SILANES

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The properties and applications of commercially important hydride functional silanes, ie, compounds having a Si–H bond; halosilanes, ie, compounds having a Si–X bond; and organosilanes, ie, compounds having a Si–C bond, are discussed herein. Compounds having Si–OSi bonds are called siloxanes or silicones. Those having a Si–OR bond are called silicon esters. Siloxanes and silicon esters are discussed elsewhere in the *Encyclopedia* (see SILICON COMPOUNDS, SILICON ESTERS; SILICON COMPOUNDS, SILICONES).

Silane [*7803-62-5*], SiH_4, is the simplest silicon compound and provides the basis of nomenclature for all silicon chemistry (1). Compounds are named as derivatives of silane. The substituents, whether inorganic or organic, are prefixed. Examples are trichlorosilane [*10025-78-2*], $HSiCl_3$; disilane [*1590-87-0*], H_3SiSiH_3; methyldichlorosilane [*75-54-7*], CH_3SiHCl_2; methylsilane [*992-94-9*], CH_3SiH_3; diethylsilane [*542-91-6*], $(C_2H_5)_2SiH_2$; and triethylsilane [*617-86-7*], $(C_2H_5)_3SiH$. Two or more substituents are listed alphabetically, adhering to the following rules: substituted organic moieties are named first, followed by simple organic fragments; alkoxy substituents are named next, followed by acyloxy, halogen, and pseudohalogen groups. For example, ethylmethylethoxysilane [*68414-52-8*], $C_2H_5(CH_3)SiH(OC_2H_5)$, and 3-chloropropylmethylchlorosilane [*33687-63-7*], $ClCH_2CH_2CH_2SiH(CH_3)Cl$, are correct. The complete rules for nomenclature are available (2).

Inorganic Hydride Functional Silanes

Hydride functional silanes are sometimes simply referred to as silanes. The classic work in the field was completed in the early 1900s and involved the study of silane and higher binary silanes, Si_nH_{2n+2}, by means of precision vacuum techniques (3). Only a few of the thousands of hydride functional silanes reported have any commercial significance. These include inorganic silanes, organic silanes, and polymeric siloxanes. Despite the small number, a wide range of applications has developed for such compounds, eg, in the manufacture of high purity and electronic-grade silicon metal (see SILICON AND SILICON ALLOYS, PURE SILICON) and in epitaxial silicon deposition (see ELECTRONIC MATERIALS; INTEGRATED CIRCUITS; SEMICONDUCTORS); as selective reducing agents; as monomers; and as elastomer intermediates (see ELASTOMERS, SYNTHETIC). Not least is the use of these materials as intermediates for production of other silanes and silicones.

The inorganic silanes of commercial importance include silane, dichlorosilane, and trichlorosilane. The last, trichlorosilane, is preponderant. It is not only the preferred intermediate for the first two, but it is also used in the production of high purity silicon metal and as an intermediate for silane adhesion promoters, coupling agents, silicone resin intermediates, and surface treatments. Other silanes that appear to have potential in solar electronics are monochlorosilane, disilane, and some silylmetal hydrides. Silicon-based thin films (qv) employed in microelectronic applications are described as hydrogenated amorphous silicon (a-Si–H). An understanding of the physical and chemical behavior of simple silicon compounds, both as precursors and models, is essential for microelectronic device fabrication. Analogously, hydrogenated amorphous silicon carbide is of interest as a wide-gap solar cell material. Siloxene [*27233-73-4*], $(H_6Si_6O_3)_x$, an inorganic polymer containing silicon hydride bonds, is of interest as a catalyst and as a model for luminescent porous silicon (4) (see METAL-CONTAINING POLYMERS (SUPPLEMENT); SOLAR ENERGY).

Physical Properties. Silanes and chlorosilanes have boiling points, melting points, and dipole moments comparable to those of simple hydrocarbons (qv) and chlorinated hydrocarbons. Moreover, both silanes and hydrocarbons are colorless gases or liquids at room temperature. The similarity ends, however, with these simple physical characteristics (5). Silane, chlorosilane, disilane, and trisilylamine are pyrophoric, igniting immediately on contact with air. The chlorosilanes react with moist air, liberating hydrogen chloride. Dichlorosilane hydrolyzes to a polymeric material that may ignite spontaneously. Even trichlorosilane is highly flammable. The ability of chlorosilanes to permeate or solvate materials of construction, coupled with their hydrolysis to corrosive hydrogen chloride, formation of abrasive silica, and ability to act as reducing agents, makes these compounds difficult to handle.

The simple inorganic silanes are similar to carbon in that each forms stable, covalent, single bonds. Double bonds involving silicon and silicon carbon are relatively unstable. Whereas examples of isolable silicon double-bond-containing materials have been reported (6,7), these do not constitute a part of industrial silane technology. Most silane materials have a tetrahedral bonding geometry consistent with formation of sp^3 hybrid orbitals. Although in some cases participation of 3*d* orbitals in five- or six-coordinate silicon compounds, eg, SiF_6^{-2}, has been invoked, the degree of participation is debated. Silicon is more electropositive than hydrogen and carbon, generally leading to a more polar bond structure than that which occurs in the carbon analogues. The expected inductive release of electrons from R_3Si, however, does not occur. Disiloxanes, for example, are less basic than ethers. A factor which may contribute to the greater reactivity of silicon compared to that of carbon is silicon's greater size.

The physical and thermodynamic properties of silane in the context of semiconductor applications have been reviewed in detail (8). Tabulations of properties of various silanes in the context of inorganic chemistry have also been published (9). Table 1 contains selected physical properties of inorganic silanes.

Thermal Properties. Silanes have less thermal stability than hydrocarbon analogues. The C–H bond energy in methane is 414 kJ/mol (98.9 kcal/mol); the

Table 1. Properties of Inorganic Silanes

Parameter	SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	H_3SiSiH_3	$H_3SiOSiH_3$	$(H_3Si)_3N$
CAS Registry Number	*[7803-62-5]*	*[13465-78-6]*	*[4109-96-0]*	*[10025-78-2]*	*[1590-87-0]*	*[13862-73-4]*	*[13862-16-3]*
mp, °C	−185	−118	−122	−126.5	−132.5	−144	−105.6
bp, °C	−111.9	−30.4	8.2	31.9	−14.5	−15.2	52
vapor pressure,[a] Pa[b]	71_{-118}		13_{-34}	$53_{14.5}$			14.5_0
ΔH_{vap}, kJ/mol[c]	12.5	20	25.2	26.6	21.2	21.6	
ΔH_{fus}, kJ/mol[c]	0.67						
critical temperature, °C	−3.5		176	234	109		
critical pressure, MPa[d]	472		455	365			
ΔH_f, kJ/mol[c]	32.6		−314	−482			
dipole moment, C·m[e] × 10^{-30}		4.347	3.913	3.24		0.8	0
density,[a] g/cm^3	0.68_{-185}	1.145_{-113}	1.22	1.34	0.69_{-15}	0.881_{-15}	0.895_{-106}
autoignition temperature, °C	*f*	*f*	55	215	*f*	<50	*f*

[a] Subscripted numbers are temperature in °C.
[b] To convert Pa to mm Hg, multiply by 7.5.
[c] To convert J to cal, divide by 4.184.
[d] To convert MPa to psi, multiply by 145.
[e] To convert C·m to debye, divide by 3.336 × 10^{-30}.
[f] Pyrophoric.

Si–H bond energy in silane is 378 kJ/mol (90.3 kcal/mol) (10). Silane, however, is one of the most thermally stable inorganic silanes. Decomposition occurs at 500°C in the absence of catalytic surfaces, at 300°C in glass vessels, and at 180°C in the presence of charcoal (11). Disilanes and other members of the binary series are less stable. Halogen-substituted silanes are subject to disproportionation reactions at higher temperatures (12).

The thermal decomposition of silanes in the presence of hydrogen into silicon for production of ultrapure, semiconductor-grade silicon has become an important art, known as the Siemens process (13). A variety of process parameters, which usually include the introduction of hydrogen, have been studied. Silane can be used to deposit silicon at temperatures below 1000°C (14). Dichlorosilane deposits silicon at 1000–1150°C (15,16). Trichlorosilane has been reported as a source for silicon deposition at >1150°C (17). Tribromosilane is ordinarily a source for silicon deposition at 600–800°C (18). Thin-film deposition of silicon metal from silane and disilane takes place at temperatures as low as 640°C, but results in amorphous hydrogenated silicon (19).

Chemical Properties. *Oxidation.* All inorganic silicon hydrides are readily oxidized. Silane and disilane are pyrophoric in air and form silicon dioxide and water as combustion products; thus, the soot from these materials is white. The activation energies of the reaction of silane with molecular and atomic oxygen have been reported (20,21). The oxidation reaction of dichlorosilane under low pressure has been used for the vapor deposition of silicon dioxide (22).

Water and Alcohols. Silanes do not react with pure water or slightly acidified water under normal conditions. A rapid reaction occurs, however, in basic solution with quantitative evolution of hydrogen (3). Alkali leached from glass is sufficient to lead to the hydrolysis of silanes.

$$SiH_4 + 2\,KOH + H_2O \longrightarrow K_2SiO_3 + 4\,H_2$$

$$Si_2H_6 + 4\,KOH + 2\,H_2O \longrightarrow 2\,K_2SiO_3 + 7\,H_2$$

Complete basic hydrolysis, followed by the quantitative measurement of hydrogen formed, can be used to determine the number of Si–H and Si–Si bonds present in a particular compound. One molecule of H_2 is liberated for each Si–H and Si–Si bond present. The total silicon content can be obtained from analysis of the resulting silicate solution.

Silane reacts with methanol at room temperature to produce methoxymonosilanes such as $Si(OCH_3)_4$ [*78-10-4*], $HSi(OCH_3)_3$, and $H_2Si(OCH_3)_2$ [*5314-52-3*], but not H_3SiOCH_3 [*2171-96-2*] (23). The reaction is catalyzed by copper metal. In the presence of alkoxide ions, SiH_4 reacts with various alcohols, except CH_3OH, to produce tetraalkoxysilanes and hydrogen (24).

Halogens, Hydrogen Halides, and Other Covalent Halides. Most compounds containing Si–H bonds react very rapidly with the free halogens. An explosive reaction takes place when chlorine or bromine is allowed to react with SiH_4 at room temperature, presumably forming halogenated silane derivatives (3). At lower temperatures, the reactions are moderated considerably, for example,

$$SiH_4 + Br_2 \xrightarrow[-80°C]{} SiH_3Br\ (+SiH_2Br_2) + HBr$$

Halogen derivatives also form when the silanes are allowed to react with anhydrous hydrogen halides, ie, HCl, HBr, or HI, in the presence of an appropriate aluminum halide catalyst (25,26). The reactions are generally quite moderate and can be carried out at room temperature or slightly above, ie, 80–100°C:

$$\mathrm{SiH_4 + 3\ HX \xrightarrow{Al_2X_6} SiHX_3 + 3\ H_2}$$

where X is Cl, Br, or I. Hydrogen bromide reacts more readily than HCl or HI. Increasing the temperature or the duration of reactions generally leads to the formation of more fully halogenated derivatives.

Metals and Metal Derivatives. Silane reacts with alkali metals dissolved in various solvents, forming as the chief product the silyl derivative of the metal, potassium being the most commonly studied, eg, $\mathrm{KSiH_3}$ [*13812-63-0*] (27–30). When 1,2-dimethoxyethane or bis(2-methoxyethyl)ether are used as solvents, two competing reactions occur, where M is an alkali metal.

$$\mathrm{SiH_4 + 2\ M^0 \longrightarrow SiH_3M + MH}$$
$$\mathrm{SiH_4 + M^0 \longrightarrow SiH_3M + 1/2\ H_2}$$

Using hexamethylphosphoramide as the solvent, only the second reaction occurs. Disilane also reacts with potassium in 1,2-dimethoxyethane to form $\mathrm{KSiH_3}$, although $\mathrm{SiH_4}$ and nonvolatile polysilanes are also produced (28,31). Pure crystalline $\mathrm{KSiH_3}$ prepared from $\mathrm{SiH_4}$ and potassium in 1,2-dimethoxyethane has been obtained by slow evaporation of the solvent. When liquid ammonia is used as the solvent, only a small fraction of $\mathrm{SiH_4}$ is converted into metal salt; most of the $\mathrm{SiH_4}$ undergoes ammonolysis (32).

Disilane undergoes disproportionation in 1,2-dimethoxyethane, forming $\mathrm{SiH_4}$ and a solid material, $\mathrm{-\!\!(SiH_2)\!\!-}_x$, when an alkali metal salt, eg, KH or LiCl, is present (33,34).

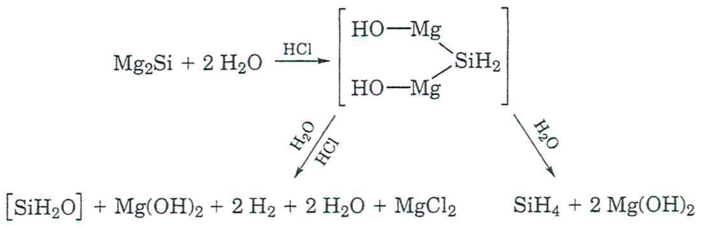
Silanes react with alkyllithium compounds, forming various alkylsilanes. Complete substitution is generally favored; however, less substituted products can be isolated by proper choice of solvent. All four methylsilanes, vinylsilane [*7291-09-1*], and divinylsilane [*18142-56-8*] have been isolated from the reaction of $\mathrm{SiH_4}$ and the appropriate alkyllithium compound with propyl ether as the solvent (35). Methylsilane and ethyldisilane [*7528-37-2*] have been obtained in a similar reaction (36).

Electrical Discharge, Irradiation, and Photolysis. Early reports of the decomposition of $\mathrm{SiH_4}$ in an electrical discharge indicated that the main products were hydrogen, solid silicon subhydrides of composition $\mathrm{SiH_{1.2-1.7}}$, and small quantities of higher silanes (37). However, more recent studies indicate that under certain conditions reasonably large quantities of higher silanes up to *n*-$\mathrm{Si_4H_{10}}$ [*7783-29-1*] and *iso*-$\mathrm{Si_4H_{10}}$ [*13597-87-0*] plus smaller amounts of various isomers of higher silanes up to $\mathrm{Si_8H_{18}}$ can be produced by this method (38–40). In addition, mixed-hydride derivatives can be prepared by subjecting mixtures of $\mathrm{SiH_4}$ and certain other volatile hydrides to such a discharge. Thus, $\mathrm{SiH_3GeH_3}$ [*13768-63-3*], $\mathrm{SiH_3PH_2}$ [*14616-47-8*], and $\mathrm{SiH_3AsH_2}$ [*15455-99-9*] have been prepared from SiH_4-GeH_4, SiH_4-PH_3, and SiH_4-AsH_3 mixtures, respectively (41,42). Although both disilylphosphine *[14616-42-3]*, $(SiH_3)_2PH$, and disilanylphosphine, $SiH_3SiH_2PH_2$, are obtained in the SiH_4-PH_3 system, these can be obtained free of each other in the discharge of $SiH_4-SiH_3PH_2$ and $Si_2H_6-PH_3$ (43). Methyldisilane *[13498-43-6]* can be isolated from the products of a $SiH_4-CH_3SiH_3$ or a $SiH_4-(CH_3)_2O$ discharge system (33,44). Hexachlorodisilane *[13465-77-5]* and hexafluorodisilane *[13830-68-7]* can be prepared from trichlorosilane and trifluorosilane *[13465-71-9]*, respectively (45). Glow discharge also provides a method for a high deposition rate of silicon from disilane (46). Silicon has been produced from silane by Penning discharge (47). Similarly, amorphous hydrogenated silicon nitride has been produced from silane–ammonia–nitrogen mixtures (48).

Photolysis studies of SiH_4 have involved a sensitizer, eg, mercury vapor, because SiH_4 does not absorb uv-radiation at wavelengths above 185 nm (49). The mercury-sensitized photolysis of SiH_4 leads to the formation of H_2, Si_2H_6, Si_3H_8 *[7783-26-8]*, and polymeric solid silanes; the quantum yields of H_2 and Si_2H_6 are ca 1.6 and 0.6, respectively (50,51). The photolysis of SiH_4 in the presence of GeH_4 or CH_3I produces SiH_3GeH_3 or CH_3SiH_3, respectively (52).

Manufacture and Processing. There are four methods of production of compounds containing a Si–H bond that are noteworthy. Silicides of magnesium, aluminum, lithium, iron, and other metals react with acids or their ammonium salts to produce silane and higher binary silanes. This method, uniquely applicable to the inorganic silanes, is the historic method for production of the silicon hydrides. Under optimum conditions, ie, the addition of magnesium silicide to dilute phosphoric acid, a 23% conversion to volatile silanes is possible (3). The composition of the silane mixture is 40 wt % SiH_4, 30 wt % Si_2H_6, 15 wt % Si_3H_8, and 15 wt % higher silanes. The highest reported yields of silicon hydrides have been achieved by treatment of magnesium silicide with NH_4Br in liquid ammonia at −33°C and $N_2H_4{\cdot}2HCl$ in hydrazine (53–55).

The formation of silane from magnesium silicide by acidic hydrolysis is thought to involve one of two paths after formation of a dihydroxymagnesiosilane intermediate (56).



The relatively low yields of silane provided by this method together with the difficulties in subsequently purifying the materials led to the discontinuation of commercial processes based on this technology in the United States in the late 1960s and early 1970s. This method was generally abandoned in favor of methods involving reduction of silicon halides. Interest in disilane has been sufficient to maintain magnesium silicide-based production in Japan. Treatment of calcium silicide with HCl–ethanol or glacial acetic acid yields the complex polymer called siloxene (57,58).

The reductions of chlorosilanes by lithium aluminum hydride, lithium hydride, and other metal hydrides, MH, offers the advantages of higher yield and purity as well as flexibility in producing a range of silicon hydrides comparable to the range of silicon halides (59). The general reaction is as follows:

$$R_nSiX_{4-n} + (4-n)\,MH \longrightarrow R_nSiH_4 + (4-n)\,MX$$

where X is a halogen. The most versatile reagent is lithium aluminum hydride; the most convenient solvent is tetrahydrofuran, followed by ethyl ether and bis(methoxyethyl)ether, although tertiary amines in hydrocarbons have also been reported as reaction media (60). The reduction occurs at room temperature. This approach is employed in the commercial production of silane from tetrafluorosilane utilizing sodium aluminum hydride (61,62). Limitations of the lithium aluminum hydride reagent system include the inability to produce partially reduced materials, eg, $SiCl_4$ is reduced completely to SiH_4 without formation of SiH_2Cl_2; and the catalytic rearrangement of susceptible bonds because of the formation of by-product aluminum chloride.

Lithium hydride is perhaps the most useful of the other metal hydrides. The principal limitation is poor solubility, which essentially limits reaction media to such solvents as dioxane and dibutyl ether. Sodium hydride, which is too insoluble to function efficiently in solvents, is an effective reducing agent for the production of silane when dissolved in a LiCl–KCl eutectic at 348°C (63–65). Magnesium hydride has also been shown to be effective in the reduction of chloro- and fluorosilanes in solvent systems (66) and eutectic melts (67).

Methods of direct reduction of chlorosilanes using hydrogen at high temperatures have historically been inefficient processes (68–70). Significant process innovations, involving the hydrogenation of silicon tetrachloride over Si–Cu at less than 2.45 MPa (500 psi), proceed in good conversion (71,72) and allow commercial processes.

$$3\,SiCl_4 + 2\,H_2 + Si^0 \xrightarrow{550\ K} 4\,HSiCl_3$$

At atmospheric pressure, the conversion to trichlorosilane is limited to about 16%. The conversion of $SiCl_4$ to $HSiCl_3$ was found to be at equilibrium. If contact time was greater than 45 s and the mole ratio of hydrogen to silicon tetrachloride 1:1, then at 14 kPa (2 psi) and 550°C, the $HSiCl_3$ mole fraction reached 0.7 but substantial formation of H_2SiCl_2 occurred (62). Enhancements in yield have been reported through preactivating the silicon mass by removal of oxides (73) and the rapid thermal quench of the effluent gas stream (74). The reduction of silicon tetrachloride in a plasma has also been reported (75).

Disproportionation reactions of silicon hydrides occur readily in the presence of a variety of catalysts. For example:

$$4\,HSiCl_3 \xrightarrow{\text{catalyst}} SiH_4 + 3\,SiCl_4$$

The most common catalysts in order of decreasing reactivity are halides of aluminum, boron, zinc, and iron (76). Alkali metals and their alcoholates, amines, nitriles, and tetraalkylureas have been used (77–80). The largest commercial processes use a resin–catalyst system (81). Trichlorosilane refluxes in a bed of anion-exchange resin containing tertiary amino or quaternary ammonium groups. Contact time can be used to control disproportionation to dichlorosilane, monochlorosilane, or silane.

Direct synthesis is the preparative method that ultimately accounts for most of the commercial silicon hydride production. This is the synthesis of halosilanes by the direct reaction of a halogen or halide with silicon metal, silicon dioxide, silicon carbide, or metal silicide without an intervening chemical step or reagent. Trichlorosilane is produced by the reaction of hydrogen chloride and silicon, ferrosilicon, or calcium silicide with or without a copper catalyst (82,83). Standard purity is produced in a static bed at 400–900°C.

$$2\ Si^0 + 7\ HCl \longrightarrow HSiCl_3 + SiCl_4 + 3\ H_2$$

Despite the apparent stoichiometry, this technology generates only 10–20% trichlorosilane. The balance is tetrachlorosilane. Trichlorosilane is in essence a recoverable by-product in a feedstock process for the production of fumed silica. High purity trichlorosilane is usually produced in a fluidized bed at 300–425°C. Hydrogen chloride is typically employed, although separate feeds of hydrogen and chlorine can be combusted in the reactor. Metallurgical silicon feedstock typically has a median particle size of 40–60 mesh (ca 420–250 μm); principal impurities are iron and aluminum as a result of primary silicon production and the milling employed in size reduction (qv) (see SILICON AND SILICON ALLOYS, CHEMICAL AND METALLURGICAL). A gas flow rate 4–20 times the minimum fluidization velocity is employed (84). A typical reactor is constructed of carbon steel, has a diameter of 0.5–0.8 m, operates at 2–5 kPa (0.3–0.7 psi), and has an output of 600–1000 kg/h. The heat of reaction, −141.8 kJ/mol (−33.9 kcal/mol) at 298°C (85), energetically propagates the initiated reaction and cooling must be provided. The conversion to trichlorosilane under these conditions is typically 80–88%; the remainder is silicon tetrachloride, 1–4% higher silicon halides consisting mainly of hexachlorodisilane and pentachlorodisilane, and 1–2% dichlorosilane. Pilot-scale technology for trichlorosilane developed independently from commercial technology has been reported in detail (86). Similarly, laboratory-scale production of tribromosilane has been reported with a fixed bed at 360–400°C (87). Additionally, inorganic silanes can be formed by cleavage reactions of aromatic organosilanes, eg, (88,89):

$$C_6H_5SiH_3 + HI \longrightarrow ISiH_3 + C_6H_6$$

Other, less satisfactory methods for forming silicon hydrogen bonds are shown below (90–94), where diphos = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.

$$Cl_3SiSiCl_3 + HCl \longrightarrow HSiCl_3 + SiCl_4$$

$$Cl_3SiSiCl_3 + NH_3 \longrightarrow HSiCl_3 + SiCl_3NH_2$$

$$SiCl_4 + HCHO \longrightarrow H_3SiCl + H_2SiCl_2 + \text{other products}$$

$$3\ SiCl_4 + 4\ Al^0 + 6\ H_2 \longrightarrow 3\ SiH_4 + 4\ AlCl_3$$

$$HSiCl_3 + (\text{diphos})_2CoH \xrightarrow{175°C} H_2SiCl_2 + (\text{diphos})_2CoCl$$

Economic Aspects. Trichlorosilane is the only inorganic silicon hydride produced in large scale. The annual U.S. production is ca 30,000–35,000 metric tons. Substantial quantities of this material are also generated in the production of silicon tetrachloride streams used in fumed silica (qv) production, but these are never isolated. The merchant cost of trichlorosilane is \$2–\$10/kg, depending on grade and container. Trichlorosilane is produced in the United States by Dow Corning, Degussa, General Electric, and Texas Instruments. Other worldwide producers are Hüls, Wacker, Chisso, Mitsubishi, Shin-etsu, and Tokoyama. Most (60–65%) trichlorosilane is used in the production of electronic-grade silicon (Fig. 1). Polycrystalline silicon processes consume most of the material, but some is used for epitaxial deposition. Hemlock Semiconductor, a joint venture

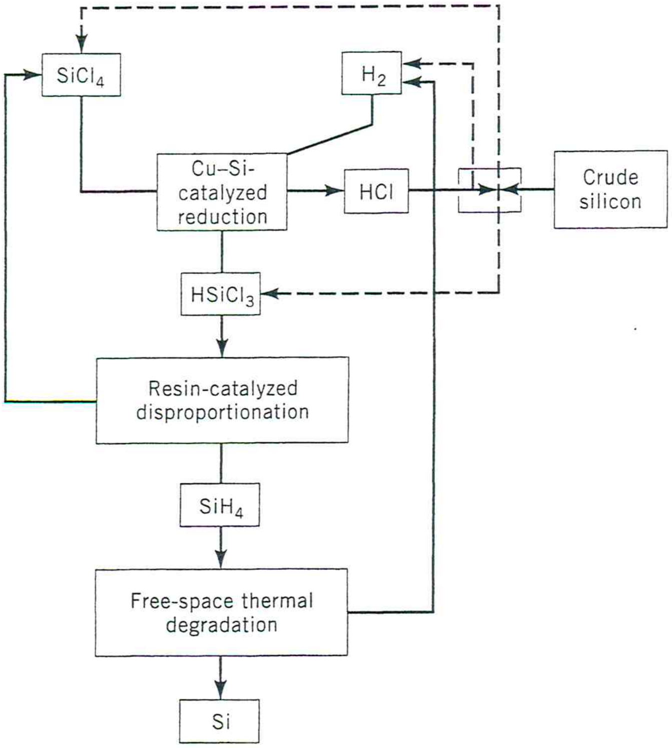


Fig. 1. Method for production of ultrapure silicon.

dominated by Dow Corning, produces polycrystalline silicon from trichlorosilane by a Siemens-type process. Hemlock Semiconductor had a nameplate capacity of 3500 t in 1995 and was scheduled to expand to 5000 t in 1997. Other producers of polycrystalline silicon from trichlorosilane by similar processes include Komatsu, Tokoyama, Mitsubishi, and Shin-etzu. Other uses for trichlorosilane include disproportionation to silicon hydrides and the conversion to organosilanes, eg, adhesion promoters.

In the United States, most of the consumption of silane is internal. Silane is consumed in a free-space polycrystalline silicon production facility (3000 t/yr) at Moses Lake, Washington. This facility was built by Union Carbide but as of 1996 was operated by Advanced Silicon Materials Inc., a joint venture controlled by Komatsu. Silane is also consumed in a fluidized-bed polycrystalline silicon production facility (1250 t/yr) in Pasadena, Texas, built by Ethyl Corporation and operated as of 1996 by MEMC, a publicly traded company 51% owned by Hüls. The world merchant market for silane is about 250 t/yr. The bulk price for silane is \$80–\$120/kg; much higher pricing is placed on small packages. The primary use of silane is in microelectronics. Minor applications exist in reprography, ie, in photocopiers, and in specialty glass technology.

Other specialty silanes used in microelectronic applications include dichlorosilane and disilane. Tribromosilane [*7789-57-3*], iodosilanes, and trisilylamine [*13862-16-3*] are of interest for microelectronics in low temperature deposition technologies.

Health and Safety Factors, Toxicology. The acute hazards of silicon hydrides are overwhelmingly important in considering worker safety. Silane is pyrophoric. Dichlorosilane, methylsilane, and dimethylsilane have demonstrated flow dynamic ignition. High levels of explosion severity have been reported under certain conditions (95). Chlorine-containing compounds generate hydrogen chloride on contact with water and other protic materials. At low concentrations, chlorosilanes affect nasal and pulmonary membranes. Only a minimal amount of toxicity information is available on these materials. The LD_{50} for trichlorosilane is 1050 mg/kg (96).

Organic Hydride Functional Silanes

The organohydrosilane of greatest commercial importance is methyldichlorosilane [*75-54-7*]. Careful hydrolysis of this material with water affords polymethylhydrosiloxanes, primarily used in the textile industry to waterproof and improve the wear resistance of fabrics (see WATERPROOFING AND WATER/OIL REPELLANCY). This polymer is also used as a waterproofing agent in the leather (qv) industry, the paper (qv) industry for sizing, electronic applications, and in construction for enhancing the water resistance of gypsum board (97–99). Similar fluids based on ethyldichlorosilane [*1789-58-8*] have been developed for commercial application in the CIS (former USSR), but as of 1996 these were not readily available elsewhere. Methyldichlorosilane is also used captively by silane and silicone producers in thermal condensation reactions to produce vinyl, phenyl, and cyanoalkyl precursors to silicone fluids. The addition reaction of methyldichlorosilane to fluorocarbon alkenes has enabled production of methyltrifluoropropyl silicone fluids, gums (qv), and rubbers. Trialkoxysilanes, eg, triethoxysilane [*998-30-1*] and trimethoxysilane [*2487-90-3*], are being used to prepare a number of organic coupling agents utilized by the plastics industry as adhesion promoters (see ADHESIVES). Organosilanes containing one or more Si–H bonds have excellent reducing capabilities (100).

Physical Properties. The physical properties of organosilanes are determined largely by the properties of the silicon atom (Table 2). Because silicon is larger and less electronegative than either carbon or hydrogen, the polarity of the Si–H bond is opposite to that of the C–H bond (Table 3). This difference in polarity imparts hydride character to the Si–H bonds of organosilanes. This difference in electronegativities is not as great as in ionic hydrides (qv), eg, LiH, NaH, and CaH_2; thus, the Si–H bond is still largely (98%) covalent. The size of the silicon atom is greater than the carbon atom, and this increase in atomic volume enables nucleophilic attack on the silicon to occur more readily than on carbon. Electrophilic attack on hydrogen bonded to silicon is also facilitated by the small steric constraints of hydrogen and the increased Si–H bond length. Additionally, the Si–H bond energy is somewhat lower than that of C–H, as is reflected in the thermal stabilities of such bonds. Organohydrosilanes begin to decompose at 440–460°C through homolytic cleavage of the Si–H bond and subsequent radical formation. The length and strength of silane bonds are also manifest in the vibrational spectra. Vibration frequencies of silanes, 2100–2260 cm^{-1}, are lower than those of C–H, 2700–3000 cm^{-1}. The presence of inductive groups, eg, halogen, vinyl, phenyl, or fluoroalkyl, on silicon increases the vibrational frequency of the Si–H bond. Conversely, the presence of alkyl substituents generally decreases the vibrational frequency because of the donation of electron density. A comparison of some physical properties of carbon and silicon and their bonds to hydrogen is given in Table 3.

Unlike carbon, the silicon atom may utilize vacant 3*d* orbitals to expand its valence beyond four, to five or six, forming additional bonds with electron donors. This is shown by isolated amine complexes. The stability of the organosilane amine complexes varies over a wide range and depends on the nature of the donor and acceptor (2).

Chemical Properties. Organohydrosilanes undergo a wide variety of chemical conversions. The Si–H bond of organohydrosilanes reacts with elements of most groups of the Periodic System, especially Groups 16(VIA) and 17(VIIA). There are no known reactions if the Si–H bond is replaced by stable bonds of silicon with elements of Groups 2(IIA), 13(IIIA), and 8–10(VIII).

Oxidation. Whereas the majority of inorganic silanes are oxidized spontaneously on contact with oxygen and air, the simplest organosilane, ie, methylsilane, is stable to air and does not spontaneously inflame, although flow-dynamic ignition has been reported. Methylsilane has been reported to explode in the presence of mercury and oxygen (102). The larger-chain alkylsilanes are more stable but ignite spontaneously when vaporized in oxygen under pressure. Phenyl and cyclohexylsilane can be distilled open to the atmosphere. Trialkyl- and triarylsilanes are more stable and have been distilled at as high as 325°C without decomposition (103). Differences between organosilanes and inorganic silanes are attributed to the electronic and steric effects of the organic substituents. The oxidizability of the Si–H bonds is much greater than that of C–H bonds. This difference is manifested by the ease

Table 2. Properties of Hydride Functional Organosilanes, Siloxanes, and Silazanes[a]

Compound	CAS Registry Number	Mol wt	Bp,[b] °C	Mp, °C	d_4^{20}	n_D^{20}
CH_3SiH_3	*[992-94-9]*	46.1	−57	−157	0.6277[c]	
$(CH_3)_3SiSiH_3$	*[18365-32-7]*	104.3	80−81			
$C_2H_5SiH_3$	*[2814-79-1]*	60.2	−14	−180	0.6396[d]	
$C_4H_9SiH_3$	*[1600-29-9]*	88.2	56	−138	0.6764	1.3922
$C_6H_5SiH_3$	*[694-53-1]*	108.2	120	<−60	0.8681	1.5125
$C_6H_{13}SiH_3$	*[1072-14-6]*	116.3	114−115	−98	0.7182	1.4129
$C_{18}H_{37}SiH_3$	*[18623-11-5]*	284.6	$195-196_2$	29		
$(CH_3)_2SiH_2$	*[1111-74-6]*	60.2	−20	−150	0.6377[e]	
$CH_3(C_6H_5)SiH_2$	*[766-08-5]*	122.2	139		0.889	1.506
$(C_2H_5)_2SiH_2$	*[542-91-6]*	88.2	56	−134	0.6832	1.3920
$(C_2H_5O)_2SiH_2$	*[18165-68-9]*	120.2	90−92			
$(C_6H_5)_2SiH_2$	*[775-12-2]*	184.3	$100-101_4$		0.9964	1.5756
$CH_3SiH(Cl)_2$	*[75-54-7]*	115.0	41−42	−93	1.105	1.422
$CH_3SiH(OCH_3)_2$	*[16881-77-9]*	106.2	61	−136	0.861	1.360
$CH_3SiH(OC_2H_5)_2$	*[2031-62-1]*	134.3	94.5		0.829[f]	1.372[f]
$CH_3SiH(Cl)N(CH_3)_2$	*[18209-60-4]*	123.7	85−87			
$CH_3SiH[N(CH_3)_2]_2$	*[3768-57-8]*	176.4	112−113			
$CH_3SiH(OOCCH_3)_2$	*[3435-15-2]*	162.2	$83-84_6$		1.1081	1.4022
$CH_3SiH(C_2H_5)Cl$	*[6374-21-6]*	108.6	67−68		0.8816	1.4020
$(CH_3)_2SiHCl$	*[1066-35-9]*	94.6	36	−111	0.851	1.3827
$(CH_3)_2SiHC_2H_5$	*[758-21-4]*	88.2	46		0.6681	1.3783
$(CH_3)_2SiHOC_2H_5$	*[14857-34-2]*	104.2	54		0.7572	1.3683
$(CH_3)_2SiHN(C_2H_5)_2$	*[13686-66-3]*	131.3	109−110			
$(CH_3)_3SiH$	*[993-07-7]*	74.2	67	−136	0.6375	
$(CH_3O)_3SiH$	*[2487-90-3]*	122.2	86−87	−114	0.860	1.3687
$C_2H_5SiH(Cl_2)$	*[1789-58-8]*	129.1	75	−107	1.0926	1.4148
$(C_2H_5)_2SiH(Cl)$	*[1609-19-4]*	122.7	100		0.889	1.4152
$(C_2H_5)_2SiH(CH_3)$	*[760-32-7]*	102.3	77−78		0.7054	1.3984
$(C_2H_5)_3SiH$	*[617-86-7]*	116.3	107−108	−157	0.7318	1.4119
$(C_2H_5O)_3SiH$	*[998-30-1]*	164.3	131.5	−170	0.875	1.337
$(2\text{-}ClC_2H_4O)_3SiH$	*[10138-79-1]*	267.6	$117-118_{0.3}$		1.2886	1.4577
$(C_3H_7)_3SiH$	*[998-29-8]*	158.4	173		0.7580	1.4272
$(C_6H_5)_2SiH(Cl)$	*[1631-83-0]*	218.8	$143_{1.3}$		1.118	1.581
$C_6H_5SiH(Cl_2)$	*[1631-84-1]*	177.1	$65-66_{1.3}$		1.212	1.526
$C_6H_5SiH(CH_3)Cl$	*[1631-82-9]*	156.7	113_{13}		1.054	1.571
$C_6H_5SiH(CH_3)_2$	*[766-77-8]*	136.3	156−157		0.8891	1.4995
$C_6H_5(H_2C{=}CH)\text{-}SiH(CH_3)$	*[17878-39-6]*	148.3	$56-57_{0.9}$		0.891	1.5115
$(C_6H_5)_2SiH(CH_3)$	*[776-76-1]*	198.3	266−267		0.9945	1.5717
$(C_6H_5)_3SiH$	*[789-25-3]*	260.4	$160-165_{0.4}$	42.4		
$(C_6H_{13})_3SiH$	*[2929-52-4]*	284.6	160−161		0.7992	1.448
$(C_8H_{17})_3SiH$	*[18765-09-8]*	368.8	$163-165_{0.02}$		0.821	1.454
$[(CH_3)_2SiH]_2O$	*[3277-26-7]*	134.3	70−71		0.757	1.370
$[(CH_3)_2SiH]_2NH$	*[15933-59-2]*	133.3	99−100		0.766	1.4044
$(CH_3)_3SiOSiH(CH_3)_2$	*[1438-82-0]*	148.4	85−86		0.7578	1.3740
$[(CH_3)_3SiO]_2SiH(CH_3)$	*[1873-88-7]*	222.5	141−142		0.8136	1.3815
$[CH_3SiHO]_4$	*[2370-88-9]*	240.5	134−135	−69	0.9912	1.3870
$[SiH(CH_3)_2]_2$	*[814-98-2]*	118.3	118.3	84−86	0.7202	1.4290

[a] Refs. 2 and 101. [b] Subscripted numbers are pressures in kPa. To convert kPa to mm Hg, multiply by 7.5. [c] At −58°C. [d] At −14°C. [e] At −20°C. [f] At 25°C.

Table 3. Physical Properties of Carbon and Silicon and Their Bonds to Hydrogen[a]

Element	Electronegativity	Covalent radius, pm	Usual coordination number	Bond with hydrogen: Bond length, pm	Bond with hydrogen: Bond energy, kJ/mol[b]
silicon	1.8	117	4	149	369–378
hydrogen	2.1	30		74	432
carbon	2.5	77	4	106–110	368–506

[a] Ref. 10, 59.
[b] To convert J to cal, divide by 4.184.

of oxidation of organohydrosilanes with metal oxides. The most noteworthy of these is mercuric oxide. Reactions of alkylsilanes with mercuric oxide in inert solvents, eg, toluene, afford nearly quantitative yields of silanols or silanediols.

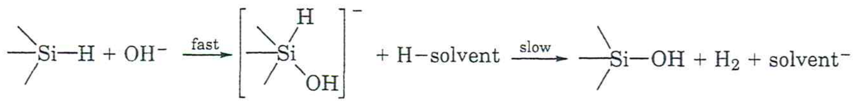
$$R_2SiH_2 + 2\ HgO \xrightarrow[-80\text{–}20°C]{\text{toluene}} R_2Si(OH)_2 + 2\ Hg^0$$

Oxidation has also been cited as occurring in the cure of polymethylhydrosiloxane [*9004-73-3*] (PMHS) on cellulose acetate fibers. Investigation of the cured, cross-linked silicone shows no evidence of the Si–H bond. The same compound under an atmosphere of nitrogen does not cure and retains the Si–H bonds (99).

Hydrolysis. As for inorganic silanes, no reaction occurs between organohydrosilanes and water. The presence of acidic or alkaline catalysts, however, brings about the reaction according to the following scheme:

$$\equiv Si\text{–}H + H_2O \xrightarrow{\text{catalyst}} \equiv Si\text{–}OH + H_2$$

The ease of hydrolysis depends on the pH and is more rapid under alkaline than acidic conditions. Organosilanes are most stable in weakly acidic media. The rate and extent of hydrolysis reactions are conveniently monitored by measurement of the rate and amount of hydrogen evolved. Alkaline hydrolysis is more widely used and has been more extensively studied. Alkaline catalysts may be organic, eg, triethylamine, pyridine, etc, or inorganic, eg, KOH, NaOH, NH_4OH, etc. The rate and completeness of these reactions depend on the nature and amount of catalyst, solvent, reagent concentration, temperature, and organic substituents of the organosilane. The substituents influence rate through steric and inductive effects. Such effects determine the ease of formation of the pentacoordinate silicon complex believed to be the transition state (104,105). The mechanism is thought to proceed through rapid attack of the base on the organohydrosilane with formation of a pentacoordinate silicon via bonding through 3*d* orbitals. Slow decomposition of this complex through interaction with a solvent proton affords the product.



Steric and inductive effects determine the rate of formation of the pentacovalent silicon reaction complex. In alkaline hydrolysis, replacement of a hydrogen by alkyl groups, which have lower electronegativity and greater steric requirements, leads to slower hydrolysis rates. Replacement of alkyl groups with bulkier alkyl substituents has the same effect. Reaction rates decrease according to:

$$C_4H_9SiH_3 > CH_3(i\text{-}C_3H_7)SiH_2 > (C_2H_5)_2SiH_2 > (C_2H_5)_3SiH > (C_3H_7)_3SiH$$

Mechanistically the rate-determining step is nucleophilic attack involving the hydroxide ion and the more positive silicon atom in the Si–H bond. This attack has been related to the Lewis acid strength of the corresponding silane, ie, to the ability to act as an acceptor for a given attacking base. Similar inductive and steric effects apply for acid hydrolysis of organosilanes (106).

Alcohols, Phenols, Silanols, and Carboxylic Acids. The catalyzed reaction of organosilanes with hydroxyl-containing organic compounds affords organoalkoxy and organoaryloxysilanes, usually in high yields (107). Alkali–metal oxides, hydrogen halides, and metal halides are most often used as catalysts. Of the metal halides, $ZnCl_2$ and $SnCl_2$ are the most commonly used:

$$\equiv Si{-}H + HOR \xrightarrow{\text{catalyst}} \equiv Si{-}OR + H_2$$

where R is an alkyl or aryl. The reaction of organosilanes with alkali metal alkoxides proceeds vigorously and in high yields. Aryloxy derivatives of silanes can be produced from phenols in yields up to 90% by catalysis with colloidal nickel and less effectively with other metals, eg, copper, cobalt, chromium, zinc, and tin (108). Reactivity increases for selected alcohols in the order $CH_3OH < C_2H_5OH < n\text{-}C_3H_7OH < n\text{-}C_4H_9OH$ (109), suggesting that the alkoxide is the active nucleophile.

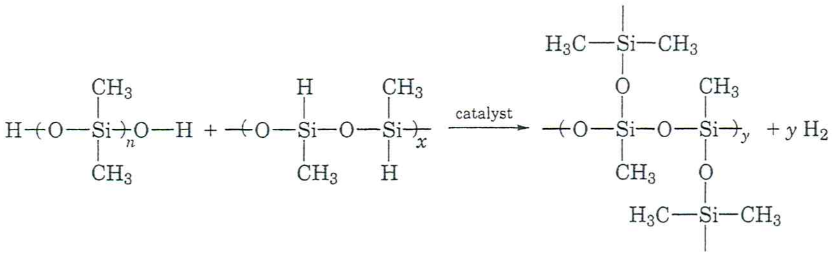
$$C_6H_5SiH_3 + 3\ ROH \longrightarrow C_6H_5Si(OR)_3 + 3\ H_2$$

Organic amines, eg, pyridine and piperidine, have also been used successfully as catalysts in the reactions of organosilanes with alcohols and silanols. The reactions of organosilanes with organosilanols lead to formation of siloxane bonds. Nickel, zinc, and tin also exhibit a catalytic effect.

$$\equiv Si{-}H + HOSi{\equiv} \xrightarrow{\text{catalyst}} \equiv Si{-}OSi{\equiv} + H_2$$

The reaction is of practical importance in the vulcanization of silicone rubbers (see RUBBER COMPOUNDING). Linear hydroxy-terminated polydimethylsiloxanes are conveniently cross-linked by reaction with methyldiethoxysilane or triethoxysilane [*998-30-1*]. Catalysts are amines, carboxylic acid salts of divalent metals such as Zn, Sn, Pb, Fe, Ba, and Ca, and organotin compounds. Hydroxy-terminated polysiloxanes react with Si–H-containing polysiloxanes to produce cross-linked materials. Metal salts of carboxylic acids are used as catalysts.

The liberated hydrogen can act as a blowing agent to produce silicone foam rubber (110).



Whereas metal salts of carboxylic acids catalyze the above reactions, these are not sufficiently basic to cleave Si–H bonds. Mercury salts of organic acids in the presence of silver perchlorate, however, do react to produce organoacyloxysilanes (111).

$$R'_3Si\text{–}H \xrightarrow{Hg(O\overset{O}{\overset{\parallel}{C}}R)_2} R'_3SiO\overset{O}{\overset{\parallel}{C}}R + R\overset{O}{\overset{\parallel}{C}}OH + Hg^0$$

Organoacyloxysilanes are also produced by reaction of organosilanes with carboxylic acids in the presence of strong mineral acids, eg, sulfuric and hydroiodic acids. Trialkylacyloxysilanes have been obtained in 81–87% yield from monocarboxylic acids in the presence of aluminum and iodine.

$$R_3SiH + HOCR' \longrightarrow R_3SiOCR' + H_2$$

Peracylation of polymethylhydrosiloxane to produce a cross-linked or cross-linkable material is achieved by reaction with acetic acid and is catalyzed by anhydrous zinc chloride (112). This reaction can be extended to monomeric organosilanes under similar conditions.

Amines and Phosphines. As in reactions of alcohols and acids with organosilanes, reaction of the Si–H bond with amines and phosphines proceeds only under catalysis. Alkali metal amides or phosphines are the catalysts of choice and effect replacement of the Si–H bond with Si–N or Si–P bonds, respectively. Catalytic activity of the alkali metals for these reactions is K > Na > Li (113). Reactions of triorganosilanes with ammonia (qv) and amines have been the most widely studied. Ammonia affords the disubstituted nitrogen compounds or disilazanes with no trisubstitution being observed. This presumably occurs because of steric crowding at nitrogen. For example, reactions for the formation of triethyldisilazane [*2117-18-2*] and triphenyldisilazane [*4158-64-9*] are as follows:

$$2\,(C_2H_5)_3SiH + NH_3 \xrightarrow{NaNH_2} ((C_2H_5)_3Si)_2NH + H_2$$

$$2\,(C_6H_5)_3SiH + NH_3 \xrightarrow{NaNH_2} ((C_6H_5)_3Si)_2NH + H_2$$

Primary organic amines react with triethylsilane in the presence of the appropriate potassium amides to produce organoaminotriethylsilanes with yields of 82–92%.

$$(C_2H_5)_3SiH + RNH_2 \xrightarrow{KNHR} (C_2H_5)_3SiNHR + H_2$$

where R is C_2H_5 [*3294-33-5*], $i\text{-}C_3H_7$ [*5277-20-3*], or C_6H_5 [*18106-48-4*]. No reaction occurs using secondary or tertiary amines under similar reaction conditions. Steric factors are also important, as branched primary amines require higher temperatures.

In the presence of hydrogen and certain precious metal and acidic catalysts, dihydridosilanes react with ammonia to form silazane oligomers (114).

$$n\ (C_2H_5)_2SiH_2 + n\ NH_3 \xrightarrow{Ru_3(CO)_{12},\ H_2} ((C_2H_5)_2SiNH)_n + n\ H_2$$

The same reaction is exploited on a commercial scale to convert higher silazanes to cyclic silazanes, but the hydride intermediate is never isolated (115).

$$(CH_3)_2SiNH)_n \longrightarrow [H(CH_3)_2SiNH_2] \xrightarrow{Pt/C,\ H_2} c\text{-}((CH_3)_2SiNH)_3$$

Halogens and Halogen Compounds. The reaction of organosilanes with halogens and halogen compounds usually proceeds in good yield through cleavage of the Si–H bond and formation of the Si–X bond. This reaction can be achieved by direct action of halogen on the organosilane or by interaction with halogen-containing organic and inorganic compounds. Reaction with fluorine, however, does not proceed satisfactorily. Cleavage not only of the Si–H bond, but also of the C–Si and C–H bonds, occurs. Fluorination of organosilanes has been achieved by reaction with inorganic fluorides, eg, AgF and SbF_3. Direct halogenation with chlorine, bromine, and iodine proceeds smoothly, however. Reactions are normally carried out in an inert solvent, eg, carbon tetrachloride, hexane, ethyl bromide, benzene, or chloroform. The reaction rate is further controlled by maintaining low reaction temperatures and controlling the rate of halogen addition. Steric requirements are not a significant factor, as evidenced by the facile iodination of tricyclohexylsilane [*1629-47-6*]. These reactions are fast and convenient and allow partial replacement of Si–H bonds (103):

$$R_3SiH + X_2 \longrightarrow R_3SiX + HX$$

$$C_6H_5SiH_3 + Br_2 \longrightarrow C_6H_5SiH_2Br + HBr$$

where R is an alkyl, a cycloalkyl, or aryl, and X_2 is Cl_2, Br_2, or I_2.

Organosilanes may react with hydrogen halides to afford organohalosilanes and hydrogen. Hydrogen fluoride is not generally used for conversion of organosilanes to organofluorosilanes. The action of hydrogen fluoride readily cleaves Si–H and Si–C bonds, forming Si–F bonds. In the presence of copper salts, however, HF fluorinates the Si–H bond without splitting the Si–C bond (100).

Using hydrogen chloride and hydrogen bromide, reactions are catalyzed by a Lewis acid, eg, $AlCl_3$, ie, where X = Cl or Br:

$$\equiv Si{-}H + HX \xrightarrow{AlX_3} \equiv Si{-}X + H_2$$

Hydrogen iodide iodinates trialkylsilanes in good yield in boiling carbon tetrachloride with no aluminum halide present (116). This can perhaps be explained on the basis that some free iodine is always present in equilibrium with hydrogen iodide.

A convenient synthesis of organochlorosilanes from organosilanes is achieved by reaction with inorganic chlorides of Hg, Pt, V, Cr, Mo, Pd, Se, Bi, Fe, Sn, Cu, and even C. The last compounds, tin tetrachloride, copper(II) chloride, and, under catalytic conditions, carbon tetrachloride (117,118), are most widely used.

$$SiH_4 + SnCl_4 \longrightarrow HSiCl_3 + SnCl_2 + HCl$$

Tin tetrachloride has been used to prepare the sterically hindered triisopropylchlorosilane [*13154-24-0*] (119). Organobromosilanes are obtained under similar conditions through reaction with cupric and mercuric bromide. These reactions are most suitable for stepwise displacement of hydrogen to form mixed hydridochlorosilanes or in systems sensitive to halogen (120). Hydrides have also been displaced using organic bromides. Heating triethylsilane and allyl bromide, propyl bromide, and methyl β-bromopropionate produces triethylbromosilane [*1112-48-7*] in 10–100% yields (121). Organochlorosilanes have been obtained from alkyl and alkenyl chlorides, eg, allyl, neopentyl, hexyl, and propyl chlorides. Unlike bromo compounds, these reactions proceed when catalyzed by small amounts of $AlCl_3$. Such reactions show potential for reduction of alkyl halides (122).

$$C_6H_{11}Cl + (C_2H_5)_3SiH \xrightarrow{AlCl_3,\ 0^\circ C} C_6H_{12} + (C_2H_5)_3SiCl$$

In the context of commercial silane production, these frequently lead to by-product reactions, as for example the production of allyldimethylsilane by a Grignard route (see GRIGNARD REACTIONS).

$$3\ CH_2{=}CHCH_2Cl + 2\ H(CH_3)_2SiCl \xrightarrow{Mg} H(CH_3)_2SiCH_2CH{=}CH_2 + HCl + 2\ MgCl_2 + CH_2{=}CHCH_2(CH_3)_2SiCH_2CH{=}CH_2$$

Even more importantly, these lead to reduction by-products in the commercial hydrosilylation reaction with allyl chloride.

$$2\ CH_2{=}CHCH_2Cl + 2\ H(CH_3)_2SiCl \xrightarrow{Pt} Cl(CH_3)_2SiCH_2CH_2CH_2Cl + CH_3CH{=}CH_2 + (CH_3)_2SiCl_2$$

Geminal polyhalides also react with organosilanes under peroxide catalysis. For example, triethylsilane affords triethylchlorosilane in good yield upon reaction with carbon tetrachloride in the presence of benzoyl peroxide (bpo) at 80°C (94,100,102).

$$(C_2H_5)_3SiH + CCl_4 \xrightarrow{\text{bpo}} (C_2H_5)_3SiCl + HCCl_3$$

Acid halides, eg, benzoyl chloride, acetyl chloride, and benzoyl bromide, have been used to prepare Si–Cl and Si–Br compounds from organosilanes. Acetyl chloride proceeds to higher yield when catalyzed by aluminum chloride.

Metals and Organometallic Compounds. There are no reports of the direct reaction of the Si–H bond in organosilanes with magnesium, zinc, mercury, aluminum, and other elements of the Groups 2(IIA), 12(IIB), and 13(IIIA) metals. The alkali metals, ie, sodium, potassium, and their alloys, react with arylsilanes in amines or ammonia to produce the arylsilyl derivatives of these metals. However, these reactions should be regarded as indirect examples of hydrogen replacement on silicon because they probably go through an amide intermediate. Direct reaction between arylsilanes and alkali metals occurs when alloys of potassium and sodium are used. The bond between the triarylsilicon moiety and the alkali metal is usually quite stable and reacts in a variety of ways (123,124). Formation of potassium triphenylsilicide [*15487-82-8*], di(triphenylsilane) [*1450-23-3*], and triphenylorganosilane occur as shown:

$$(C_6H_5)_3SiH \xrightarrow{\text{Na/K}} (C_6H_5)_3SiK + NaH$$

$$(C_6H_5)_3SiK + (C_6H_5)_3SiH \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_3$$

$$(C_6H_5)_3SiK + RX \longrightarrow (C_6H_5)_3SiR + KX$$

where R is CH_3 [*791-29-7*], C_6H_5 [*1048-08-4*], or $(CH_3)_3Si$ [*1450-18-6*], and X is Cl or Br.

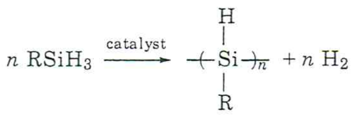
The preparation of cyclic polysilanes from dialkylchlorosilanes and lithium metal in tetrahydrofuran presumably involves a silicon–lithium intermediate (125).

$$5\text{-}7\ (CH_3)_2SiHCl \xrightarrow{\text{Li}} [(CH_3)_2Si]_{5-7} + 5\text{-}7\ HCl$$

Alkylation and arylation of organosilanes occur readily with alkyl and aryl alkali metal compounds. Yields from these reactions are good but are influenced by steric requirements on both silane and metal compounds. There is little inductive effect by the organic groups attached to silicon, as measured by the yield of products (126,127). These reactions proceed more readily in tetrahydrofuran and ethyl ether than in ligroin or petroleum ether, where R and R′ are alkyl or aryl and M is Li, Na, or K.

$$R_nSiH_{(4-n)} + (4-n)\,R'M \longrightarrow R_nSiR'_{4-n} + (4-n)\,MH$$

Dehydrogenative Coupling of Hydride Functional Silanes. The autocoupling of dihydridosilanes was first observed using Wilkinson's catalyst (128). A considerable effort has been undertaken to enhance catalyst turnover and increase the molecular weight of polysilane products (129) because the materials have commercial potential in ceramic, photoresist, and conductive polymer technology.

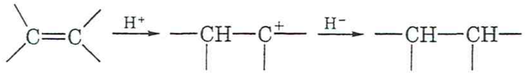


$$n\,\mathrm{RSiH_3} \xrightarrow{\text{catalyst}} \left(\underset{\mathrm{R}}{\overset{\mathrm{H}}{\mathrm{Si}}}\right)_n + n\,\mathrm{H_2}$$

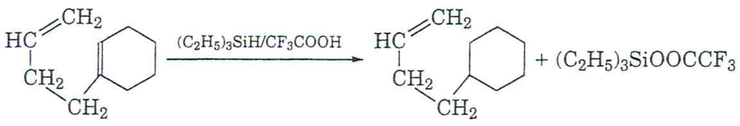
There appear to be two general classes of catalysts. Cyclopentadienyl (Cp) transition-metal catalysts of the general structure Cp_xMR_y were introduced first (130) and then highly elaborated (131). A second class of catalyst has the general structure Cl_xML_y, where M is an electron-rich metal. A typical example is $ClRh(P(C_6H_5)_3)_3$. The latter class also leads to disproportionation reactions of silanes.

Organosilanes as Reducing Agents. The two principal categories of reductive chemistry of hydridosilanes are hydrosilylation and ionic reduction. Hydrosilylation is the catalyzed addition of a hydridosilane to a multiply bonded system. This chemistry is a principal technology in silicon–carbon bond formation. Ionic reduction by silanes, a class of chemistry more properly considered within the context of organic synthesis, is the subject of detailed reviews (132).

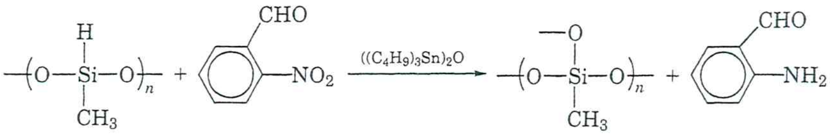
The hybridic nature of the Si–H bond is utilized to generate C–H bonds by ionic hydrogenation according to the following general mechanism, in which a hydride is transferred to a carbocation.



A catalyst, usually acid, is required to promote chemoselective and regioselective reduction under mild conditions. A variety of organosilanes can be used, but triethylsilane in the presence of trifluoroacetic acid is the most frequently reported. Use of this reagent enables reduction of alkenes to alkanes. Branched alkenes are reduced more readily than unbranched ones. Selective hydrogenation of branched dienes is also possible.



Carboxylic acids, esters, amides, nitriles, nitro groups and most aromatic nuclei are not reduced under ionic hydrogenation conditions (133). An organosiloxane, polymethylhydrosiloxane [*9004-73-3*] (PMHS), is most economically favored for large-scale reductions. Polymethylhydrosiloxane is a versatile low cost hydride transfer reagent having a hydride equivalent weight of 60. Reactions are catalyzed by Pd^0 or dibutyltinoxide. The choice of reaction conditions leads to chemoselective reduction, eg, allyl reductions in the presence of ketones and aldehydes (134–136). Esters are reduced to primary alcohols in the presence of titanium isopropoxide (137).

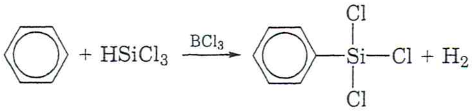


An incomplete summary of silanes as reducing agents is provided in Table 4.

Silicon–Carbon Bond-Forming Reactions. After the Rochow-Müller direct process, the hydrosilylation reaction (139),

$$RCH{=}CH_2 + HSiCl_3 \xrightarrow{Pt} RCH_2CH_2SiCl_3$$

and the Barry arylation (140,141),



account for the most significant commercial production of organosilanes.

Manufacture and Processing. *Direct Process.* The preparation of organosilanes by the direct process, first reported in 1945, is the primary

Table 4. Organosilanes as Reducing Agents[a,b]

Substrate[c]	$(C_2H_5)_3SiH$	$(C_6H_5)_3SiH$	$(C_6H_5)_2SiH_2$	PMHS[d]	Products[c]
C=C	++				CHCH
CX	+	+			CH
C=O	++	+	+	+	CH_2, CHOH, COR
ROH	+	++	+		RH
RC(=O)Cl	++				RCHO
RCOOR′	++				RCH_2OR'
$RCONR'_2$	+				$RCH_2NR'_2$
RCN	++				RCHO
RNCO	+				RNHCHO
$ArNO_2$				+	$ArNH_2$
RCH=NR′	+		+		RCH_2NHR'
P=O, PCl		+	++	+	PH

[a] Ref. 138.
[b] ++ = recommended; + = reported.
[c] X = halogen; Ar = aryl.
[d] PMHS = polymethylhydrosiloxane.

method used commercially (142,143). Organosilanes in the United States, France, Germany, Japan, and the CIS are prepared by this method, including CH_3SiHCl_2, $(CH_3)_2SiHCl$, and $C_2H_5SiHCl_2$. Those materials are utilized as polymers and reactive intermediates. The synthesis involves the reaction of alkyl halides, eg, methyl and ethyl chloride, with silicon metal or silicon alloys in a fluidized bed at 250–450°C:

$$x\,\mathrm{RX} + y\,\mathrm{Si}^0 \xrightarrow{250\text{–}450^\circ\mathrm{C}} \mathrm{R_3SiX} + \mathrm{R_2SiX_2} + \mathrm{RSiX_3} + \mathrm{RSiHX_2} + \mathrm{R_2SiHX} + \mathrm{R_4Si}$$

where R is CH_3 or C_2H_5. The yields of the desired products can be maximized by adjusting temperature, contact time, catalyst (usually copper or copper salts), and catalyst content. Methyldichlorosilane yields can also be increased by the addition of hydrogen to the methyl chloride (144,145). The use of alloys of silicon with copper or cobalt activated with copper chloride permits higher yields of $C_2H_5SiH(Cl_2)$ and $(C_2H_5)_2SiH(Cl)$ (146). Direct process still residues, which contain large amounts of methyldisilanes, can be converted to methylchlorosilanes by reaction with HCl. Yields are low, however, and the process is of little preparative value. The direct process has been extended to the production of alkoxysilanes. Reaction of silicon with ethanol or methanol containing less than 2000 ppm water produces $(C_2H_5O)_3SiH$ and $(CH_3O)_3SiH$ using cuprous chloride as the catalyst. Yields of trialkoxysilane in the instances where methyl and ethyl alcohols are employed are 86 and 91%, respectively (147,148).

$$3\,\mathrm{ROH} + \mathrm{Si}^0 \xrightarrow{\mathrm{CuCl},\ 220^\circ\mathrm{C}} \mathrm{(RO)_3SiH} + \mathrm{H_2}$$

Dialkylamino-substituted silanes have also been obtained by a similar process (149–151).

$$3\,\mathrm{(CH_3)_2NH} + \mathrm{Si}^0 \xrightarrow{250^\circ\mathrm{C}} \mathrm{((CH_3)_2N)_3SiH} + \mathrm{H_2}$$

Reduction with Metal Hydrides. Organosilanes can be synthesized most conveniently on pilot, bench, and laboratory scale by reduction of organic-substituted halo- and alkoxysilanes, using metal hydrides. As for inorganic silanes, the most effective reducing agent is lithium aluminum hydride, which offers advantages of reduction under mild conditions, high yield, and good purity of reaction products. Commonly employed solvents are ether and tetrahydrofuran. Mechanistically, the reaction is

$$4\,\mathrm{R}_n\mathrm{SiX}_{(4-n)} + (4-n)\,\mathrm{LiAlH_4} \longrightarrow 4\,\mathrm{R}_n\mathrm{SiH}_{(4-n)} + (4-n)\,\mathrm{LiX} + (4-n)\,\mathrm{AlX_3}$$

where X = F, Cl, Br, I, OR, OC_6H_5SR, or NR_2.

The versatility of lithium aluminum hydride permits synthesis of alkyl, alkenyl, and arylsilanes. Silanes containing functional groups, such as chloro, amino, and alkoxyl in the organic substituents, can also be prepared. Mixed compounds containing both SiCl and SiH cannot be prepared from organopolyhalosilanes using lithium aluminum hydride. Reduction is invariably complete.

Other reducing agents that have been used to prepare organosilanes are lithium hydride, sodium hydride, and the lithium, sodium, potassium, and aluminum borohydrides. Of these reagents, lithium hydride has been most widely used. This compound is a weaker reducing agent than lithium aluminum hydride and lower yields are generally obtained. Satisfactory reductions generally require higher temperatures, prolonged reaction times, and excess LiH. Reductions are run in high boiling solvents, eg, dioxane and dibutyl ether. This reducing agent is usually employed where there is a danger of side reactions with the aluminum halides formed as by-products from lithium aluminum hydride reductions. Similarly, magnesium hydride *[7693-27-8]*, which has been shown to reduce fluoro- and chlorosilanes, appears to have significant potential where catalytically inactive by-products are required (152). Yields of organohalosilanes and organoalkoxysilanes are listed in Table 5.

Organosilanes are also produced by reaction of organohalosilanes and organoalkoxysilanes with organometallic compounds. Sterically hindered Grignard reagents having a proton in the beta position relative to MgX are the most effective for this type of reduction (153,154). Although it was used to prepare the first isolated organosilanes, this method is of limited value. Organolithium reagents, eg, *t*-butyllithium, have also produced organohydrosilanes on reaction with organochlorosilanes and tetrahalosilanes. Tri-*t*-butylsilane *[18159-55-2]*, which cannot be prepared by other reaction methods, is synthesized successfully by this route beginning with *t*-butyltrichlorosilane *[18171-74-9]* (155). Success of this reaction is attributed to the *t*-butyllithium acting as a reducing agent.

$$t\text{-}C_4H_9SiCl_3 + 3\ t\text{-}C_4H_9Li \longrightarrow \underset{10\%}{(t\text{-}C_4H_9)_3SiH} + (CH_3)_2C{=}CH_2 + 3\ LiCl$$

$$SiF_4 + 4\ t\text{-}C_4H_9Li \longrightarrow \underset{80\%}{(t\text{-}C_4H_9)_3SiH} + (CH_3)_2C{=}CH_2 + 4\ LiF$$

Table 5. Yields of Organosilanes via Reduction with LiAlH and LiH[a]

		Yield, %	
Compound	CAS Registry Number	$LiAlH_4$	LiH
CH_3SiH_3	*[992-94-9]*	80–90	
$ClCH_2SiH_3$	*[10112-09-1]*	80	
$C_2H_5SiH_3$	*[2814-79-1]*	80–90	
$(C_2H_5)_2SiH_2$	*[542-91-6]*	80–90	66
$(C_2H_5)_3SiH$	*[617-86-7]*	80–90	20
$(C_2H_3)_3SiH$	*[2372-31-8]*	52	39
$C_2H_5(CH_2{=}CH)SiH_2$	*[18243-33-9]*		24
$C_4H_9SiH_3$	*[1600-29-9]*	80–90	
$\underline{CH_2(CH_2)_3SiH_2}$	*[288-06-2]*	47	27
$C_3H_7SiH_3$	*[13154-66-0]*	80	
$C_6H_5SiH_3$	*[694-53-1]*	86	
$(C_6H_5)_2SiH_2$	*[775-12-2]*	78	
$C_6H_{13}SiH_3$	*[1072-14-6]*		65
$(C_6H_{13})_3SiH$	*[2929-52-4]*	94	

[a] Ref. 59.

Disproportionation. Disproportionation reactions have also been used to prepare organosilanes. These reactions involve interaction of organosilanes and other silicon compounds containing organic, alkoxy, and halogen groups bound to silicon. Reactions are catalyzed by a variety of materials, including alkali metals, alkali metal alcoholates, and Lewis acids, eg, aluminum, zinc, iron, and boron halides (156). Aluminum chloride is the most active and widely used catalyst. It enables facile preparation of various alkyl and dialkylsilanes according to the following scheme:

$$R_nSiX_{(4-n)} + (4-n)\,R'_3SiH \longrightarrow R_nSiH_{(4-n)} + (4-n)\,R'_3SiX$$

where R and R′ are alkyl, X is Cl or Br, and $n = 1$ or 2.

Organochlorosilanes containing Si–H disproportionate in the presence of aluminum chloride without addition of more organosilane. Organic groups can be replaced by hydrogen (157). For example, tetraphenylsilane [*1048-08-4*] can be made from phenylmethylsilane [*766-08-5*].

$$C_6H_5(CH_3)SiH_2 \xrightarrow{AlCl_3} (C_6H_5)_4Si + CH_3SiH_3 + (CH_3)_2SiH_2$$

Similar disproportionation reactions are catalyzed by organic catalysts, eg, adiponitrile, pyridine, and dimethylacetamide. Methods for the redistribution of methylhydridosilane mixtures from the direct process have been developed to enhance the yield of dimethylchlorosilane (158).

Grignard Reagents. Grignard reagents are utilized to transfer organic groups to silicon. In contrast to more basic organometallic compounds such as alkyl lithium reagents, cleavage of the Si–H bond does not occur. However, in tetrahydrofuran at elevated temperature and in the case of polyhydridosilanes in diethyl ether, the hydride can be displaced (159).

$$C_6H_5SiH_3 + C_6H_5MgBr \longrightarrow (C_6H_5)_2SiH_2$$

In general, Grignard reagents are useful in the synthesis of mixed hydridochlorosilanes because these reagents can effect stepwise substitution of the halogen, eg,

$$HSiCl_3 + 2\ i\text{-}C_3H_7MgCl \longrightarrow (i\text{-}C_3H_7)_2SiHCl + 2\ MgCl_2$$

Addition to Olefins. Organohydrosilanes can also be prepared by addition of halosilanes and organosilanes containing multiple Si–H bonds to olefins. These reactions are catalyzed by platinum, platinum salts, peroxides, ultraviolet light, or ionizing radiation.

$$H_2SiCl_2 + RCH{=}CH_2 \xrightarrow{H_2PtCl_6} RCH_2CH_2SiHCl_2$$

$$RSiH_3 + R'CH{=}CH_2 \longrightarrow R'CH_2CH_2SiH_2(R)$$

Economic Aspects. The only organic silane that is produced on a large scale is methyldichlorosilane. It is a by-product in the direct process for methylchlorosilane production, representing 0.5–3.0% of the overall output. An estimate of worldwide methyldichlorosilane production for 1995 is in the 3,000–20,000 t/yr range. Because there is no distinct process technology operated for the production of methyldichlorosilane, its availability varies in accord with both overall methylchlorosilane production and its demand in silicon production. Domestic producers of methyldichlorosilane are General Electric and Dow Corning. Pricing is $4–$6/kg. Polymethylhydrosiloxane, the polymeric derivative of methyldichlorosilane, is also available from these suppliers. Prices are $7–$10/kg. Other specialty organic silicon hydrides bear much higher pricing. The most significant products are dimethylchlorosilane, tetramethyldisiloxane, tetramethylcyclotetrasiloxane, triethylsilane, diethylmethylsilane, methylsilane, diphenylsilane, and various hydride-containing silicone copolymers. The cost of these materials varies between $35–$400/kg. Producers of these materials are Dow Corning, General Electric, Gelest, Harris Specialty Chemicals, and Hüls.

Halosilanes

Only three inorganic halosilanes are produced on a large industrial scale, ie, tetrachlorosilane [*10026-04-7*], tetrafluorosilane [*7783-61-1*], and trichlorosilane.

Physical Properties. The bonds between silicon and halogen are predominantly covalent in character, exhibiting bond energies consistent with good thermal stability. The bond energy of Si–F is >550 kJ/mol (131 kcal/mol) making Si–F one of the strongest covalent bonds. The extreme polarization of the bonds, however, results in materials that are extremely sensitive to nucleophilic attack. All halosilanes, for example, fume in air from the presence of moisture liberating the hydrogen halide. These compounds are thus extremely corrosive materials in open environments. The parent halogen is soluble in tetrahalosilanes. For example, chlorine is soluble to the extent of 1% in tetrachlorosilane. Physical properties for halosilanes of commercial significance are given in Table 6.

Chemical Properties. *Oxidation.* Silicon halides are stable to oxygen at room temperature, but react at elevated temperatures to form, in the case of

Table 6. Properties of Halosilanes

Property	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
CAS Registry Number	[*7783-61-1*]	[*10026-04-7*]	[*7789-66-4*]	[*13465-84-4*]
mp, °C	−90.3	−70.4	5.4	120.5
bp, °C	−95.7 sub	57	155	287.5
vapor pressure,[a] kPa[b]	68.6_{-100}	25.9_{20}	0.24_{0}	
H_{vap}, kJ/mol[c]	18.7	28.7	37.9	26.6
bond energy, kJ/mol[c]	565	381	310	244
critical temperature, °C	−14.15	233.6	383	
critical pressure, kPa[d]	37.3	36.8		
density,[a] g/cm^3	1.598_{-80}	1.4707	2.771	4.2

[a] The subscripted numbers are temperature in °C.
[b] To convert kPa to mm Hg, multiply by 7.5.
[c] To convert J to cal, divide by 4.184.
[d] To convert kPa to psi, multiply by 0.145.

chlorides, oxychlorosilanes. Tetrachlorosilane reacts at 950–970°C to form hexachlorodisiloxane (160,161).

$$2\ SiCl_4 + 1/2\ O_2 \longrightarrow Cl_3SiOSiCl_3 + Cl_2$$

Tetrabromosilane reacts with oxygen at 670–695°C to form polybromosiloxanes and at 900°C to form silicon dioxide.

Reaction with Silicon. At elevated temperature (1000°C) tetrachlorosilane attacks pure crystalline silicon to form a mixture of higher chlorosilanes including Si_2Cl_6, Si_3Cl_8, and Si_4Cl_{10}. Under vacuum at 1000°C, silicon tetrafluoride reacts with silicon to form difluorosilene (162), which, using a rapid thermal quench below −60°C, forms polydifluorosilane, a wax-like polymer. The polydifluorosilane reverts to silicon and silicon tetrafluoride at moderate temperature.

$$Si^0 + SiF_4 \xrightarrow{1000^\circ C} SiF_2 \xrightarrow{-76^\circ C} (SiF_2)_n \xrightarrow{0^\circ C} n/2\ Si^0 + n/2\ SiF_4$$

In principle, this technology represents a possible alternative for closed-loop purification of silicon, but transport and purification efficiencies are not sufficient to be enabling (163).

Protic Materials. The hydrolytic behavior of tetrachlorosilane was described by Mendeleyev (164), and is summarized herein. Orthosilicic acid formed by the action of water on tetrachlorosilane:

> does not remain in that form, but loses part of its water with extraordinary ease... The hydrate formed is not actually obtained with as high a water content as corresponds to $Si(OH)_4$. . .In the hydrates $n SiO_2 \cdot m H_2O$, m becomes smaller than n... This loss of water proceeds, in the natural hydrates, in perfect sequence, and so to speak, imperceptibly, until n becomes incomparably greater than m.... The structure of silica is polymeric, complex, instead of simple, as it is expressed by its empirical formula.

The heat of reaction of tetrachlorosilane with an excess of water is 290.0 kJ/mol (69.3 kcal/mol). The reaction of tetrafluorosilane with excess water contrasts with the other halosilanes, because it leads to formation of hexafluorosilicic acid and a hydrous silica.

$$2\ SiF_4 + 2\ H_2O \longrightarrow H_2SiF_6 + SiO_2 + 2\ HF$$

The reaction of halosilanes with alcohols proceeds analogously. Difunctional amines react with tetrahalosilanes to yield tetrakis(dialkylamino)silanes.

$$8\ (CH_3)_2NH + SiCl_4 \longrightarrow Si(N(CH_3)_2)_4 + 4\ (CH_3)_2NH_2^+ + 4\ Cl^-$$

The analogous reaction with ammonia leads ultimately to silicon nitride. In the past, hydrocarbon soluble fractions of the ammonolysis were incorrectly referred to as silicon diimide. This improper designation occasionally persists as of the mid-1990s.

Reduction/Reaction with Hydrogen. Tetrafluorosilane reacts with hydrogen only above 2000°C. Tetrachlorosilane can be reduced by hydrogen at 1200°C. Tetraiodosilane can be reduced to silicon at 1000°C (165). Reduction of tetrafluorosilane with potassium metal to silicon was the first method used to prepare silicon (see SILICON AND SILICON ALLOYS). The reduction of silicon tetrachloride by zinc metal led to the first semiconductor-grade silicon (166,167).

$$K_2SiF_6 + 4\ K \longrightarrow 6\ KF + Si$$

$$SiCl_4 + 2\ Zn \longrightarrow 2\ ZnCl_2 + Si$$

Sodium and magnesium do not react with tetrachlorosilane at room temperature, but do so at elevated temperatures and in the presence of polar aprotic solvents at moderately elevated temperatures. The Wurtz-Fittig coupling of organosilanes to form disilanes (168) and polysilanes (169) is usually accomplished using molten sodium in toluene or xylene.

$$2\ R_3SiCl + 2\ Na \longrightarrow R_3SiSiR_3 + 2\ NaCl$$

$$n\ R_2SiCl_2 + 2n\ Na \longrightarrow (R_2Si)_n + 2n\ NaCl$$

Reduction of halosilanes with hydrides leads to the formation of hydride functional silanes and is considered in that section.

Reaction With Hydrogen and Oxygen. The combustion of silicon tetrachloride in a hydrogen oxygen (air) flame is an important technology leading to fumed or pyrogenic silica.

$$SiCl_4 + 2\ H_2 + O_2 \longrightarrow SiO_2 + 4\ HCl$$

The mechanism for the formation of silica is complex because oxidation, reduction, and hydrolysis pathways are all possible.

Organometallics. Halosilanes undergo substitution reactions with alkali metal organics, Grignard reagents, and alkylaluminums. These reactions lead to carbon–silicon bond formation.

$$RMgCl + R'SiCl_3 \longrightarrow RR'SiCl_2 + 2\ MgCl_2$$

$$4\ RLi + SiCl_4 \longrightarrow R_4Si + 4\ LiCl$$

$$AlR_3 + 3\ R'_3SiCl \longrightarrow 3\ RR'_3Si + AlCl_3$$

Manufacturing. Tetrachlorosilane can be manufactured directly by the reaction of chlorine on silicon metal or ferrosilicon at 500°C or silicon carbide (170).

$$Si + 2\ Cl_2 \longrightarrow SiCl_4$$

$$SiC + 2\ Cl_2 \longrightarrow SiCl_4 + C$$

The production of silicon tetrachloride by these methods was abandoned worldwide in the early 1980s. Industrial tetrachlorosilane derives from two processes associated with trichlorosilane, the direct reaction of hydrogen chloride on silicon primarily produced as an intermediate for fumed silica production, and as a by-product in the disproportionation reaction of trichlorosilane to silane utilized in microelectronics. Substantial quantities of tetrachlorosilane are produced as a by-product in the production of zirconium tetrachloride, but this source has decreased in the 1990s owing to reduction in demand for zirconium in nuclear facilities (see NUCLEAR REACTORS). The price of tetrachlorosilane varies between \$1/kg and \$25/kg, depending on grade and container.

Tetrabromosilane and tetraiodosilane are produced by the direct reaction between silicon and bromine at 500°C and silicon and iodine at 600°C. There is no commercial production of these materials as of mid-1996.

Although tetrafluorosilane can be readily produced by the action of hydrogen fluoride on silica, its production is a by-product of HF production by the reaction of fluorospar and sulfuric acid and as a by-product from phosphate fertilizer production by the treatment of fluoroapatite with sulfuric acid (171). The most significant U.S. production is by IMC-Agrico at Uncle Sam, Louisiana.

$$4\ Ca_5(PO_4)_3F + 4\ H_2SO_4 + SiO_2 \longrightarrow 4\ Ca_5(PO_4)_3HSO_4 + 2\ H_2O + SiF_4$$

A small by-product stream is also realized in Europe from glass-etching by HF. Laboratory-scale production is readily accomplished by exchange between metal fluorides and chlorosilanes (172).

$$SiCl_4 + 2\ PbF_2 \longrightarrow SiF_4 + PbCl_2$$

$$n\text{-}(C_4H_9)_3SnF + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiF + n\text{-}(C_4H_9)_3SnCl$$

Halosilanes can also be produced by displacement of amines with a hydrogen halide (173).

$$SiH(NHC_6H_5)_3 + 6\ HI \longrightarrow SiHI_3 + 3\ (C_6H_5NH_3)I$$

Mixed halosilanes are produced by warming a mixture of tetrahydrosilanes.

$$SiCl_4 + SiBr_4 \longrightarrow 2\ SiCl_2Br_2$$

Alternatively, they can be prepared by the reaction of hydridohalosilanes with halogen (174).

Health and Safety. Halosilane vapors react with moist air to produce the respective hydrohalogen acid mist. Federal standards have not set exposure to halosilanes, but it is generally believed that there is no serious risk if vapor concentrations are maintained below a level that produces an irritating concentration of acid mist. The exposure threshold limit value (TLV) for HCl is 5 ppm, expressed as a ceiling limit. Because most people experience odor and irritation at or below 5 ppm, HCl is considered to have good warning properties.

Uses. The overwhelming use for tetrachlorosilane is in the production of fumed silica. The tetrachlorosilane used as a raw material for fumed silica is of generally low purity (80–95%) and typically contains some trichlorosilane as well as methyltrichlorosilane (introduced from other manufacturing sources). Tetrachlorosilane utilized as an intermediate for tetraalkoxysilanes is typically >98% pure. Extremely high purity grades of >99.99% having controlled metal contents below 1 ppm are utilized in the production of silica fiber optic waveguides. Tetrafluorosilane is primarily an intermediate for the production of fluorosilicic acid, used as a sterilant for glass bottles, and in electroplating applications (see FLUORINE COMPOUNDS, INORGANIC). Commercial production of silane from tetrafluorosilane accounts for about 5000 t/yr at the MEMC facility located at Pasadena, Texas.

BIBLIOGRAPHY

"Silicon Compounds" in *ECT* 1st ed., Vol. 12, pp. 365–392, by E. G. Rochow, Harvard University; "Silicon Compounds, Silanes" in *ECT* 2nd ed., pp. 172–215, by C. H. Van Dyke, Carnegie-Mellon University; in *ECT* 3rd ed., Vol. 20, pp. 887–911, by B. Arkles and W. R. Peterson, Jr., Petrarch Systems, Inc.

1. P. E. Verkade, *Chem. Weekbl.* **47**, 309 (1951).
2. V. Bazant, V. Chvalovsky, and J. Rathovsky, *Organosilicon Compounds*, Vol. 1, Academic Press, Inc., New York, 1965.
3. A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N.Y., 1933.
4. Y. Yamaguchi, *Mol. Eng.* **3**, 301–309 (1994).
5. R. West and T. Barton, *Chem. Ed.* **57**, 165, 364 (1980).
6. R. West and J. Michl, *Science* **214**, 1344 (1980).
7. A. G. Brook, F. Abdesaken, and B. Gutekunst, in *Proceedings of the XV Silicon Symposium*, Mar. 1981, Duke University, Durham, N.C.; A. G. Brook and co-workers, *J. Am. Chem. Soc.* **104**, 5667 (1982).
8. R. Borreson and co-workers, *Solid State Technol.* **21**, 43 (1978).
9. E. Rochow in *Comprehensive Inorganic Chemistry*, Vol. 1, Pergamon Press, Inc., Elmsford, N.Y., 1973, p. 1353.
10. R. Walsh, *Accounts Chem. Res.* **14**, 246 (1981).
11. D. G. White and E. G. Rochow, *J. Am. Chem. Soc.* **76**, 3897 (1954).
12. S. N. Borisov, M. G. Voronkov, and B. N. Dolgov, *Dokl. Akad. Nauk SSSR* **93**, 114 (1957).
13. Ger. Offen. 1,102,117 (May 18, 1954) (to Siemens-Haska AG).
14. W. Claassen and J. Bloehm, *Phillips J. Res.* **36**(2), 122 (1981).
15. D. J. DeLong, *Solid State Technol.* **15**(10), 43 (Aug. 19, 1972).
16. U.S. Pat. 3,400,660 (Aug. 19, 1975), H. Bradley (to Union Carbide).
17. W. R. Runyan, *Silicon Semiconductor Technology*, McGraw-Hill Book Co., Inc., New York, 1965.
18. U.S. Pat. 4,318,942, L. M. Woerner and E. B. Moore (to J. C. Schumacher Co.).
19. B. A. Scott, D. R. Estes, and D. B. Beach in J. Y. Corey, E. R. Corey, and P. P. Gaspar, eds., *Silicon Chemistry*, Ellis Horwood/Wiley, Chichester, U.K., 1988, p. 369.
20. S. A. Arutyunyan and E. N. Sarkisyan, *Arm. Khim. Zh.* **34**(1), 3 (1981).
21. T. G. Mkryan, E. N. Sarkisyan, and S. A. Arutyunyan, *Arm. Khim. Zh.* **34**(1), 3 (1981).
22. U.S. Pat. 4,239,811 (Dec. 16, 1980), B. M. Kiemlage (to IBM).
23. B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.* **81**, 5109 (1959).
24. J. S. Peake and W. H. Nebergall, Y. T. Chen, *J. Am. Chem. Soc.* **74**, 1526 (1952).
25. L. G. L. Ward and A. G. MacDiarmid, *J. Am. Chem. Soc.* **82**, 2151 (1960).

26. M. Aberdini, C. H. VanDyke, and A. G. MacDiarmid, *J. Inorg. Nuc. Chem.* **28**, 1373 (1966).
27. S. Cradock, G. A. Gibbon, and C. H. Van Dyke, *Inorg. Chem.*, **6**, 1751 (1967).
28. E. Amberger and E. Mulhofer, *J. Organomet. Chem.*, **12**, 557 (1968).
29. E. Amberger, R. Romer, and A. Layer, *J. Organomet. Chem.* **12**, 417 (1968).
30. M. A. Ring and D. M. Ritter, *J. Am. Chem. Soc.* **83**, 802 (1961).
31. S. P. Garrity and M. A. Ring, *Inorg. Nucl. Chem. Lett.* **4**, 77 (1968).
32. D. S. Rustad and W. L. Jolly, *Inorg. Chem.* **6**, 1986 (1967).
33. R. C. Kennedy, L. P. Freeman, A. P. Fox, M. A. Ring, *J. Inorg. Nucl. Chem.* **28**, 1373 (1966).
34. J. A. Morrison and M. A. Ring, *Inorg. Chem.* **6**, 100 (1967).
35. E. A. Groschwitz, W. M. Ingle, and M. A. Ring, *J. Organomet. Chem.* **9**, 1373 (1966).
36. W. J. Boldue and M. A. Ring, *J. Organomet. Chem.* **9**, 421 (1967).
37. R. Schwarz and F. Heinrich, *Z. Anorg. Chem.* **221**, 227 (1935).
38. S. D. Gokhale and W. L. Jolly, *Inorg. Chem.* **3**, 946 (1964).
39. E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 432 (1962).
40. S. D. Gokhale, J. E. Drake, and W. L. Jolly, *J. Inorg. Nuc. Chem.* **27**, 1911 (1965).
41. E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.* **2**, 215 (1963).
42. S. D. Gokhale and W. L. Jolly, *Inorg. Chem.* **3**, 1141 (1964).
43. S. D. Gokhale and W. L. Jolly, *Inorg. Chem.* **4**, 596 (1965).
44. M. Abedini and A. G. MacDiarmid, *Inorg. Chem.* **5**, 2040 (1966).
45. A. A. Kirpichinikova and co-workers, *Zh. Vses. Khim. Obshchest.* **22**, 465 (1977).
46. B. Scott and M. Brodsky, *Bull. Am. Phys. Soc.* **25**, 299 (1980).
47. T. Hiiao and co-workers, *J. Appl. Phys.* **52**(12), 7453 (1981).
48. M. J. Loboda and J. A. Seifferly, *J. Mater. Res.* **11**, 391 (1996).
49. H. J. Emeleus and K. Stewart, *Trans. Farady Soc.* **32**, 1677 (1936).
50. N. Nihi and G. J. Mains, *J. Phys. Chem.* **68**, 304 (1964).
51. B. Reimann and R. Potzinger, *Ber. Bunsenges. Phys. Chem.* **80**, 565 (1976).
52. G. A. Gobbon, T. Rosseau, C. H. VanDyke, and G. J. Mains, *Inorg. Chem.* **5**, 114 (1966).
53. W. C. Johnson and J. R. Hogness, *J. Am. Chem. Soc.* **56**, 1252 (1934).
54. W. C. Johnson and S. Isenberg, *J. Am. Chem. Soc.* **57**, 1359 (1935).
55. F. Feher and W. Tromm, *Z. Anorg. Allgem., Chem.* **282**, 29 (1955).
56. R. Schwarz and E. Konrad, *Ber.* **55**, 3242 (1952); *Z. Anorg. Allg. Chem.* **215**, 288 (1938).
57. G. Scott and D. Naumann, *Z. Anorg. Allg. Chem.* **291**, 103, 112 (1957).
58. Y. Ono, Y. Sndoda, and T. Keii, *J. Am. Chem. Soc.* **97**, 5284 (1975).
59. A. D. Petrov, B. F. Mironov, V. A. Ponomorenko, and R. A. Cherpyshev, *Synthesis of Organosilicon Monomers*, Consultants Bureau, New York, 1964.
60. U.S. Pat. 4,927,616, E. M. Marlett (to Ethyl Corp.).
61. Eur. Par. Appl. EP 87-116243, E. M. Marlett and F. W. Frey (to Ethyl).
62. Eur. Pat. Appl. EP 89-14115, J. E. Boone, D. M. Richards, and J. Bossier (to Ethyl Corp.).
63. W. Sundermeyer and O. Glemser, *Angew. Chem.* **70**, 625 (1958).
64. O. Glemser and W. Lohman, *Z. Anorg. Allg. Chem.* **275**, 260 (1964).
65. U.S. Pat. 4,051,136 (Aug. 9, 1977), R. E. Franklin, W. A. Francis, and G. Tanaron (to Union Carbide).
66. Can. Pat. 2,121,931 (1994), K. Klein and co-workers; Germ. Offen. 43 13 130.1-44 (1993).
67. Ger. Offen. DE 3409172 W. Porcham (to Swarovski).
68. D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1545 (1945).
69. U.S. Pat. 2,458,703 (Jan. 11, 1949), D. B. Hatcher (to Libby-Owens-Ford).
70. D. L. Bailey, personal communication. This work was performed by E. O. Brimm at Union Carbide in the 1940s.

71. J. Y. P. Mui, Low Cost Solar Array Project, NASA/JPL Contract 954334, Union Carbide Corp., June 1979.
72. J. Y. P. Mui and D. Seyferth, *Investigation of the Hydrogenation of Silicon Tetrachloride*, DOE/JPL/955382-79/8, Department of Energy, Washington, D.C., 1981.
73. Ger. Offen. DE 3341340 A1 (May 23, 1985), A. Schnegg and R. Rurlaender.
74. Ger. DE3809784 C1 (July 13, 1988), K. Ruff.
75. PCT Int. Appl. WO 81-03168 (Nov. 12, 1981), K. R. Sarma and M. J. Rice, Jr. (to Motorola).
76. U.S. Pat. 2,627,451 (Feb. 3, 1953); U.S. Pat. 2,735,861, C. E. Erikson and G. H. Wagner (to Union Carbide).
77. U.S. Pat. 2,745,860 (May 15, 1956), D. L. Bailey (to Union Carbide).
78. H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).
79. U.S. Pat. 2,732,282 (Jan. 24, 1956), D. L. Bailey, G. H. Wagner, and P. W. Shafer (to Union Carbide).
80. Ger. Offen. 2,550,076 (1976), G. Marin.
81. U.S. Pat. 3,968,199 (July 6, 1976), C. J. Bakey (to Union Carbide).
82. E. Helfrich and J. Hausen, *Ber.* **57B**, 795 (1924).
83. W. C. Breneman, in K. M. Lewis and D. G. Rethwish, eds., *Catalyzed Direct Reactions of Silicon*, Elsevier Science, Inc., New York, 1993, p. 441.
84. Jpn. Kokai Tokkyo Koho JP 63/170210 A2 [88/170210] (July 14, 1988), H. Yamada, H. Ogawa, T. Hosokawa, and M. Tachikawa.
85. D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, National Bureau of Standards, Washington, D.C., 1971.
86. J. A. Cervantes and co-workers, in Ref. 83, p. 459.
87. W. C. Schumb, *Inorg. Synth.* **1**, 38 (1939).
88. L. G. L. Ward, *Inorg. Synth.* **11**, 159 (1968).
89. G. Tamizhmani, M. Cocivera, R. T. Oakley, and P. Del Bel Belluz, *Chem. Mat.* **2**, 473 (1990).
90. C. J. Wilkins, *J. Chem. Soc.*, 3409 (1953).
91. H. Brederman, T. J. Thor, and H. J. Waterman, *Research* **7**, 829 (1959).
92. D. J. Hurd, *J. Am. Chem. Soc.* **67**, 1545 (1945).
93. H. L. Jackson, F. D. Marsh, and E. L. Muetterties, *Inorg. Chem.* **2**, 43 (1963).
94. N. J. Archer, R. N. Hazeldine, and R. V. Parish, *J. Orgmet. Chem.* **81**, 335 (1974).
95. K. Sharp, A. Arvidson, and T. C. Elvey, *J. Electrochem. Soc.* **129**, 2346 (1982).
96. *Registry of Toxic Effects of Chemical Substances*, National Institute of Occupational Safety and Health, (NIOSH), Washington, D.C., 1976.
97. F. Fortes, *Ind. Eng. Chem.* **46**, 2325 (1954).
98. R. R. McGregor, *Silicones and Their Uses*, McGraw-Hill Book Co., Inc., New York, 1954.
99. W. Noll, *Chemistry and Technology of Silicones*, Academic Press, Inc., New York, 1968.
100. Y. Nagai, *Org. Prep. Proc. Int.* **12**, 15 (1980).
101. B. Arkles, *Silicon, Germanium, Tin, and Lead Compounds: A Survey of Properties and Chemistry*, Gelest Inc., Tullytown, Pa., 1995.
102. H. J. Emeleus and K. Stewart, *Nature*, 397 (1935).
103. C. Eaborn, *Organosilicon Compounds*, Buttersworth Scientific Publications, Lander, U.K., 1960.
104. J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 4023 (1955).
105. L. H. Sommer, O. Bennet, P. G. Campbell, and D. R. Weyenberg, *J. Am. Chem. Soc.* **79**, 3295 (1957).
106. J. E. Baines and C. Eaborn, *J. Chem. Soc.*, 7436 (1956).
107. E. Lukevics and M. Dzintara, *J. Organomet. Chem.* **295**, 265 (1985).
108. W. S. Miller, J. S. Peake, and W. H. Nebergall, *J. Am. Chem. Soc.* **79**, 5604 (1957).

109. L. H. Sommer and C. L. Frye, *J. Am. Chem. Soc.* **79**, 3295 (1957).
110. C. L. Lee, R. G. Niemi, and K. M. Kelley, *J. Cell. Plast.* **13**, 62 (1977).
111. C. Eaborn, *J. Chem. Soc.*, 23517 (1955).
112. U.S. Pat. 2,658,908 (Nov. 10, 1953), S. Nitzsche and E. Pirson (to Wacker).
113. B. N. Dolgov, N. P. Kharitonov, and M. G. Voronkov, *Zh. Obsch. Khim.* **24**, 678 (1954).
114. U.S. Pat. 4,612,383 (1986); U.S. Pat. 4,788,309 (1988), R. Laine and Y. Blum (to SRI).
115. U.S. Pat. 4,577,039 (Mar. 18, 1986), B. Arkles and B. Hamon (to Petrarch Systems).
116. M. G. Voronkov and Yu I. Khudobin, *Izv. Akad. Nauk SSSR*, 805 (1956).
117. Y. Nagai, H. Matsumoto, T. Yagihara, and K. Moxishita, *Kogyo Kagaku Zasshi* **71**, 1112 (1968).
118. R. Boukherroub, C. Chatgilialoglu, and G. Manuel, *Organometallics* **15**, 1508 (1996).
119. R. G. Cunico and L. Bedell, *J. Org. Chem.* **45**, 4797 (1980).
120. H. H. Anderson, *J. Am. Chem. Soc.* **69**, 2600 (1958).
121. H. Westermark, *Acta Chem. Scand.* **8**, 1086 (1954).
122. M. P. Doyle and C. T. West, *J. Org. Chem.* **41**, 1393 (1976).
123. R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.* **74**, 648 (1952).
124. R. A. Benkeser and D. J. Foster, *J. Am. Chem. Soc.* **74**, 4200 (1952).
125. U.S. Pat. 4,276,424 (June 30, 1981), B. Arkles and W. R. Peterson, Jr. (to Petrarch Systems).
126. R. A. Benkeser and F. J. Riel, *J. Am. Chem. Soc.* **73**, 3472 (1951).
127. H. Gilman and J. J. Goodman, *J. Org. Chem.* **22**, 45 (1957).
128. I. Ojima, S.-I. Inabe, T. Kogure, and Y. Nagai, *J. Organomet. Chem.* **55**, C7 (1973).
129. J. Y. Corey, *Adv. Silicon Chem.* **1**, 327 (1991).
130. C. Aitken, J. Harrod, and E. Samuel, *J. Am. Chem. Soc.* **108**, 4059 (1986).
131. T. D. Tilley, *Acc. Chem. Res.* **26**, 22 (1993).
132. W. P. Weber, *Silicon Reagents for Organic Synthesis*, Springer-Verlag, New York, 1983, p. 273.
133. D. N. Kursanov, Z. N. Parnes, and N. M. Loim, *Synthesis*, 633 (1974).
134. J. Lipowitz and co-workers, *J. Org. Chem.* **38**, 162 (1973).
135. E. Keinan and co-workers, *Israel. J. Chem.* **24**, 82 (1984); *J. Org. Chem.* **48**, 3545 (1983).
136. T. Mukaiyama and co-workers, *Chem. Lett.*, 1727 (1983).
137. M. Reding and co-workers, *J. Org. Chem.* **60**, 7884 (1995).
138. *Hydrosilanes as Reducing Agents*, Technical Bulletin, Chisso Corp., Tokyo, Japan, 1980.
139. B. Marciniec, *Comprehensive Handbook of Hydrosilylation*, Pergamon Press, New York, 1992.
140. U.S. Pat. 2,494,560 (1950); U.S. Pat. 2,626,929 (1953), A. J. Barry (to Dow Corning).
141. A. J. Barry, J. W. Gilkey, D. E. Hook, *Metal-Organic Compounds*, ACS Advances in Chemistry, Vol. 23, American Chemical Society, Washington, D.C., 1959, p. 246.
142. E. G. Rochow, *J. Am. Chem. Soc.* **67**, 693 (1945).
143. U.S. Pat. 2,380,995 (Aug. 7, 1945), E. G. Rochow (to General Electric).
144. U.S. Pat. 2,380,998 (Aug. 7, 1945), M. M. Sprung and W. F. Gilliam (to General Electric).
145. U.S. Pat. 4,973,725 (Nov. 27, 1990), K. Lewis, J. Larnard, and B. Kanner (to Union Carbide).
146. Brit. Pat. 681,387 (1952) R. Decker and H. Holz.
147. Jpn. Kokai Tokkyo Koho 80 28,928 (Apr. 6, 1980), S. Suzuki, T. Imaki, and T. Yamamura (to Mitsubishi).
148. Jpn. Kokai Tokkyo Koho 80 28,929 (Apr. 6, 1980), S. Suzuki, T. Imaki, and T. Yamamura (to Mitsubishi).
149. B. Kanner, W. B. Herdle, J. M. Quirk, in J. Y. Corey, E. R. Corey, and P. P. Gaspar, eds., *Silicon Chemistry*, Ellis Horwood/Wiley, Chichester, U.K., 1988, p. 123.

150. U.S. Pat. 4,255,348 (Mar. 10, 1981), B. Kanner and W. B. Herdle (to Union Carbide).
151. K. M. Lewis, B. K. C. Tan, T. E. Childress, and D. McLeod, in K. M. Lewis and D. G. Rethwisc, eds., *Catalyzed Direct Reactions of Silicon*, Elsevier Science, Inc., New York, 1993, p. 559.
152. Can. Pat. 2,121,931 (1994); Ger. Offen. P 43 13 130.1–44 (1993), K. Klein and co-workers.
153. M. C. Harvey, W. H. Nebergall, and J. S. Peake, *J. Am. Chem. Soc.* **79**, 7762 (1957).
154. M. B. Lacout-Loustalet, J. P. Dupin, F. Metras, and J. Valade, *J. Organomet. Chem.* **31**, 337 (1971).
155. E. M. Dexheimer and L. Spialter, *Tetrahedron Lett.*, 1771 (1975).
156. U.S. Pat. 2,745,860 (May 15, 1956), D. L. Bailey (to Union Carbide).
157. J. L. Speier and R. E. Zimmerman, *J. Am. Chem. Soc.* **77**, 6395 (1955).
158. U.S. Pat. 5,493,043 (Feb. 20, 1996), O. W. Marko (to Dow Corning).
159. H. Gilman and E. A. Zeuch, *J. Am. Chem. Soc.* **79**, 4560 (1957).
160. A. D. Gaunt, H. Mackle, and L. E. Sutton, *Trans. Faraday Soc.* **47**, 943 (1954).
161. B. A. Grigor and C. J. Wilkins, *Inorg. Syn.* **7**, 23 (1963).
162. P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.* **87**, 2824 (1965).
163. W. Ingle, R. Rosler, S. Thompson, and R. Chaney, *Semiconductor-Grade Solar Silicon Purification Project*, NASA-CR-158868, Rept.-2257/12, Cape Canavral, Fla., 1979.
164. D. I. Mendeleyev, *Principles of Chemistry*, St. Petersburg, CIS, 1871.
165. U.S. Pat. 3,006,737 (Oct. 31, 1961), G. H. Moats, B. Rubin, and W. B. Jackson.
166. D. W. Lyon, C. M. Olso, and E. D. Lewis, *J. Electrochem. Soc.* **96**, 359 (1949).
167. U.S. Pat. 2,773,745 (Dec. 11, 1956), K. Butler and C. M. Olson (to DuPont).
168. H. Gilman and T. C. Wu, *J. Am. Chem. Soc.* **75**, 3762 (1953).
169. R. D. Miller and co-workers, in L. F. Tompson and C. G. Wilson, eds., *Materials for Microlithography*, ACS Symposium Series 266, American Chemical Society, Washington, D.C., 1984, p. 293.
170. K. A. Andrianov, *Dokl. Akad. Nauk SSSR* **28**, 66 (1940).
171. U.S. Pat. 2,833,628 (1958), Molstad (to W. R. Grace).
172. D. K. Padma, B. S. Suresh, and A. R. Vasudevamurthy, *J. Fluoro. Chem.* **14**, 327 (1979).
173. E. Hengge and F. Höfler, *Z. Naturforsch.* **26a**, 768 (1971).
174. R. West and E. G. Rochow, *Inorg. Syn.* **4**, 41 (1953).

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Gelest, Inc.