied. Thus, it would be useful to have analytical procedures for some elements of silane that would be sensitive to the part-per-trillion level or better. Several techniques that might be developed into usable analytical methods for determining the boron, phosphorus, arsenic, and antimony levels in silane are presented.

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ABSTRACT

This report contains information on the improvements in the quality of monosilane and disilane now commercially available. Suppliers' analyses are tabulated along with capacity data. Suppliers currently have a higher purity grade of silane than previously, which yields a deposited silicon film with a resistivity of more than 1000 ohm-cm. Prices and grades are listed for the silane gases available in the United States and Japan. The silent electric discharge method of preparing disilane from silane is reviewed, with references. Properties and stability data for disilane are given. Handling and shipping of the silane gases are discussed, along with data on health hazards. Analytical procedures for determining impurities in silanes are listed; sensitivities are generally only to the 1 ppm level. Analyses for boron, phosphorus, arsenic, and antimony in silane would be useful for photovoltaic work at the parts-per-trillon level: suggestions are given for possible techniques that might be developed to achieve this.

SECTION 1.0

INTRODUCTION

A SERI consultant report issued in December 1983 [1] identified methods of preparing and purifying silane and disilane in the United States and Japan. Manufacturers, commercial availability, quality, and price ranges were listed. Now, amorphous silicon solar cells are being produced in Japan, and production is also starting in the United States. This and other new, potential uses have increased the competition for silane, in both the United States and Japan. Three U.S. companies (Liquid Carbonic, Matheson, and Union Carbide) and one in Japan (Komatsu) currently produce over 80% of the world's silane. Interest is also increasing in disilane for photovoltaics and other uses, and this has encouraged four Japanese companies to begin disilane production. Several Japanese firms are now seeking U.S. and European distributors. The quality of both the silane and disilane has improved. As to disilane, increased stability in cylinders is evident, due in large part to much lower amounts of impurities.

The world market for silane has been growing at some 15% to 20% per year. Current and potential uses are projected to triple by the year 1990 from the 1984 world use of 74 metric tons. This is still a rather small market in the chemical world, but an attractive one. In Japan, there has been one domestic producer of silane for the past 12 years; now there are four, and three more are poised to start production. While photovoltaic uses for silanes are less than 2% of the total market, this could change rapidly in the next 6 years.

This report updates the 1983 report, with special emphasis on disilane preparation and properties. The status of silane and disilane in the United States and in Japan is also discussed in the following areas:

- Market data
- Production capacities and prices
- Commercial availability and quality
- Safety and shipping
- Analysis of impurities.

Telephone and personal interviews were used to obtain the market data. A Chemical Abstracts computer search was employed for the safety and analysis sections. These were supplemented by communications with consultants concerning handling and analytical areas.

SECTION 2.0

UPDATE ON THE STATUS OF SILANE

2.1 STATUS IN THE UNITED STATES

2.1.1 Market Summary

The commercial market for silane in the United States is still dominated by the electronics industry. These uses--epitaxial silicon, silicon oxide, or silicon nitride deposits--continue to grow with the semiconductor industry at some 12% to 15% per year. As shown in Table 2-1, 44 metric tons of silane were used in electronics in the United States in 1983, and over 52 metric tons are expected to be used in 1984. These are the author's data, since no industry figures are available. However, ARCO Solar, Chronar Corporation, Energy Conversion Devices, Inc., and Solarex Corporation have announced that they will start production of amorphous silicon solar cells in 1984.

Union Carbide Corporation's Electronics Division did begin producing polysilicon from silane in their 100-ton Washougal pilot plant in 1983. Most of this silane will be converted on-site to polysilicon, but some will also be marketed by the Linde Division. The Linde Specialty Gases group has received some shipments of silane from this plant for resale and is expected to get larger quantities once the 1400-ton Moses Lake plant is started, late in 1984.

The seven U.S. producers of silane have increased their capacities somewhat from last year, and most of them have also improved their products' quality. Thus, adequate supplies of silane continue to be available for photovoltaics and other uses that could emerge.

Silane prices have been very stable over the past year in the United States. This trend is expected to continue. It is likely that prices will remain in their current ranges, with continued improvements in the quality of the products.

Table 2-1. Silane Merchant Markets in the United States and Japan
(metric tons)

	United States			Japan			
Year	Electronics	PV	Total	Electronics	PV	Copy Machines	Total
1981	34	-	34	8	-	-	8
1982	40	-	40	12	0.5	-	12.5
1983	44	-	44	15	1.0	0.4	16.4
1984 estimates	52	-	52	18	2.5	1.2	21.7

The first indication of foreign competition with the U.S. silane market occurred in 1984. Mitsui Toatsu Chemical Company is seeking to enter the U.S. market by supplying some of the established producers/sellers. Other Japanese companies may also seek current sellers as distributors or even set up their own outlets. Even so, however, no market upsets are expected.

Additional markets for silane, other than for semiconductor, polysilicon, and photovoltaic uses, are expected to develop. One is a new, charged couple device that contains a layer of amorphous silicon between two silicon/silicon oxide layers [2]. Silane is already being used in the production of copy machines in Japan (see Section 2.2.1); production in the United States could begin in 1985. Silane suppliers indicate that U.S. and Japanese companies are evaluating the use of amorphous silicon as light-emitting diodes on flat display panels. The growth of these uses could help increase the demand for silane.

2.1.2 Commercial Availability

Silane is produced in the United States, as it was in 1983, by seven manufacturers: Airco Industrial Gases, Air Products and Chemicals, Inc., Union Carbide Corporation (Linde Division), Liquid Carbonic Corporation, Matheson Gas Products, Scientific Gas Products, Inc., and Synthatron Corporation. These companies have silane-producing capabilities (Table 2-2) but not all are operating their plants at this time. Historically, the smaller producers have opted to buy silane to meet some or all of their needs and purify the purchased gas to their specifications. Liquid Carbonic, Matheson, and Union Carbide dominate production, and no new producers have come on-stream in 1984. Allied Chemical has a pilot plant and a process, but has chosen to try to license others rather than to produce the gas itself. Chronar indicates that it is considering entering the silane market by 1985. Union Carbide's 120-ton silane/polysilicon pilot plant at Washougal, Washington, did provide 4 to 6 tons of silane to its Linde Division for marketing in 1983. Linde reports that this silane is the purest it has seen. Larger quantities were expected to be available for resale from this unit in 1984. In 1985, Union Carbide's large, 1400-ton silane/polysilicon plant is scheduled to be on-stream. The silane plant is being commissioned totally, and the polysilicon reactors will be brought up incrementally. Several hundred tons of this silane could be available for resale.

CBI Industries, Inc., has purchased Liquid Carbonic Corporation from Houston Natural Gas Corporation. No changes in operation are currently planned. In October 1984, Liquid Air Corporation announced its purchase of Ideal Gas Company, which will now operate in the Alphagaz Division. Eagle-Picher announced it would be selling high-purity gases, including silane, starting in 1985. It will buy silane and purify it further with a proprietary process.

As the volumes of silanes increase, additional sellers or distributors can be expected to have the product available. L'Air Liquide has announced its start-up of silane plants in France and in Japan; so, we might expect its U.S. affiliate, Liquid Air, to add silane gas to its product line.

Table 2-2. Silane Manufacturing Capacities, for Resale
(est. metric tons)

United States	1984	1986
Airco	2	25
Air Products	7	15
Linde-UCC	20 [120][a]	200 [1540][a]
Liquid Carbonic	20	30
Matheson	12	20
Scientific Gas	3	10
Synthatron	5	10
Totals	69	310
Japan	1984	1986
Komatsu	50 [120][b]	140 [200][b]
Mitsui	7	20
Honjo	3	6
Teisan	3	5
Showa Denko	1	5
Totals	64	176

[a] Union Carbide Electronics Division's silane capacities at its polysilicon plants are shown in the brackets. An estimated 20% of this silane could be available for resale.

[b] Komatsu's total silane capacity is in brackets; 60 tons used for polysilicon.

While there was little change in their total production capabilities, all producers did improve their silane's quality. Some of the products were already better than indicated in the author's 1983 report [1]. On pages 10-12 of that report, data are given on 12 cylinders of Matheson silane, with a range of impurities from 11,500 ppm to zero. Note that the cylinders with high impurities were intentionally prepared for special studies. The commercial silane then available from Matheson was fairly represented by the analyses of cylinders M6, M6A, M7, and M8 [1, pp. 11-12].

Silane prices (Table 2-3) have been fairly stable during the past year. All suppliers now offer a "super" grade of silane, and the price of this grade has generally decreased. We noted three-tier pricing: the "standard" semiconductor grade sells at $0.15 to $0.32 per gram; the "improved" grade, at $0.50 to $0.85; and the "super" grade, at $1.30 to $2.00 per gram. Products priced over $1.00 per gram are used mainly as standards. It appears that high-quality silane with a deposited film resistivity of over 500 ohm-cm will continue to be available in the $0.50-per-gram range. In general, the trend is toward better-quality silane at current prices.

Table 2-3. Monosilane in the United States
(list prices, August 1984)

Company	Grade Name	Price Range[a] ($/g)
Airco	Electronic	0.32 - 0.76
	VLSI	0.80
	CCD	1.20 - 1.50
	Nitride	1.75
Air Products	Semiconductor	0.29 - 0.90
	Nitride	0.50 - 0.75
	Mitsui	0.70
Linde-UCC	Electronic	0.17 - 0.41
	Ultra-plus	0.50 - 1.00
Liquid Carbonic	Epitaxial	0.15-1.50
	HRS	0.15-1.50
Matheson	Semiconductor	0.24 - 0.88
	Matheson Purity	2.00
Scientific Gas	Semiconductor	0.32 - 0.90
	Epitaxial	0.36 - 0.95
	Nitride	0.55 - 1.15
	VLSI	1.30 - 1.43
Synthatron	Epi/Nitride	0.30 - 0.50
	Ultra-high	0.80
Ideal Gas Div., Liquid Air	Electronic	0.27 - 0.40
	CCD	0.85 - 5.00
	Ideal	2.00

[a] These are list prices quoted by the suppliers. Quantity or contract uses are usually negotiated. Cylinder deposits, demurrage, and shipping costs should be obtained from the supplier.

Most companies have improved their quality and some have reset their available grades (Table 2-4). The minimum resistivity for regular epitaxial or semiconductor use is now 100 ohm-cm; two companies even offer 500 ohm-cm as the minimum resistivity for this quality. The high-purity grades have a film resistivity range from 1000 to 10,000 ohm-cm. While resistivity is only one of the important parameters of silane, it is an indicator of the relative quantities of donors (like phosphorus) or acceptors (like boron). Silanes will generally yield an n-type silicon deposit, indicating an excess of phosphorus or arsenic over the boron. For most solar cell applications, silanes having a film resistivity of 500 to 2000 ohm-cm will perform well. However, users still

Table 2-4. Silane Analyses From Supplier's Data (ppm)

	Ohm-cm	N_2	O_2	H_2O	THC	CO	H_2	Rare	ClSi[a]	Cl-	Siloxane
Airco											
Electronic	100	b	10	3	50	20	5000	b	1000	b	b
VLSI	500	b	10	3	30	5	1000	b	100	b	b
CCD	2500	2	1	1	1	2	200	1	1	b	b
Nitride	10000	b	b	b	b	b	b	b	b	b	b
Air Products											
Semiconductor	100	100	10	1	10	5	1000	40	10	b	b
Nitride	100	40	10	1	10	5	500	40	b	10	b
Mitsui	1000-2000	<2	<0.5	<1	<1	<1	300	10	b	<3	<0.1
Lice-UCC											
Electronic	150	100	10	3	50	10	200	40	b	50	50
Ultra-plus	1000	40	10	3	5	3	10	40	b	c	c
Liquid Air, Ideal Gas Products											
Electronic	500	b	b	b	b	b	b	b	b	b	b
CCD	2500	b	b	b	b	b	b	b	b	b	b
Ideal	10000	10	b	2	2	b	100	b	c	b	b
Liquid Carbonic											
Semiconductor	500	10	1	b	2	0.5	5	b	b	1	1-5
HRS	1000	5	1	1	c	0.2	3	b	b	<1	<1
Matheson											
Semiconductor	500	b	5	2	40	b	500	b	10	b	b
Purity	10000	b	0.9	b	b	b	b	b	0	b	b
Scientific Gas											
Semiconductor	50	20	10	3	50	b	2000	b	1000	b	b
Epitaxial	100	40	10	3	40	b	1000	40	1000	b	b
Nitride	100	b	10	3	10	b	500	40	10	b	b
VLSI	1500	10	5	1	5	b	4500	10	10	b	b
Synthatron											
Epi/CCD	100	b	1	2	10	10	50	5	5	b	b
Ultra-high	800	c	c	c	c	c	300	c	c	c	b

[a] Chlorosilanes.
[b] Not reported.
[c] Not detected.

indicate that since the quality of all grades of silane varies in cylinder-to-cylinder purity, there is a troublesome problem in maintaining production uniformity.

The effects of impurities in silane on the optoelectronic properties of glow-discharge-deposited amorphous silicon have been reported recently by Corderman and Vanier [3]. Their paper reviews the previously published data and presents their data obtained at Brookhaven National Laboratory on amorphous silicon cells with chlorine- and oxygen-containing impurities. They found that chlorine-containing impurities act as weak p-type dopants in the amorphous silicon. These results are discussed further in Section 6.0. They conclude that chlorine-containing molecules (usually HCl and chlorosilanes) and oxygen-containing species (mostly oxysilanes) are detrimental to solar cell efficiency. Thus, the silane used for hydrogenated amorphous silicon thin films should contain minimum amounts of these impurities. Table 2-4 lists the impurity contents of the silanes, as presented in the company data sheets or letters. Note that most of the highest-quality grades of silane--those over 1000 ohm-cm resistivity--are generally low in chlorides and chlorosilanes.

2.1.3 Further Comments on Silane Producers and Sellers

Current U.S. silane producers and sellers are listed in the Appendix. Producers have generally kept their original, "electronic" grade of silane at its original purity and have added other grades. This is understandable, since silane at this quality performs adequately in epitaxial uses. The higher-quality grades--often showing a ten- to twentyfold reduction in impurities--were added to the product line. The two largest U.S. producers--Union Carbide and Liquid Carbonic--now offer just two grades. This will probably be the trend of the future.

Air Products has signed a distributor contract with Mitsui Toatsu Chemical Company for exclusive rights to sell Mitsui monosilane in the United States and Canada, with a nonexclusive right for disilane. And Synthatron has announced it will be seeking to import silanes from Japan.

2.2 STATUS IN JAPAN

2.2.1 Market Summary

The market for silane in Japan is still dominated by the semiconductor industry, but with photovoltaics and the copy machine uses developing rapidly. As noted in Table 2-1, electronic uses are growing with the market at 20% to 30% per year. The 15 metric tons of silane used in 1983 was expected to grow to 18 tons in 1984. The photovoltaic industry used almost 1 ton of silane in 1983, almost entirely in amorphous cells for the small calculator and watch-charging markets. This use will more than double in 1984, since all the amorphous cell producers are expanding. However, the dark horse in the silane market in Japan is copy machine use. A German patent [4] details this particular use. Canon, in its Keno plant at Nagoya, is now making plain paper copiers using amorphous silicon as the photoconductive material instead of the conventional selenium or cadmium. Silane suppliers expect that this commercial use will exceed 1 ton per year in 1984.

As silane uses grow, one would expect to see more companies enter the market. And, indeed, this is already happening. Komatsu, which has had over a 70% market share of the merchant silane sales in Japan, continues to hold that share. Komatsu expanded its silane capacity in 1984 and plans to almost double it by 1986 (Table 2-2). Union Carbide has held its nearly 26% of the market in Japan, leaving very little for Matheson or the new domestic producers. Mitsui Toatsu has expanded its pilot plant for silane and will try to enter the U.S. market. At least three other companies are now making silane on a scale of 1 to 5 tons per year.

Prices are fairly stable, varying slightly with the value of the dollar. They range from $0.29 to $0.63 per gram for semiconductor grade to $0.50 to $0.63 for VLSI grades. With more producers coming into the market, we can expect a trend toward one medium-priced, good-quality grade.

2.2.2 Commercial Availability

The commercial silane market in Japan has not changed much from 1983. Komatsu continues to hold its 70% market share, and Union Carbide is the only major importer. Wacker Chemie, Germany, has surveyed the market, but is apparently not able to ship 100% silane because of the country's laws. Four other companies are currently engaged in small-scale silane production: Mitsui Toatsu, Honjo, Teisan, and Showa Denko. Other firms interested in the silane market that could be preparing to enter it include Shin Etsu, Seitetsu, and Tokuyama Soda. Komatsu's large expansions in silane capacity appear to ensure adequate capacity in Japan for at least the next 8 years.

2.2.2.1 Komatsu Electronic Metals Company, Ltd., Hiratsuka

Komatsu continues to dominate the domestic markets. Its process for making silane is fully automated and efficient. Starting with magnesium and silicon, Komatsu makes magnesium silicide, which is reacted with ammonium chloride in liquid ammonia. Its purification techniques yield a very pure silane. Komatsu reports a deposited silicon resistivity of 2000 ohm-cm. The company states that it has now expanded its silane production to 140 tons per year and will expand again by 1985 to 200 tons capacity. Sixty tons of Komatsu's silane capacity is allocated to producing polysilicon; the rest is for resale. Komatsu appears to be geared up for all uses of silane and either keeping or expanding its market share. All of this expansion is apparently for merchant silane sales, as the firm is apparently not adding more polysilicon capacity.

2.2.2.2 Honjo Chemical Corporation, Osaka

Honjo Chemical makes specialty metal compounds, zinc and zinc oxides, lithium and strontium compounds, and magnesium anodes. Honjo started producing silane in 1982 under a license from Matheson. Its data sheet outlines its process: the reaction of lithium hydride with trichlorosilane in molten salt. The lithium chloride is converted back to lithium and then to lithium hydride. Using this process, Honjo would need very efficient purification processes to approach Komatsu's product's purity. Honjo started with a 2- to 3-ton plant and is rumored to be expanding to 5 to 6 tons by 1986. Honjo is seeking to distribute its products in Europe and the United States.

2.2.2.3 Mitsui Toatsu Chemicals, Inc., Tokyo

Mitsui started up a 5-ton silane plant in 1983, using an undisclosed process. The company reports that it will be capable of making 10 tons per year in 1984 and 20 tons per year by 1986. It claims only one grade of silane, with an average resistivity of 800 to 1200 ohm-cm as-deposited. Mitsui's data sheet lists only hydrogen as an impurity, with all other metals, gases, and hydrocarbons undetected down to 1 or 0.5 ppm.

Mitsui seems to have serious plans to enter the business, since it recently formed a new Electronic, Information, and Energy Materials Development Division. It has also listed offices in New York and Dusseldorf for this group. Mitsui has signed Air Products and Chemicals to be its exclusive monosilane and nonexclusive disilane distributor in the United States and Canada.

2.2.2.4 Teisan KK, Tokyo

Teisan, a subsidary of L'Air Liquide Group, Chalon Sur Saone, France, has begun silane production in a 3-ton unit. The parent company is also starting up a 10-ton silane unit in France. We believe it uses the lithium hydride process. The quality of Teisan's product is unknown at this time.

2.2.2.5 Showa Denko, Tokyo

This company has just started a 1-ton silane unit. Process, quality, and future production plans are not yet known. Showa Aluminum did participate in the Sunshine Solar Project, conducting silicon materials research.

2.2.2.6 Tokuyama Soda, Tokuyama City

This company is planning to enter the polysilicon market, having purchased the know-how from the General Electric Company. Tokuyama Soda is still developing its silane process, perhaps for an integrated product line or for internal uses. The firm could enter the silane market at any time.

2.2.2.7 Shin-Etsu Handotai, Tokyo

Shin-Etsu Handotai (SEH) has manufactured silicon products for many years and is a large silicon wafer supplier. It has a wafer facility in Vancouver, Washington, for example. The production of silane for internal use or perhaps to expand the company's epitaxial wafer line seems likely. Future plans and timing are not yet known, but Shin-Etsu is believed to be seeking markets outside Japan.

2.3 STATUS IN EUROPE

In Europe there are currently three producers of silane: Germany's Wacker, Airgo of Sweden, and British Oxygen. Recently, Air Products and Chemicals set up Air Products, Ltd., to market silane produced by Epichem Ltd., Cheshire, England [5] under an exclusive international agreement. The parent company will also provide operating support on the lithium hydride-silicon tetrachloride process for silane. In June 1984, L'Air Liquide announced start-up of a 10-ton silane plant in France to serve the electronics industry. All of these producers use the lithium hydride process.

SECTION 3.0

UPDATE ON THE STATUS OF DISILANE

3.1 INTRODUCTION

Disilane has several advantages in the preparation of amorphous silicon solar cells. Many researchers have made disilane in the laboratory and have utilized products of varying degrees of purity. When disilane first became commercially available several years ago, the stability of the gas in the cylinders was quite variable, due in part to the variable purity of the disilane. However, disilane had some interesting properties and was investigated for making solar cells.

Interest in disilane continues because of these indications of its usefulness and advantages. Research workers such as the IBM group [6] have reported much higher deposition rates of amorphous silicon when they use higher order silanes instead of monosilane. Other firms and universities have been working in the field of disilane on their own or under SERI contracts. Data on the purity and preparation of early disilanes were reported in 1983 [1], in which analyses of Chronar and Matheson (KOR) disilanes were given. Actually, these data were out of date by the time the report was printed, as much purer products became available. Current, improved products are discussed in Section 3.3. Disilane produced in the United States was dramatically improved in 1983; this has been documented by the Institute of Energy Conversion [7]. These researchers reported that disilane purchased early in 1983 showed up to 12 extra peaks on a gas chromatogram, each indicating an impurity of about 0.1%. The newer materials, however, exhibited only one impurity peak.

Meanwhile, Mitsui Toatsu in Japan has moved into disilane production and plans to make its material available in the United States and Europe.

As is the case with silane, as quality materials become readily available, other uses for disilane should develop. In addition to solar cell uses, suppliers indicate that disilane is also being evaluated for semiconductor use for depositing epitaxial films as well as for copy-machine uses. Currently, only 50- or 100-gram cylinders are available; 500-gram cylinders should be offered soon. Prices will also be reduced as commercial volumes grow.

Sales to date have been only of R&D quantities in 50- or 100-gram cylinders. Of course, paying \$60 to \$100 per gram, one would use the material with care. List prices of disilane in the United States in 1984 have ranged from \$25 to \$30 per gram, a marked reduction from the \$40 to \$130 per gram listed in 1982-83. High-quality disilane is now selling in Japan at under \$5 per gram, however. Disilane imported into the United States could thus be priced below the current \$10 to \$15 per gram.

3.2 PREPARATION AND PROPERTIES

3.2.1 Preparation

The preparation of disilane has been discussed in the earlier report on silanes [1]. Since that report, interest has been expressed in the electrical discharge process of converting silane to disilane. Thus, some comments on that process would be in order.

In 1962, Spanier, as part of his doctoral thesis with MacDiarmid at the University of Pennsylvania, published a paper [8] on making disilane by passing silane through an ozone-type electrical discharge. They found that a mixture of silanes resulted: 66% disilane, 23% trisilane, and 11% higher silanes.

In 1965, Gokhole and coworkers at the University of California's Lawrence Radiation Laboratory published a paper [9] on preparing disilane by passing silane through a silent electrical discharge. They separated the products by gas chromatography and listed only "good" yields. These two papers, along with data, are detailed in the book Preparative Inorganic Reactions [10].

Smith and Milne [11] studied the conversion of silane to disilane by the glow-discharge method. They achieved from 5% to 14% conversion under various feed ratios and power variations. Wiberg and Amberger [12] presented a comprehensive review of the preparation of silane and higher silanes. They discussed articles by Zakharkin et al. [13] and Obi et al. [14] in which both groups reported making monosilane by lithium aluminum hydride reaction with silicon tetrachloride in diglyme solvent (diethylene glycol dimethyl ether) for easier separation of products. This solvent could also be used to produce disilane from hexachlorodisilane and lithium aluminum hydride.

Wiberg [12] also provided some data from his unpublished notes (co-authored by Newman) in which yields of disilane from the lithium aluminum hydride-chlorosilane reaction in diethyl ether are given. They found 88% disilane at -50°C and at -120°C, 98% yield. Monosilane was the other major product of this process.

Regardless of the solvent used with the chlorosilane process, small amounts of contaminants are still possible. Of course, improved purfication processes can certainly minimize or even eliminate these impurities. With the silent electrical discharge method, the disilane product should be as pure as the feed silane. The process can be tuned for maximum disilane production. The small amounts of higher silanes formed are not detrimental to solar cell use. In fact Alan Delahoy, Director of Research and Development at Chronar Corp. [15], feels that for chemical vapor deposition from disilane, the presence of trisilane and other higher order silanes is desirable. A review by Mikhail et al. [16] of research on the use of disilane to deposit amorphous silicon films by chemical vapor deposition indicates that most of the research to date has been on disilane mixed with higher order silanes.

3.2.2 Properties

Disilane is a colorless gas at room temperature that ignites spontaneously in air. If one could get a whiff of disilane before it ignited, it probably would have the same pungent odor as silane [17]. The chemical reactions are similar to those of silane, but reaction rates are faster [18]. Mitsui's brochure [17] summarizes some of these data for chemical and physical properties.

The melting and boiling points of the silanes (from reference [19]) are as follows:

	Melting Point (°C)	Boiling Point (°C)
SiH_4	-185.0	-111.9
Si_2H_6	-132.5	-14.5
Si_3H_8	-117.8	52.9
nSi_4H_{10}	-89.9	108.4
$isoSi_4H_{10}$	-99.0	101.4

Because of its boiling point of -14.5°C, disilane can exist as a liquid in systems under slight pressure. It will ignite in air at almost all concentrations. Mitsui's data [17] suggest that concentrations under 0.1% may not ignite when exposed to air. No explosion limits have been determined; thus, it is suggested that one should consider that all concentrations of disilane from 0% to 100% will ignite or explode when they are exposed to air.

The first disilane products sold in cylinders degraded rather rapidly, since disilane is sensitive to small, catalytic amounts of contaminants. As with many silicon compounds, catalytic rearrangement is caused by many acidic or basic impurities. The end products of the disilane redistribution are silane and hydrogen, with a resulting build-up of pressure in the cylinder.

Harper and coworkers at duPont published some stability data in 1961 [20]. They prepared disilane by reacting lithium aluminum hydride with hexachlorodisilane. One sample was purified by trap distillation; this analyzed to 88 mol % Si_2H_6, 7% SiH_4, 0.1% SiH_2Cl_2, 0.1% $SiHCl_3$, 0.1% $SiCl_4$, 3% diethyl ether (the reaction media), 2% water, and 2% nitrogen. A second sample was purified by gas-phase chromatography. This is a good analysis process, where the disilane is preferentailly trapped in the packing and later is eluted as essentially 100% pure product. Table 3-1 gives the mol % of disilane remaining after the listed days in stainless steel cylinders held at the listed temperatures. The 88% disilane prepared by distillation decomposed more rapidly than did the nearly pure disilane. The authors conclude that the rate of decomposition is influenced by the presence of contaminants.

Table 3-1. Disilane Stability
(mol %)

Days	Distilled	Gas Chromatograph	
	(-30°C)	(-30°C)	(-78°C)
Start	97	100	100
49	93.9	100	100
154	84.2	97	98.5
244	75	97.5	98.6

Source: Harper 1961 [20].

Mitsui's brochure [17] lists data that indicate that no decomposition of their essentially 100%-pure disilane occurs over 165 days at room temperatures. Details of the test are not given, but the Mitsui product is usually shipped in nickel-lined cylinders. Mitsui predicts that its disilane will be stable for at least 6 months. Studies are continuing at Mistui and Matheson on the long-term stability of disilane.

Wiberg [12] lists the decomposition products of disilane as silane, polysilanes [$(SiH_2)_x$, SiH], and hydrogen. Thus, even if some decomposition does occur, which would be evidenced by a slight build-up of pressure, the deposited silicon purity should not be affected. There could be, however, a significant problem with the consistency of the composition of the gas flow from the cylinder, as the lighter gases would tend to exit first.

3.3 COMMERCIAL AVAILABILITY IN THE UNITED STATES

There are still only two producers of disilane in the United States. Chronar sells its product through Airco, and Matheson Gas sells its own disilane. Both companies improved their processes late last year and greatly improved the quality of their disilane. Mitsui Toatsu disilane is now sold in the United States by Air Products and Chemicals, Inc. Synthatron is discussing disilane imports with several Japanese companies.

Data from disilane analyses were given in the 1983 report [1, p. 13]. Concentrations of various impurities were cited as 120 to 48750 ppm, as analyzed on a modulated beam mass spectrometer. Analyses on currently available disilanes show that very few impurities are present. Current suppliers' data are listed in Table 3-2 for each producer. Total impurities, except hydrogen and higher silanes, range from 10 to 67 ppm. Users suggest that cylinders be analyzed before use, since variations in cylinder composition have been noted. Most manufacturers have been responsive to users' concerns about suspected impurities when these elements are detected in specific cylinders.

Prices have fallen dramatically during the past year, as shown in Table 3-3, for a purer product. Indications are that further price reductions can be expected. If volume uses develop, prices could fall below $5 per gram by

Table 3-2. Disilane Analyses from Suppliers' Data

Component	Chronar (Airco)	Matheson	Air Products, Mitsui	Synthatron
SiH_4	0 to 8%	0.1%	<0.1 vol. %	<0.1%
Si_2H_6	95.5%[a]	97+%	>99.9 vol. %	99.9%
Si_3H_8	4.0%	0.1%	<0.1 vol. %	<0.1%
Si_4H_{10}	0.1%	0.1%	b	b
Chlorosilanes	c	c	c	b
Oxysilanes	67 ppm	c	b	b
Hydrocarbons	c	c	<10 ppm	<10 ppm
CO, CO_2	c	c	c	c
N_2	10 ppm	10 ppm	c	c
Oxygen	c	c	c	c
Chlorides	c	c	c	c
Hydrogen	b	<500 ppm	<100 ppm	b

[a] Can supply single component on request.
[b] Data not supplied.
[c] The "not detected" level varies with producers. This could be 0.1 or 1.0 ppm, depending on the sensitivity of the method used for analysis.

Table 3-3. List Prices and Capacities for U.S. Disilane
(November 1984)

	Price Range ($/g)		Production Capacity (kg/yr)
	1983	1984[a]	
Airco	55-65	60	20 (Chronar)
Matheson	45	22.50	10
Synthatron	85-130	25	Imports
Air Products	—	7	Imports

[a] Prices are for 25- or 100-gram cylinders; data for larger sizes or quantities will be supplied on request.

1985. Pricing will depend on a great deal on the ability of producers to scale up their process. Calculations by several suppliers indicate that a disilane price of $2 to $4 per gram could make it cost-effective with silane for most uses.

The companies listed in the table all indicate that they can expand capacity to meet demands. This statement will have to be tested; for companies using the hexachlorodisilane process, commercial volumes of this material are not readily available.

Although there are only two producers of disilane in the United States, several other gas suppliers list disilane in their product line. Other suppliers have indicated that they can handle disilane upon customer request. Two companies indicated that they would be importing disilane from Japan beginning in late 1984.

3.3.1 Chronar Corporation

Chronar produces disilane by the magnesium silicide and by the silent electric discharge methods for in-house use and for resale by Airco. The quality of its product has dramatically improved with the new process. A cylinder of the company's disilane was analyzed by Brookhaven National Laboratory, under a private contract, in March 1984. The data, released by Chronar [15], indicate the following:

Si_2H_6	95.5%
Si_3H_8	4.0%
Si_4H_{10}	0.1%
$Si_2H_5OSiH_3$	67 ppm
Chlorosilanes	ND .

Chronar's own analysis indicates 8% monosilane and 10% nitrogen, with hydrocarbons and carbon oxides not detected. Chronar does have the capability to supply a single-component disilane on request.

3.3.2 Matheson Gas Products

Matheson makes and sells disilane. This firm has also considered the silent electrical discharge method. It offers 25- and 100-gram cylinders, but will consider larger sizes on request. Matheson's disilane is 97% Si_2H_6 and 3% total higher silanes and silane. Except for hydrogen and nitrogen, other impurities are not detected (to 0.1 ppm).

3.3.3 Synthatron Corporation

Synthatron has been purchasing its disilane requirements from a domestic company. Now, it is negotiating to import the product from a Japanese firm. In any case, Synthatron expects to have a quality disilane in its product line. It lists a 99.9% product with 0.1% silane and trisilane and less than 10 ppm hydrocarbons as the only detected impurities.

3.3.4 Air Products and Chemicals, Inc.

Air Products is adding disilane to its line in 1984. The firm will import the product from Mitsui Toatsu. This is a quality product and Air Products expects to price it at about $7 per gram (see Table 3-2).

3.4 COMMERCIAL AVAILABILITY IN JAPAN

Three domestic companies began producing disilane in Japan in 1983: Mitsui Toatsu, Shin-Etsu, and Showa Denko. Previously, a small amount of Chronar disilane had been imported. Apparently, there is not yet a commercial use for disilane in Japan. It is still under the new industrial chemical material regulation, which limits total sales to 100 kg. However, there is a lot of interest in disilane in Japan; Komatsu, Seitestu Chemical, Teisan, and Tokuyama Soda are investigating processes. The quality of the disilane is largely unknown; only Mitsui has printed any data. These data indicate that Mitsui is producing a very pure product.

Prices are currently much lower in Japan than in the United States. This seems to indicate a market strategy of encouraging rapid evaluation and there is a possibility that disilane may be cost-competitive with silane in the future. Prices and capacities are listed in Table 3-4.

3.4.1 Mitsui Toatsu Chemicals, Inc.

Mitsui has been conducting R&D in this area for some years, as well as investigating production of solar cells. In 1983, Mistui started up a pilot plant for silane and progressed into disilane. In 1984, it formed a new division, the Electronic Information and Energy Material Development Division, headed by Kazuyoshi Isogaya. This is an indication of the firm's dedication to get into this area. Mitsui currently offers silane, disilane, and silicon tetrafluoride.

Table 3-4. List Prices and Capacities for Disilane in Japan
(June 1984)

	Price ($/g)	Capacity (kg/yr)
Mitsui Toatsu[a]	4.50-6.00	100 1000 by 1985 (proposed)
Shin-Etsu	9.00	30
Showa Denko	9.00	30

[a] Although several companies have stated that they make and sell disilane in Japan, data have been available only for the Mitsui product.

Mitsui's current data sheets indicate products of high quality. On disilane, it lists 99.9 vol % disilane, with less than 0.1% silane and trisilane, less than 100 ppm hydrogen and hydrocarbons, less than 3 ppm total chloride, and undetected (less than 1 ppm) amounts of oxygen, nitrogen, argon, and carbon oxides. Because of this purity, and because nickel-lined steel cylinders are used, Mitsui claims shelf-life in the cylinders of over 6 months. It projects no deterioration over a year's time [17]. As shown in Table 3-4, Mitsui states that it has a capacity for 100 kg of disilane per year and will expand to 1 metric ton (1000 kg) by 1985. Mitsui has signed Air Products and Chemicals, Inc., as a nonexclusive seller of its disilane in the United States and Canada.

3.4.2 Shin-Etsu Handotai

This company has been in chemicals, silicones, and silicon wafers for many years. It produces and sells wafers in the United States as SEH, America. It also has a 24% equity in Dow Corning's Hemlock Polysilicon plant in Michigan. Thus, it is not surprising that Shin Etsu would be planning to produce silanes. No data sheets or analyses were available at this writing. The firm probably has an internal use for making epitaxial wafers. Shin-Etsu is seeking market outlets in Europe and in the United States.

3.4.3 Showa Denko

This company is just starting to operate a 100-kg facility. The quality of its product and future plans are not known.

3.4.4 Honjo Chemical Corporation

Honjo makes small quantities of disilane, and it is setting up United States distributors. The quality of its disilane is not yet known.

SECTION 4.0

HANDLING AND SHIPPING SILANE

4.1 INTRODUCTION

Silane is a colorless gas, with a choking, repulsive odor. It is flammable and often spontaneously ignitable. Silane at 100% and as a diluted mixture of gases has been used in the semiconductor industry for over 15 years. Since only grams of silane are used and the total volume produced has been relatively small, specific handling and shipping categories have not been established. The president of Larry Fluer, Inc., a firm specializing in safety-related issues associated with industrial storage, handling, and use of hazardous materials, states, "Good manufacturing practice has, in effect, been left to end users, who have forged ahead with guidance, support and common sense of plant safety personnel and the gas suppliers [21]."

There is evidence that some efforts are being made to set up guidance procedures and standards for silane. In 1979, the Semiconductor Equipment and Materials Institute began developing standards for compressed gases used in the industry. More recently, Battelle Laboratories proposed a multiclient study on silane gas safety [22]. This two-year study was to begin in 1984, if sufficient client funding had been found, to look at silane purity versus reactivity, silane oxidation and silane flames, use of flame arrestors, and the nature of leak deposits.

4.2 HANDLING AND USING SILANE

Silane is shipped in cylinders holding 100 to 16,000 grams. Thus, the practices for handling compressed gases [23] could be used as guidelines. The National Research Council (NRC) has published Prudent Practices for Disposal of Chemicals from Laboratories [24]. Written by the Committee on Hazardous Substances of the NRC, this book discusses recommended procedures and outlines the exposure limits for chemicals. A more recent edition published in 1983 [25] is a comprehensive guide to hazardous waste management. Silane is mentioned in the book, but the prudent procedures discussed are useful for all gases.

As guidelines for safe use, the American Conference of Governmental Industrial Hygienists, Inc., (ACGIH) publishes threshold limits for many chemicals [26]. As shown in Table 4-1, the threshold limit value--time-weighted average (TLV-TWA) for silane is 5 ppm. This value is the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be exposed day after day without adverse effect. This value for silane was recently increased from the earlier 0.5 ppm value. It was probably increased because the hydrolysis products of silane are only hydrogen and silica. When any silicon compound, such as chlorosilane, silane, or chloride, is reacted with water, silicon dioxide or silica gel (hydrated silica) is formed. This product, SiO_2, is formed very rapidly so small particles result. These particles have a high surface area and are very absorbent. When the particles come in contact with human skin, they quickly pull

Table 4-1. Health and Shipping Categories for Silane Gases

	Silane	Disilane[a]	Reference
TLV-TWA[b]	5 ppm	--	26
TLV-STEL[c]	1 ppm	--	26
DOT PIN[d]	UN 1954	--	30
UFC class[e]	2-Health hazard 4-Flammable 4-Pyrophoric	-- -- --	27[f]
Hazard class	F-Flammable P-Pyrophoric	-- --	27[f]
DOT[g] label	Flammable gas	Flammable gas	28
DOT name	Compressed gas NOS	Compressed gas	28
Odor	Repulsive-choking	--	--

[a] Disilane values and categories have not been set, so for now, the silane values should be considered guidelines.
[b] TLV-TWA = threshold limit value--time-weighted average.
[c] TLV-STEL = threshold limit value--short-term exposure limit.
[d] DOT PIN = Department of Transportation product identification number.
[e] UFC = uniform fire code.
[f] Silane is not specifically characterized by the National Fire Protection Association, nor by the reference. Hazard ranking is suggested by Fluer [29], based on experience and his file data.
[g] DOT = Department of Transportation.

moisture from it, causing a dry feeling. The silica particles were shown to be amorphous by X-ray analysis, indicating that they will not cause the severe physiological damage associated with crystalline particles. Thus, the dominant effect of exposure would be dehydration of the skin or mucous membranes.

Another value listed by the ACGIH [26] is the threshold limit value--short-term exposure limit (TLV-STEL). This is the amount to which a person could be exposed for 15 minutes up to 4 times a day, with no effect. This value for silane (Table 4-1) is 1 ppm. This 1983 volume is currently being revised. It should be noted that silane mixtures, such as with arsine or phosphine, would have a different TLV number.

The 1984 Matheson catalogue [31] lists the following effects of silane in man: "Little is known of the toxicity of silane except that breathing the gas may cause headaches and nausea. The hydrolysis of silane in the body tissues would form silicic acid or hydrated silica. The offensive odors of most of these gases should be taken as a warning of the persence of dangerous concentrations of the gases." Matheson also publishes a book, Effects of Exposure to Toxic Gases: First Aid and Medical Treatment (Second Edition), which is a practical first aid reference guide.

The storage of silane cylinders is another area in which several company practices have developed and there is no "standard accepted practice." For example, should one use a gas storage cabinet for storing silane cylinders? Some users insist on cabinets; others say they could add to the hazard. IBM Corporation has sponsored several studies on this issue to define explosion limits under stated conditions [32,33]. These reports are generally released upon request. The Hazards Research Study [32] presents data on leakage of pure silane in gas cabinets and ducts. The SWI study [33] provides data on silane dilutions of of.5%, 7.5%, 10%, and 15% with nitrogen, concerning ignition or explosions.

At the Semiconductor Safety Association meeting in May 1984 [29], a show of hands by users of silane indicated that about 60% used gas cabinets and about 40% did not. Some used a restrictive orifice in the silane line, because some data indicate that smaller flows do not ignite. Others viewed this practice as a hazard. A few companies replace their regulators every 8 to 10 months, as they detected the flows creeping up and loss of precise control. Many companies use double piping for their distribution systems, usually welded stainless steel with a nitrogen pressure in the outer tubing. All agree that proper purging procedures for the system are essential. New valves for use with silanes are now being offered on request by some suppliers. These will contain a restricted-orifice flow restrictor and filter. Other valve improvements are also being developed in work being sponsored by the Semiconductor Safety Association. Their goal is completely automatic shutdown inside the cylinder when needed.

Fluer [21] reports, "Although the potential for serious fires or dangerous exposure from chemicals certainly exists within the industry, the operating history reveals that process and safety engineers have coped adequately with the problems by keeping the incidents to a minimum. While there have been a number of fire losses reported where flammable gases were involved (notably silane), major losses occurred primarily in unsprinklered buildings. Whether inside or outside storage is provided, automatic sprinkler coverage is a prudent choice."

In setting up a new process line or revamping an old one, advice and suggestions can be obtained from the gas supplier, from insurers such as Factory Mutual, and from qualified consultants.

4.3 SHIPPING SILANE

Most silane is shipped in steel cylinders. When properly passified, the steel surfaces are quite inert to silane. Federal regulations require that such pressure vessels be hydrostatically tested every five years; they must then be repassified with care. Aluminum cylinders are being used by several companies, mostly with high-purity products. There is some indication that it is easier to maintain these very high purities in aluminum containers. However, the aluminum alloys are somewhat weaker than steel, so dents in handling do occur. One company has solved this problem by overcoating its aluminum cylinders with a fiberglass-resin layer. Steel cylinders can also be plated inside with nickel or other resistant metals.

As shown in Table 4-1, silane has a Department of Transportation (DOT) name of "Compressed Gas NOS" and a flammable gas label must be used. Silane is really pyrophoric, but DOT does not have such a category. The DOT product identification number (PIN), UN 1954, is a reference number to aid emergency agencies in quickly finding procedures in the DOT Emergency Response Guidebook [30]. Many gas suppliers have a special HELP (Hazardous Emergency Leaks Procedures) number to call if an emergency arises with their gases; almost all have a 24-hour number available for aid.

Currently, without industry standard operating procedures, the best source for handling and shipping procedures is the gas and equipment supplier.

SECTION 5.0

HANDLING AND SHIPPING DISILANE

5.1 INTRODUCTION

Disilane is a colorless, flammable gas that ignites spontaneously when exposed to air and is a relatively new product in the commercial market. It is sold only in quantities of 50, 100, or 500 grams. As a result, almost no regulations exist that apply to disilane. Because disilane is considered to be similar to silane, however, the same classifications can be used. Currently, disilane is sold for use in research projects. Chronar Corporation uses most of its disilane internally for solar cell production. Until more uses for disilane develop, we do not expect procedures and regulations to be standardized.

5.2 HANDLING AND USING DISILANE

There are very few articles on the safe use of disilane. Matheson's [34] and Mitsui's [17] product data brochures both give suggestions on procedures for handling disilane. Current users should probably consult their suppliers to find out the best handling procedures.

Disilane cylinders should always be stored and used upright, as the disilane in the cylinder is a liquefied gas. If the cylinder is horizontal when the disilane is withdrawn, pockets of liquid disilane would be forced into the system. Slight warming of the liquid would cause a rapid pressure build-up, which could rupture the system. Disilane and silane can be safely stored as liquids, but should always be moved in a system as gases. To date, the toxic limits for disilane have not been set. It has been suggested that the limits set for monosilane be used as guidelines (see Table 4-1).

When it is released in low concentrations into the atmosphere, disilane will hydrolyze without ignition, giving off a very visible, white, silicon dioxide plume. This is a good indicator of a leak! Although there are no data to confirm the resulting silica character, it should be similar to the silica resulting from silane burning in air. This silica is amorphous to X-rays; that is, it is not crystalline or abrasive. Contact with this silica will result only in a severe dehydrating reaction--unpleasant, but not generally life-threatening.

Users should be aware, however, that small pockets of liquid disilane could condense in turns or low parts of a system. The lines should be adequately purged, then, before they are opened. If users deposit silicon films from disilane, they should expect to find higher order polysilanes in the exit lines. These are usually yellow or brown solids or heavy liquids that are quite unstable; heat, shock, or air will cause them to detonate. Thorough purging or treating the lines with a caustic solution to react with or dilute these materials are good disposal procedures.

5.3 SHIPPING DISILANE

Disilane is shipped in steel cylinders lined with nickel or stainless steel. Quantities of 50, 100, or 500 grams are now available. Shipping data are shown in Table 4-1. Since criteria have not yet been established for shipping regulations, those for silane are now used. Suppliers should be contacted for proper procedures in case of leaking cylinders or for returning used cylinders.

Mitsui Toatsu Chemical Company is planning to sell its silanes in the United States through domestic companies. Since there is no standard industrial classification for disilane, it can be imported under one of several general silicon material categories, such as silanols. There should not be a problem with the small containers.

The stability of disilane in cylinders is of prime importance in the development of commercial uses for this gas (see Section 3.2.2). Suppliers and producers are gathering data on the long-term stability of their products. Indications are that the purity of the disilane and the choice of cylinders affect its stability. Mitsui Toatsu data [17] suggest at least a 6-month stable cylinder life for disilane at room temperature. Mitsui also projects a possible 1- to 2-year maximum stability. Matheson suggests a minimum stability of 6 months, and their studies continue. So it appears that, under proper conditions, disilane in cylinders would have adequate stability for many commercial uses.

SECTION 6.0

ANALYSES OF IMPURITIES IN SILANE

6.1 INTRODUCTION

Silane was introduced into the semiconductor industry in the late 1950s for epitaxial deposits on wafers; the controlling property of interest was the resistivity of a deposited film of silicon. Even a 30 to 50 ohm-cm resistivity was acceptable in the early days. Over the years, silane suppliers have responded to growing market needs and have provided purer and cleaner silanes. The analysis methods used on most electronic gases--basically gas chromatography and infrared spectroscopy--were also used on silane. These methods are sensitive at the ppm level for gases, hydrocarbons, chlorosilanes, and carbon oxides. The basic electrical test is to deposit a silicon layer on a wafer and measure the compensated resistivity. Since donors and acceptors neutralize one another, an excess of one or the other determines resisitivity and polarity. There is no current method of determining the concentration of each donor or acceptor at the ppb level, either in the silicon film or in the silane.

In photovoltaic work, "semiconductor"-grade silane was used, but researchers soon found that their results were not uniform. Some impurities that did not affect the epitaxial semiconductor layers did, however, affect the properties of solar cells. Purer silanes are now available and have been useful in these applications.

In amorphous silicon solar cell work, researchers are finding that impurities and levels of doping do affect a cell's properties. D. E. Carlson et al., in their final report on an amorphous silicon solar cell program [35], determined the diffusion lengths in amorphous siicon due to various contaminants; they discuss the effects of these impurities. They report that less than 0.06% of PH_3 (vol. %) caused an 80% reduction in the open-circuit voltage and a 75% reduction in the current. Doping with diborane at a low level also caused reductions in voltage and current. It follows that, for solar cell use, silane with the minimum possible amounts of boron and phosphorus would be desirable.

It thus appears to be useful to know the levels of the donors and acceptors in as-received silanes. Donors could be antimony, arsenic, lithium, or phosphorus; acceptors could be nickel, aluminum, or boron. Copper and silver can go either way. The heavier metals usually show up in various analyses, but at present there is no direct method for determining phosphorus, antimony, arsenic, or boron in silane.

If suitable analytical methods were to become available to determine impurities in silanes, we should be able to predict the effects and durability of the resulting solar cells. The influence of the impurities could be differentiated from the influence of the other parameters of the manufacturing process. We might even be able to understand some of the probable causes of the light-induced instability (Staebler-Wronski effect) of amorphous silicon cells. The level of detection for impurities in silane will have to be extended to at least ppb to be useful in screening raw materials. A sensitivity level of 10 parts per trillion would be even more helpful.

6.2 CURRENT METHODS FOR DETERMINING IMPURITIES

Suppliers of silane would normally use one of the following methods to detect impurities. Most of these descriptions are taken from a Linde booklet [36].

6.2.1 Detecting Moisture

Dew point or frost point detection. Dew point is determined by cooling an inert metallic mirror until dew is detected by an optical sensor. The partial pressure of water is obtained from tables and converted to ppm of moisture.

Electrolytic cell. Moisture is detected by an electrolytic cell that contains precious-metal wires coated with phosphorus pentoxide. A DC potential is applied across the wire and the dissociation current is read.

Capacitance analyzer. The capacitance analyzer can be placed directly in a pipeline or gas stream. The sensor is made made from an aluminum strip that is anodized and coated with gold. The impedance charge is a logarithmic function of the dew point.

Piezoelectric sensor. This sensor is a quartz crystal that is coated with an absorbent material. As the crystal is alternately exposed to a dry gas and the sample gas, it oscillates; its frequency can be displayed and converted to moisture content.

6.2.2 Detecting Oxygen

Electrochemical analyzer. This analyzer acts like a battery in which oxygen from the sample is reduced and the resulting electric current (in amperes) is a measure of the oxygen concentration.

Ceramic sensor. This analyzer depends on the voltage developed between the sample gas and a reference gas.

Coulometric sensor. This is a fuel cell in which oxygen is reduced and the resulting electric current (in amperes) is a measure of the oxygen concentration.

6.2.3 Detecting Hydrocarbons

Flame ionization detector. Adding a hydrocarbon to a hydrogen flame, which has a negligible amount of ions, creates a large number of ions. Applying an electrical potential between the hydrogen burner and an ion collector plate produces an ion current that is proportional to the hydrocarbon content. Results are presented as methane equivalents; the sensitivity level is to about 1 ppm.

Infrared detectors. These analyzers measure the absorption of specific wavelengths of light as an infrared beam passes through the gas sample. The dispersive type scans the entire wavelength range, while a nondispersive analyzer uses a specific infrared wavelength.

Gas chromatograph. This is the most popular instrument for analyzing hydrocarbons; it is sensitive to ppm levels. One chromatography method involves using an ascarite (powdered sodium hydroxide) column to block the passage of silane, followed by a silica gel column to separate the hydrocarbons [37]. This method can also detect nitrogen and hydrogen.

6.2.4 Detecting Other Materials

An emission spectroscopy method is usually used to detect heavy metals, but it is sensitive only to ppm. The concentration levels that are measurable are element-specific and vary appreciably among the methods. Thus, no single method is suitable for a complete analysis for concentrations near the ppb levels.

No direct methods of analyzing for phosphorus, boron, or arsenic in silane are practiced today. Electrical properties are evaluated by depositing a layer of silicon from the silane sample on a silicon wafer. The resistivity is measured by a two- or four-point probe or by a spreading resistance analysis. Measurement of resistivities over 500 ohm-cm requires very good techniques so that results will be reproducible.

Researchers at Union Carbide Corporation, under subcontract to DOE/JPL [37], developed a method to determine trace levels of phosphine in silane. Utilizing a gas chromatograph with a photo ionization detector, they found detection limits to be about 6 ppb. That technique did not work to detect diborane in the silane, however.

Corderman [38] has analyzed silanes for chloride, chlorosilanes, siloxanes, and higher silanes using a modulated molecular beam mass spectrometry, sensitive to 1 ppm. Corderman also details the equipment and procedures used. Currently, this method is limited to the species listed.

Boubel et al. [39] have a French patent that claims direct analysis of trace gaseous hydrides in air. They react the sample with ozone, pass it through an optical filter (495-6000 angstroms), and read it through a tube photomultiplier. They claim sensitivity to 0.3 ppm for phosphine and 3.8 ppm for diborane.

Two Russian articles are listed for reference. Trokhachenkova et al. [40] claimed a wet method for detecting phosphorus, boron, and antimony in silane. By reacting the silane with nitric acid, evaporating it, and treating it with poly methylphenyl siloxane, they state that they have reached a detection level of 4-10 ppm by emission spectroscopy.

Ezheleva et al. [41] claim the analysis of hydrogen, oxygen, carbon oxides, hydrogen chloride, ammonia, diborane, germane, phosphine, arsine, and hydrogen sulfide in silane by gas chromatography using flame photometric and thermal conditioned detectors. Detection limits are in the 3 ppm range.

Analytical processes should be capable of detecting impurities to the 0.01 ppm level or lower.

6.3 POSSIBLE NEW TECHNIQUES

Development of new analytical methods is a high-risk, costly activity. In conversations and readings, some germs of ideas were found which might be developed into methods for analyzing for the donors and acceptors in silane or the deposited films.

6.3.1 Photoluminescence

Photoluminescence is a newly applied method [42] of analyzing group III and V donor and acceptor elements in single-crystal silicon. It is not yet an accepted ASTM method but is being considered. With this method, impurities at 0.01 to 50.0 ppb levels can be measured in a quick, nondestructive test.

It might be possible to adapt this method to analyze the silicon film deposited from silane, using the wafer made for resistivity measurements. The theory of operation is that the group III and V elements are fully ionized at room temperature; when they are cooled to 4.5 K, they are neutralized. The sample is then illuminated; this causes a recombination process in which luminescent photons are emitted. The ratio of the intensity of the intrinsic line to that of the dopants indicates the concentration of the impurities. This method is self-standardizing and, with photomultipliers, can be made direct-reading. After the sample is prepared, it takes about 15 minutes to run the analysis. This method is being adopted by major polysilicon producers and some wafer manufacturers, replacing time-consuming, seven-pass, float-zone refining techniques. Since only a few top atomic layers of silicon are excited in this process, it should be possible to analyze the film deposited on a wafer. Equipment is now commercially available for this method.

6.3.2 Wet Chemistry

Wet chemistry techniques work well with trichlorosilane. To measure concentrations at the ppb level, the procedure is to use IR spectroscopy to measure impurity levels in samples that have been prepared from large volume solutions of 5 to 10 gallons by evaporative concentration. Low-temperature operation is required in analyzing silane, and the techniques need to be very precise. This type of method takes several days to run and requires a skilled operator to achieve reproducible results. However, it does not seem to be a practical method to use for silanes.

6.3.3 Other Techniques

Analyzing for the elements B, As, Sb, and P in silane presents special problems. Several possible new techniques were suggested by R. G. Pankhurst, an analytical consultant [43].

6.3.3.1 Analyzing for Boron

An inductively coupled, argon plasma emission spectroscopy (ICPES) procedure might be used to determine boron in silane. This would employ a preconcentration technique based on the fact that silane does not react with slightly acidic water, but diborane readily does. The procedure would consist of passing a measured volume of silane into a small volume of water through a properly designed nozzle under temperature, pressure, and flow-rate conditions that permit complete absorption of diborane; the boron content of the resulting solution would be measured by ICPES. Since the detection limit for boron in water by ICPES is 5 ppm [44], the sensitivity that can be achieved depends on the volume of silane taken for analysis.

The ICPES technique consists of aspirating a liquid sample through a nebulizer to form a mist that passes through an argon plasma, which excites the analyte into emitting its spectrum. The spectral energy of the selected emission line is collected in a phototube, thereby converting it to an electrical signal for quantification.

The aspiration-nebulization result in a nominally 4% of the aspirated sample reaching the plasma for excitation. If a discrete sample could be excited in its entirety, a 25-fold gain could be realized. Discrete sampling approaches to various systems have been reported [45-47].

6.3.3.2 Analyzing for Arsenic and Antimony

Two methods could be considered for analyzing arsenic and antimony in silane: graphite furnace atomic absorption spectroscopy (GFAA), as detailed by Winefordner et al. [44], or hydride generation atomic absorption spectroscopy (HGAA). These may be sensitive to 0.5 ppb or so. An electroanalytical methodology [48] has been reported to have sensitivities of 0.2 ppb for both arsine and stibine, but not all of the components of the instrumentation are available commercially.

Atomic absorption spectroscopy involves conversion of the analyte to atoms by suitable means (flame, furnace, or thermal dissociation of hydride) and exciting the atoms with monochromatic radiation appropriate to the concentration of the analyte in the sample. The graphite furnace technique consists of applying a portion of the solution (10-100 microliters) to the inside of a hollow graphite tube. This is resistively heated to evaporate the solvent; the analyte is atomized by rapid heating to 2500°C.

Hydride generation followed by atomic absorption spectroscopic quantitation of the thermally dissociated hydrides can be used for As, Sb, Pb, Se, Te, and Bi. The hydrides of these elements are generated by treating a suitable solution containing the analytes with sodium borohydride. The hydrides along with the cogenerated hydrogen are swept into a thermally heated quartz tube positioned in the optical path of the spectrometer.

More detailed information about these atomic absorption techniques is available from the equipment manufacturers [49].

6.3.3.3 Analyzing for Phosphorus

Arsine, phosphine, and stibine are reportedly absorbed from silane by nitric acid, and the solution is evaporated with graphite for emission spectroscopy analysis [40]. Sensitivities are listed as 4-10 ppm. If the absorption is effective at the ppb level and alternative techniques are used, this may offer an approach to analyzing silane for trace elements from a single, preconcentrated sample. ICPES would be used to detect boron and phosphorus, and HGAA to detect arsenic and antimony.

6.3.3.4 Possibilities for the Future

There are distinct differences in the physical and chemical properties of silane, arsine, diborane, stibine, and phosphine that could be potential routes to obtaining preconcentrations and simultaneous or subsequent direct determinations. One of these might be cryogenic selective absorption-desorption followed by element-selective detection in a gas chromatographic system. Krull and Jordan [50] discuss these systems, and they present a helpful bibliography. Other possibilities might be to use low-temperature infrared spectroscopy or isotope dilution mass spectroscopy. These techniques will need to be researched to determine which ones should be developed specifically for silane.

SECTION 7.0

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APPENDIX

MAJOR U.S. PRODUCERS AND SELLERS OF SILANES

Airco Industrial Gases
P. O. Box 272
Riverton, NJ 08077
609-829-7878

Air Products and Chemicals, Inc.
P. O. Box 1104
Allentown, PA 18105
215-481-5776

Chronar Corporation
P. O. Box 177
Princeton, NJ 08540
609-587-8000

Liquid Air Corporation
Ideal Gas Products, Inc.
Division of Alphagaz
P. O. Box 709
Edison, NJ 08818
210-287-8766

Liquid Carbonic Corp.
135 LaSalle St.
Chicago, IL 60603
312-855-2500

Matheson Gas Products
30 Seaview Drive
Secaucus, NJ 07094
201-867-4100

Scientific Gas Products, Inc.
2330 Hamilton Blvd.
So. Plainfield, NJ 07080
201-754-7700

Synthatron Corporation
50 Intervale Road
Parsippany, NJ 07054
201-335-5000

Union Carbide Corporation
Linde Specialty Gas Products
P.O. Box 444
Somerset, NJ 08873
201-356-8000