Silicon Compounds, Inorganic

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1. Introduction

A number of inorganic compounds of silicon have gone through a remarkable development in the past years, prompted chiefly by the electronics industry and efforts of environmental protection. A tremendous growth of knowledge in physics and chemistry, as well as technical applications, has taken place around certain hydrides, halides, and oxides of silicon. Progress in solid state physics, the material sciences, and an increase in unwanted byproduct formation in the course of production of large-scale silicon compounds have necessitated that one look anew at process engineering. Energy consideration is of direct bearing in this technology since most processes in technical silicon chemistry require high temperature.

Environmental protection and elimination of safety hazards during production and handling of the above silicon products has been the concern of all ever since these compounds became large-scale technical products. The moisture sensitivity of the halides, the oxygen sensitivity of the hydrides, and pyrophoric properties of some of the distillation residues from reaction steps involving elementary silicon or silicides have caused waste problems and particular emphasis on process safety. Greater flexibility of chemical transformation within at least partly recycling procedures have both decreased waste and enhanced safety. Making use of byproducts has been extended to comprise substances of the system C – Si – O – Hal, its phases and transformations. Alongside product making, byproduct formation, its investigation, suppression, or transformation into useful silicon derivatives has been to some degree due to efforts of environment protection.

With respect to use, many new applications were found for special inorganic silicon compounds,

optical fibers and solar cells being example for both surface as well as bulk properties.

Surface treatments, not necessarily confined to protective coatings but including migration beneath the surface, are carried out to increase hardness, thermal stability, to influence cohesion and adhesion, to resist oxidation, erosion, corrosion, and to enhance reflexion, etc. Interfaces and multilayer cermets and plastics need silicon in various bonding states as intermediates during production or permanently in a final product.

2. Silicon Hydrides

Silicon hydrides are sensitive to hydrolysis and oxidation; volatile higher silanes are spontaneously flammable [1–3]. The first five members of the homologous series Si_nH_{2n+2} are known in the pure state (see Table 1).

All silanes are decomposed in reactions of the type:

$$SiH_4 \nearrow^{2\,O_2} SiO_2 + 2\,H_2O$$
$$\searrow_{4\,H_2O} Si(OH)_4 + 4\,H_2$$
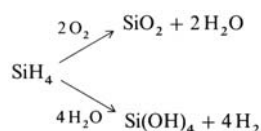
The thermal decomposition of monosilane takes place as follows:

$$SiH_4 \xrightarrow{>600\,°C} Si + 2\,H_2$$
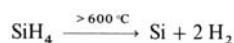
Higher silanes decompose at lower temperature.

High-purity silicon can be produced in this way from pure silanes. Organosilicon compounds can be obtained by addition of silanes to unsaturated organic compounds.

2.1. Monosilane

Monosilane, SiH_4, is formed by the hydrolysis of magnesium silicide (Mg_2Si) with 10 % hydrochloric acid at 50 °C. It is, however, accompanied by higher homologues which must be removed by high-vacuum fractionation [4], [5]. However, if magnesium silicide is hydrolyzed with ammonium chloride in anhydrous ammonia under its own vapor pressure at room temperature, SiH_4 is obtained exclusively [6]. Ammonium bromide has also been used [7]. The ammonia is condensed out as far as possible, and any remaining traces are removed by washing the silane with dilute nitric acid.

Silane can readily be prepared from silicon halides and metal hydrides. The most convenient laboratory method is the reaction of $SiCl_4$ with lithium aluminum hydride in diethyl ether [8] or THF [9].

$$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiCl + AlCl_3$$
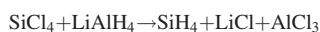
The hydrogenation can also be performed with alkali metal hydride/aluminum alkoxide or alkali metal hydride/boron triethyl in paraffin oil [10], or by alkali metal aluminum hydride/calcium aluminum hydride in other organic solvents [11], [12].

The alkali or alkaline-earth metal hydrides can be formed in situ by passing silicon tetrachloride and hydrogen into an electrolyzed melt of the metal halide [13].

In a two-step process, in which the rate of silane formation is adjusted by means of the temperature difference between the two stages, silicon halides other than the tetrafluoride are first reacted with excess alkali metal hydride or alkali metal aluminum hydride, followed by degassing and then contacting the solid reaction product with excess silicon halide [14]. Monosilane is obtained in low yield but with sufficient purity to be used in the manufacture of semiconductors with toluene as a solvent instead of ethers [15].

Benzyltriethylammonium chloride or other quaternary ammonium salts are used as catalysts in concentrations up to 25 mol %. High yields of monosilane are obtained from the reaction of silicon halides with a mixture of aluminum products containing dialkyl aluminum hydrides, trialkylaluminum, ethylaluminum chloride, and aluminum powder in liquid paraffin at 40 °C.

Catalytic disproportionation of chlorosilane mixtures originating from various sources in the silicon industry provides a route to monosilane for the manufacture of polycrystalline solar silicon. For a mixture of trichloro- and dichlorosi-

Table 1. Silanes Si_nH_{2n+2}

	M_r	mp, °C	bp, °C	d_4^{20}
SiH_4	32.12	−185	−112	0.68
Si_2H_6	62.23	−130	− 14.5	0.69
Si_3H_8	92.33	−117	− 53	0.72
Si_4H_{10}	122.44	− 91	−108	0.79

lane, copper [16], a mixture of silica and alumina at 300 °C [17], and quaternary ammonium groups bonded to carbon in an ion-exchange resin have been reported as catalysts for the main reactionleading to monosilane [18].
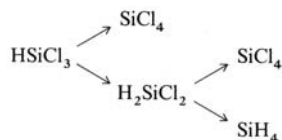
The catalytic conversion of intermediate dichlorosilane can also be accomplished by alkyl or aryl nitriles on carbon carriers at 50 °C [19]. Boron catalysts, however, enhance the formation of dichlorosilane in chlorosilane mixtures obtained by high-pressure plasma hydrogenation of tetrachlorosilane [20]:

$$SiCl_4 + H_2 \rightarrow HSiCl_3 + H_2SiCl_2$$

In-process purification is achieved by contacting part of the monosilane produced with the starting mixture of chlorosilanes, which contains the impurities as chlorides, chiefly those of arsenic, phosphorus, and boron. This procedure converts the contaminants into their more volatile hydrides, which are removed with the off-gas [18].

Properties and physical data of monosilane, particularly with regard to obtaining high-purity silicon by chemical vapor deposition, are compiled in [21].

2.2. Disilane

Increasing amounts of hexachlorodisilane are being produced as a byproduct of the chlorosilane industry. Since it is of no immediate use, it is subjected to hydrogenation or disproportionation to convert it to useful derivatives, mainly tetra- or trichlorosilane. When the production of amorphous silicon from disilane became commercially viable, the hydrogenation of hexachlorosilane became a feasible alternative to disproportionation. The production of disilane resembles that of monosilane, the reducing agents being metal hydrides, mainly lithium aluminum hydride. The use of di-*n*-butyl ether as a solvent is reported to give a smooth reaction at 35 °C [22]. Addition of lithium hydride increases the yield molar ratios

LiH : LiAlH$_4$ of 0.8, 2.0, 12.0, 20.0, and 40.0 resulted in yields of 83, 88, 90, 89, and 70 %, respectively. Lithium hydride can be used as the sole reducing agent if aluminum bromide or chloride is added to the ether solvent [23]. Lithium aluminum hydride in refluxing diethyl or diisopropyl ether gave disilane in 88 % yield [24].

2.3. Purification

Removal of boron compounds from silanes that are to be used for the production of high-purity silicon is very important. When SiH$_4$ is produced from alkali metal hydrides [12], it is recommended that water should be added to hydrolyze boron hydrides under the alkaline reaction conditions. Water vapor is added during distillation for the same reason [25]. Boron compounds can be removed from SiH$_4$ by adsorption from the gas phase onto activated carbon or silica carriers loaded with compounds that form complexes with boron compounds (AlCl$_3$, FeCl$_3$, C$_2$H$_5$CN, NH$_2$CN, PCl$_3$) [26].

If alkali metal hydrides MH are reacted in organic solvents, it is often unnecessary to include a special stage for removing boron compounds from the silicon compounds, as the former react to form boranate complexes under the following conditions:

$$SiCl_4 + 2\,BCl_3 + 10\,MH \rightarrow 10\,MCl + SiH_4 + B_2H_6$$

$$B_2H_6 + 2\,MH \rightarrow 2\,MBH_4$$
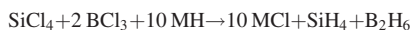
A systematic study has been carried out on the liquid – vapor distribution coefficients of volatile trace impurities in the hydrides of boron, silicon, phosphorus, arsenic, sulfur, and selenium. Experimental and calculated data are reported for the temperature range between the boiling point and critical temperature. Linear regression coefficients for the temperature dependence of the impurity distribution coefficients are included [27].

2.4. Uses

Direct use of silicon hydrides involves their decomposition on surfaces, leading to deposition of elemental silicon or silicon compounds. Polycrystalline films of elemental silicon of control-

lable grain size are deposited on glass or silica-coated surfaces by heating them to 450 – 800 °C in an atmosphere consisting of monosilane and tetrabromo- or tetraiodosilane [28]. Chemical vapor deposition is generally followed by annealing and recrystallization with an energy beam. This is used to deposit silicon on insulator surfaces [29]. Amorphous silicon photoconducting layers on electrophotographic plates are made by using a plasma for silane decomposition and silicon deposition [30]. Liquid crystal displays, based on thin film transistors, for screens in monitoring devices, are made from amorphous silicon which is produced on alkali-free glass surfaces in situ by an electric discharge in an atmosphere of monosilane at reduced pressure. Residual bonds are saturated by hydrogen atoms to avoid diminishing the semiconductor effect [31]. On the surfaces of transition metals, cleaned by sputtering in an argon atmosphere, monosilane and the higher silicon hydrides can be thermally decomposed at ca. 300 °C to form metal silicides [32]. Exposure to air leads to the formation of silicon oxides.

2.5. Safety Measures

Silicon hydrides are combustible; the lower members are spontaneously flammable. Particular attention has been given to the system monosilane – oxygen and its explosibility [33]. Oxygen-rich mixtures (>70 % O_2) give water and silicon dioxide as combustion products. As the mixtures become richer in monosilane, hydrogen replaces water as a combustion product. For monosilane-rich mixtures (>70 % SiH_4) the products are hydrogen, silicon, and silicon oxides. The explosion of monosilane-rich mixtures is primarily a thermal explosion of monosilane itself.

Hazardous waste gases containing silicon hydrides and halides are passed through columns containing pelletized oxidants to remove the silicon compounds. The oxidants are made by treating a mixture of copper and zinc nitrate with sodium carbonate [34].

2.6. Photochemistry

Irradiation of silanes and silyl compounds leads to fragments, namely the silylene

(: SiH_2) intermediate. Silane mixtures with boron trichloride [35] and hydrogen chloride [36] have been investigated with infrared laser techniques.

Monosilane and boron trichloride react along two pathways, one being hydrogenation of boron compounds, leading to boron dichloride, diborane, and trichlorosilane. In a side reaction, decomposition of silane takes place, forming hydrogen and amorphous silicon. Carrying out this procedure with methane instead of silane leads to a pyrolysis of methane, the released hydrogen partly converting the boron trichloride to hydrides.

In the presence of hydrogen chloride, the primary reaction seems to be the formation of intermediate silylene which in turn reacts with silane and hydrogen chloride. Simultaneous formation of chlorosilanes also occurs. The activation energy for the insertion of silylene into hydrogen chloride was determined to be <1.3 kcal/mol. In general, silylene insertions are considered in the context of a triplet state, and symmetry allows insertions to proceed without excitation energy when the antibonding orbital, relating to the bond into which the insertion occurs, is symmetrical with respect to the reaction coordinate [37].

3. Silicon Halides

Silicon halides (see Table 2) are mostly colorless liquids that fume in air, are readily hydrolyzed,

Table 2. Melting and boiling points of halogenosilanes

|	M_r	mp, °C	bp, °C
SiH_3F	69.12		−98.6
SiH_2F_2	106.11	−119	−77.5
$SiHF_3$	143.10	−131.5	−97.5
SiF_4	180.09	−90.2[a]	−98.6
SiH_3Cl	66.57	−118	−30.5
SiH_2Cl_2	101.01	−122	− 8.5
$SiHCl_3$	135.45	−134	36.5
$SiCl_4$	169.89	−70	57.6
SiH_3Br	111.04	−94	2.0
SiH_2Br_2	189.95	−70	66
$SiHBr_3$	268.86	−73.5	112
$SiBr_4$	347.77	5	153
SiH_3I	158.02	−56.5	46
SiH_2I_2	283.91	−1	149.5
$SiHI_3$	409.80	8	220
SiI_4	535.69	121	290

[a] At 1753 mbar triple point.

and consequently have an irritating effect on the mucous membranes. Silicon hydridohalides with a high hydrogen content are spontaneously flammable. All 18 mixed silicon halides with the composition $SiHal^1_n Hal^2_m (n+m = 4)$ are known.

3.1. Trichlorosilane

Trichlorosilane, $HSiCl_3$, M_r 135.4, mp −134 °C, bp 36.5 °C (Table 2) is the most important silicon hydridohalide. The vapor is highly flammable; mixtures with oxygen or air explode violently on ignition or on contact with a hot surface. It is decomposed by water with the evolution of hydrogen.

3.1.1. Preparation from Elemental Silicon

Trichlorosilane was first prepared by F. WÖHLER, who used the same method as that now used for laboratory and industrial scale production [38]:

$$Si + n\,HCl \rightarrow HSiCl_3 + SiCl_4$$
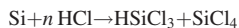
A mixture of chlorinated silanes is produced when a mixture of hydrogen chloride and hydrogen at ca. 250 – 400 °C is passed over high-silicon (ca. 97 % Si) ferrosilicon or silicon mixed with aluminum, nickel, or copper(I) chloride [39]. The process is sometimes carried out in a turbulent [40–42] or nonturbulent fluidized bed [43], [44].

Due to the growing demand for pure precursors for high-purity silicon, process improvements have been made continuously to raise the yield of trichlorosilane and to lower energy consumption as the chief cost cutting measures in production. The fluidized-bed reactor [45–54] has become the predominant process base for the manufacture of trichlorosilane from metallurgical-grade silicon or other silicon solids. Additional feed gases, both inert (e.g., nitrogen, argon, and helium) or reactive (e.g., chlorine) have been used [45], [46]; feeding hydrogen chloride in pulses is reported to give a higher yield [47]. Tetrachlorosilane added to the feed gas serves as a carrier and fluidizing agent when silicon residues are utilized as a source of silicon [48]. These residues can originate from the direct synthesis of organochlorosilanes (→ Silicon Compounds, Organic). Higher temperature in the fluidized bed followed by rapid quenching are reported to increase yield 1.8-fold. Quenching is effected by spraying the top of the bed with tetrachlorosilane at 20 °C such that the reaction gases leaving the reactor are cooled to 400 °C in less than one second [50].

Extremely fine particles of silicon (50 – 800 µm), obtained by atomizing molten elemental silicon in a nitrogen atmosphere, are claimed to give a high yield of trichlorosilane [51]. A screw conveyor has also been used for producing trichlorosilane from ferrosilicon [55]. Depending on the cooling rate the tetrachlorosilane to trichlorosilane ratio can be adjusted between 4 : 1 to 0.2 : 5.

In a two-step [56] process silicon is first reacted with tetrachlorosilane at 1100 – 1300 °C and the resulting product is treated with hydrogen chloride. The conversion of tetrachlorosilane to trichlorosilane is 50 – 60 %.

Adding tetrachlorosilane to the hydrogen chloride prior to contact with powdered silicon is claimed to enable complete conversion to trichlorosilane [57].

Silicon powder with 2 % copper [58] or 6 % copper [59], has been used at 350 – 600 °C. The yield of trichlorosilane was 7 – 27 mol % for 2 % Cu, and 80 – 90 mol % for 6 % Cu. Much lower temperatures (down to 260 °C) were possible when antimony pentachloride was used as a cocatalyst with copper; the trichlorosilane yield was 21 % [60].

Silicon residues from direct synthesis of organochlorosilanes can also be reacted with hydrogen chloride to give trichlorosilane [61].

3.1.2. Preparation from Tetrachlorosilane

Tetrachlorosilane, up to now used as a starting material for silica fillers, quartz, and special glasses, has become an important precursor for trichlorosilane. The basic reaction is

$$1.5\,SiCl_4 + H_2 + 0.5\,Si \rightarrow 2\,HSiCl_3 \qquad (1)$$

Although use of a graphite heating element at 1100 – 1400 °C has been reported [62], most processes are operated between 800 and 1400 °C. The residence time is critical and is adjusted by quenching or by using a two-step

process. The residence time of the feed should be <2.5 s [63], and quenching carried out below 600 °C within <1 s [64]. A feed stream of tetrachlorosilane – hydrogen mixture with a molar ratio of 1 : 2 in the absence of silicon at 1100, 1200, and 1500 °C, gave trichlorosilane in 27, 31, and 35 %, respectively.

In two-stage processes the reaction with silicon is carried out at lower temperature in the second-stage reactor.

Typical temperatures are 500 – 700 °C for the first stage, and 300 – 350 °C for the second [65]. The yield of trichlorosilane can be doubled by adding hydrogen chloride to the gas from the first reactor prior to entering the second [66]. A reaction mixture obtained by passing tetrachlorosilane and hydrogen through a reactor at 1050 – 1250 °C is then cooled to 250 – 350 °C and reacted with silicon in a second reactor [67], giving a product containing 38 % trichlorosilane and 61 % tetrachlorosilane. It is also possible to react the intermediate dichlorosilylene with hydrogen in a separate reaction chamber [68].

Single-step processes are mostly carried out in fluidized-bed reactors [69], [70] with quenching of the gaseous reaction products. For furnaces operating at ambient pressure, preheating the reactant gases [71], and removing surface oxide coatings from the silicon powder with aqueous acid or alkaline hydrogen fluoride solution raises the trichlorosilane yield to 70 % [72]. Pretreatment of silicon can also be carried out with gaseous hydrogen chloride [73]. While particle size of the silicon and its distribution seems to have little influence on the reaction [74], it is strongly affected by catalysts. Copper, the main catalyst, is added as such to the silicon [75–81]. The reaction kinetics have been studied in the presence of copper chloride [82]. The hydrogenation of tetrachlorosilane has an activation energy of 20 – 25 kcal/mol which is lowered to 10 – 15 kcal/mol by the catalyst; conversion and throughput are improved.

Copper has also been used with cocatalysts such as metal oxides [83] and metal halides. Aluminum halides give trichlorosilane yields of 20 – 30 mol % [84–86]; iron and vanadium halides give comparable yields [87–89].

Using nickel salts as cocatalysts [90], [91] between 500 and 600 °C gave trichlorosilane yields of 36 % whereas powdered nickel alone gave 27 % [92]. Antimony chloride in a pressure reactor gave 21 % [93].

Platinum compounds have also been used [94], [95]. Silicon with addition of 10^{-3} mol % platinum black [96] catalyzes tetrachlorosilane conversion at 550 °C to give an 80 % yield of trichlorosilane. At the same temperature, platinum on carbon gives a mere 5 % yield [97]. Carbon as the sole catalyst has also been reported in a two-step process [98], in a fluidized-bed reactor [99], and in a packed-bed reaction chamber [100], the latter two giving trichlorosilane yields of 20 vol % and 11 mol %, respectively.

The conversion of tetrachlorosilane to trichlorosilane has also been effected electrolytically [101] with 1,2-dimethoxyethane as a solvent, hydroquinone as hydrogen donor, and tetrabutylammonium perchlorate as supporting electrolyte.

3.1.3. Purification

Extreme purification of trichlorosilane is necessary if it is to be used for production of high-purity silicon for semiconductors or photoconductors. This is mainly to remove impurities such as chlorides of calcium, aluminum, titanium, copper, magnesium, iron, boron, and phosphorus, which would remain in the silicon formed by hydrogen reduction. The trichlorosilane is treated with complexing agents such as thioglycolic acid, β-naphthylamine, and salts of ethylenediaminetetraacetic acid [102]. An extremely pure product is obtained by extraction with CH_3CN [103]. Other methods include adsorption of the impurities on columns of activated silica [104], activated carbon, ion exchangers [105], [106], titanium sponge [107], or by treatment with acetals [108] or salt hydrates, which cause partial hydrolysis of the impurities [109–111]. The purification of trichlorosilane [112], [113], the development of purity criteria, and industrial control of purity [114] are well developed subjects.

The ultimate aim in trichlorosilane purification is the elimination of trace amounts of boron and phosphorus. Both elements are retained in chemical processing in sufficient amounts to impede or even prohibit certain uses in electronics. Boron impurities are first converted from volatile halides or hydrides to nonvolatile acids or oxides, for example, by passing moist nitrogen

into the boilers of a multistage distillation [115]. The addition of 0.1 – 1.0 g/t of trichlorosilane decreased the boron content from 1.6 ppm to 0.2 ppb. A similar procedure [116] gave 12 ppb residual boron in a one-step distillation. The addition of silica with at least 0.25 wt % of total hydroxyl groups is also claimed to effect partial hydrolysis [117].

Phosphorus, the other chief contaminant of silicon compounds, is present in chlorosilanes as phosphorous trichloride. During their distillation, it is trapped in the high-boiling residue by complex formation with molybdenum oxychloride and covalent nickel compounds. The phosphorus-metal complexes are thermally stable. Residual phosphorus contents of chlorosilanes distilled were below the analytical detection limit [118], [119]. Manganese dioxide is also reported as a purification agent. It forms phosphorus oxychloride which has a much higher boiling point than phosphorus trichloride and hence remains in the distillation residues [120]. Boron and phosphorus impurities in trichloro- or dichlorosilane can be oxidized with oxygen to give less volatile compounds [121]. Polycrystalline silicon prepared from purified chlorosilanes had residual impurities of 0.1 ppb boron and 0.18 ppb phosphorus.

3.1.4. Waste Disposal

The in-plant, partly on-line conversion of waste from chlorosilane manufacture and use has two chief sources: distillation residues and off-gases which are both hazardous materials. To provide safety, environment protection, and an economic conversion of material that can be used elsewhere or safely deposited, several procedures have been adopted. Distillation sludge is evaporated in the presence of metal chloride slurries giving chlorosilanes [122] and then hydrolyzed with steam in azeotropic hydrogen chloride which continuously gives additional hydrogen chloride [123].

3.1.5. Uses

The purity of trichlorosilane greatly influences its end use. High purity silicon is produced by the pyrolysis of trichlorosilane in the presence of hydrogen [124], [125], for which a large number of techniques have been used, e.g., pyrolysis in a fluidized bed [126], pyrolysis in or over molten silicon [127–129], and epitaxial growth on silicon [130–132] or graphite [133]. Other processes reported include the production of polycrystalline silicon by the pyrolysis of trichlorosilane [134–137], the production of amorphous silicon coatings by CVD [138], and the production of solar silicon [139], [140]. A reactor made of silicon has been described for the pyrolytic process [141].

In fluidized-bed reactors caking of silicon on the inner wall is prevented by starting with a bed of polycrystalline silicon of grain size 700 – 3000 µm, fluidized by a mixture of trichlorosilane and hydrogen [142]. The polycrystalline silicon granules are continuously removed from the reactor.

Other important uses for trichlorosilane include the manufacture of very finely divided ("micronized") silica for use as a filler [143], the manufacture of silicon nitride ceramics, sometimes together with metal nitrides [144], the surface treatment of boron and borides [145], the production of free-flowing granulated fertilizers [146], and in screen printing [147].

3.2. Tetrachlorosilane

Silicon tetrachloride, $SiCl_4$, M_r 169.9, mp -69.4 °C, bp 57.3 °C, T_c 234.0, p_c 37.5 bar, V_c 326.3 cm g^{-1} mol^{-1}, is a clear, colorless liquid that fumes strongly in air and hydrolyzes rapidly in water, producing SiO_2 gel. When dry, it does not attack steel, and can therefore be transported in steel tanks. It is soluble in benzene, ether, chloroform, and petroleum ether. It reacts with alcohols to give esters of silicic acid. On partial hydrolysis (e.g., with ether – water mixtures), silicon oxychlorides, $Si_nO_{n-1}Cl_{2n+2}$, are formed as colorless, viscous liquids. These oxychlorides, together with the corresponding metallic chlorides, are formed when silicon tetrachloride reacts with metal oxides (e.g., of Mn, Cu, Ca, Zn, Mg, Ag, or Hg) in organic solvents [148].

3.2.1. Production

Silicon tetrachloride is prepared in the laboratory by the reaction of silicon or high-silicon ferrosil-

icon with dry chlorine at $>400\ ^\circ C$. At lower temperature, Si_2Cl_6 and other subchlorides are also formed [15].

In industry, $SiCl_4$ is mainly produced by reacting ferrosilicon, pure silicon, or silicon carbide with chlorine. Other possible processes include the reaction of SiO_2 or a SiO_2/SiC mixture with carbon and chlorine (or with $COCl_2$ or CO/Cl_2 mixture). This older process, which uses silica sand as the cheap raw material, has attracted renewed interest since the introduction of the fluidized-bed reactors.

From Ferrosilicon ($>90\ \%$ Si) or Pure Silicon and Chlorine. The reaction between silicon and chlorine is exothermic. Therefore, after the reaction has been initiated, cooling must be provided. Ferrosilicon, with a high silicon content, is cheaper than pure silicon, and due to the greater reactivity of the iron, is more readily chlorinated. However, the temperature must be maintained at $>400\ ^\circ C$ so that the $FeCl_3$ formed is removed, and blockages in the pipework are prevented.

In the Dynamit Nobel process, large pieces of ferrosilicon containing $>90\ \%$ silicon are continuously fed into a furnace at $>500\ ^\circ C$ fitted with a cooling jacket. Silicon tetrachloride is formed together with iron chloride and the chlorides of the other elements present in the ferrosilicon, mainly aluminum chloride, calcium chloride, and titanium tetrachloride. The nonvolatile chlorides (e.g., $CaCl_2$) remain in the furnace, and are removed from time to time together with unchlorinated components (e.g., SiO_2).

The volatile chlorides pass out of the furnace and are then partially condensed by cooling. The collecting vessel is maintained at such a temperature that the $SiCl_4$ distils over while the $FeCl_3$ and $AlCl_3$ remain behind. Most of the $SiCl_4$ is then condensed out, and the residual gases are cooled to $-35\ ^\circ C$, causing any remaining tetrachloride to separate.

The crude silicon tetrachloride still contains small quantities of iron and aluminum chlorides, and also some chlorine, titanium tetrachloride, and hexachlorodisiloxane formed by partial hydrolysis of $SiCl_4$ by the traces of water that enter the furnace during charging. This is purified by simple evaporation and condensation, followed by fractional distillation. In the evaporation process, which is also applied to the residues from

the fractional distillation, chlorides of iron and aluminum remain behind along with some of the medium boiling point compounds, i.e., hexachlorodisiloxane and titanium tetrachloride. The crude distillate obtained is fractionated in a double distillation column.

It has been proposed that a molten salt reaction medium should be used [149], and that inert materials such as carbon, aluminum oxide, and silica should be added in both the batch [150] and the continuous process [151].
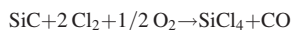
From Silicon Carbide and Chlorine.

$$SiC + 2\,Cl_2 \rightarrow SiCl_4 + C$$
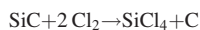
The advantage of using the readily available industrial-grade silicon carbide as the starting material must be balanced against the disadvantages that the reaction with chlorine starts at a higher temperature, and the heat of reaction is not sufficient to maintain the material at the reaction temperature without heating. Also, the carbon formed remains behind as a residue.

Silicon is added to the silicon carbide to facilitate the reaction. The chlorination is carried out in a vertical shaft furnace made of steel or cast iron lined with carbon plates. The downstream condensation system includes a spray of liquid silicon tetrachloride to prevent blockage by the iron and aluminum chlorides formed from impurities in the raw material [152].

In a modified process, the chlorine is mixed with oxygen, which oxidizes some of the carbon formed in the reaction to carbon monoxide [153], [154]:

$$SiC + 2\,Cl_2 + 1/2\,O_2 \rightarrow SiCl_4 + CO$$

From Silica, Carbon, and Chlorine. Information on the temperature required for the reaction of various silica modifications with chlorine and carbon is given in [155].

Chlorides of alkali metals or alkaline earths can be mixed with the finely powdered coke and kieselguhr or other silica-containing materials to lower the reaction temperature. The mixture is treated with chlorine at red heat [156]. In a variation of the process, the energy is provided by an electric arc, which is applied to the reaction mixture in a fixed [157] or fluidized bed [158].

As the reaction of SiO_2 with carbon and chlorine is endothermic, it is necessary to couple it with an energy-producing process, e.g., silicon and chlorine, ferrosilicon and chlorine, or silicon carbide and chlorine. In the Stauffer process [159], silicon carbide, silica sand, and coke are treated with chlorine gas in a fluidized-bed reactor. A separator removes any solid material from the gaseous reaction product, which is then cooled in heat exchangers. Silicon tetrachloride condenses out and is purified by the usual distillation process.

Other Processes. These include: treatment of silicon or a Si – Cu alloy with CCl_4 vapor at 260 – 300 °C [160], reaction of alkali metal silicofluorides (e.g., Na_2SiF_6) with $AlCl_3$ at 280 °C [161] or with $MgCl_2$ at 500 – 1000 °C [162], and recovery of byproduct silicon tetrachloride from the production of methylchlorosilanes (→ Silicon Compounds, Organic).

The formation of incrustations in a fluidized-bed reactor can be prevented if a mixture of metallurgical silicon and silicon carbide with silicates of iron, titanium, vanadium, or chromium is used. Increases in yield of up to 12 % have been observed [163].

Lower reaction temperatures, down to 200 °C, and the use of silicides, preferably calcium silicide, yields substantial amounts of tetrachlorosilane together with an appreciable amount of hexachlorodisilane [164], [165]. The conversion of higher chlorosilanes into tetrachlorosilane is effected by tertiary amines in catalytic amounts below 160 °C. Refluxing of hexachlorodisilane with 0.8 vol % of pyridine gave tetrachlorosilane [166].

3.2.2. Purification

The main aim of purification is to remove halides of boron and phosphorus by preferential hydrolysis, complexing agents, or the incorporation of adsorption stages in the distillation process. Examples include preferential hydrolysis of BCl_3 by adding water or ice [167], [168], adding substances to the distillation process that combine with BCl_3 such as CH_3CN and $(C_6H_5)_3CF$ [169], [170], substances that combine with PCl_3 such as $AlCl_3$ [171], and passing the silicon tetrachloride through adsorption columns charged with substances containing tertiary amine groups, quaternary ammonium groups [172], or water-containing oxides or silicates [173]. A countercurrent zone-melting process has also been developed for the purification of $SiCl_4$ [174].

Removing boron impurities is also accomplished by high-temperature hydrogenation, which converts boron trichloride, the chief impurity to volatile diborane [175]. The fact that considerable amounts of silicon hydrides, chiefly trichlorosilane and dichlorosilane, are formed as byproducts, is of no apparent disadvantage since both can now be used in high-purity silicon manufacture.

Low-loss optical fibers require precursors with extremely low contents of hydroxyl-containing impurities. These are probably chloro – hydroxy complexes of metals, mainly iron. They are removed by partial hydrolysis of the tetrachlorosilane with adsorption of the impurities on the in situ precipitated silica gel. The residual contaminant content is 12 ppm Fe, 2 ppm OH, and 18 ppm HCl [176].

3.2.3. Uses

High-purity silicon is produced by the thermal decomposition of $SiCl_4$ in the presence of hydrogen, and highly dispersed silica is produced by flame hydrolysis of $SiCl_4$ (→ Silica, Section 6.1.1.).

Corrosion-resistant silicon coatings are produced on metal surfaces, e.g., steel and iron [177], [178], molybdenum, tungsten, tantalum [179], molybdenum, or tungsten [180] by heating the metal component in an atmosphere of $SiCl_4$ – H_2 or $SiCl_4$ at 1000 – 1400 °C.

3.3. Hexachlorodisilane

For years, hexachlorodisilane was a typical byproduct; its formation was suppressed as far as possible or a conversion to more versatile products carried out. It is now a compound of its own standing leading directly to the production of several special silicon products. The manufacturing processes, however, are still dominated by the basic reaction of silicon or silicides with chlorine giving a number of chlorosilanes, hexachlorodisilane being just one.

3.3.1. Production

To obtain hexachlorodisilane as a high share in a crude chlorosilane product mixture, conversion or degradation processes have been designed. Calcium silicide is the preferred raw material and a low reaction temperature of 200 °C is used [181]. Continuous production in a multicolumn reactor [182], and batch production [183] with a comproportionation step have been described:

$$Si_3Cl_8 + SiCl_4 \rightarrow 2\, Si_2Cl_6$$

Reaction of ferrosilicon, with a silicon content of 50 %, and chlorine at 160 °C in a vibrating reactor gave 55 wt % hexachlorodisilane, and 44 wt % tetrachlorosilane with a 70 % ferrosilicon conversion [184], [185].

High-boiling residues, predominantly containing polychloropolysilanes, are cleaved by chlorine in a fluidized bed [186] at 250 – 450 °C.

$$2\, Si_3Cl_8 + Cl_2 \rightarrow 3\, Si_2Cl_6$$
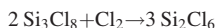
At 500 °C on α-alumina beads [187] comproportion of tetrachlorosilane is readily achieved, with a conversion of 70 %. The reverse reaction is carried out at a temperature of 700 °C aided by lithium – magnesium double oxides as catalysts and alumina as the carrier.

$$2\, SiCl_4 \rightarrow Si_2Cl_6 + Cl_2$$
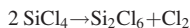
The reaction product consists of 50 % unchanged tetrachlorosilane, 40 % hexachlorodisilane, and 10 % higher homologues [188].

Liquid-phase chlorination allows a lower reaction temperature to be used. Using elemental silicon and a catalyst consisting of the chlorides of sodium, potassium, and zinc gives a product mixture that contains tetrachlorosilane, hexachlorodisilane, and tetrachlorodisilane in a weight ratio of 12 : 17 : 11 [189]. Suspension of silicides and antimony pentachloride can be chlorinated to hexachlorodisilane with 34 % conversion [190]. In a solvent mixture in which some components exhibit catalytic properties [e.g., perfluoroalkanes, tris(perfluoroalkyl) amines, and cyclic perfluoroalkyl ethers] elemental silicon reacts with chlorine at 150 °C [191] to give hexachlorodisilane and octachlorotrisilane.

3.3.2. Uses

In most of its applications, hexachlorodilane can be replaced by other special silicon compounds, but in some cases, the reactions take place at much lower temperature than with tetrachlorosilane or trichlorosilane. The deposition of elemental silicon by purely thermal decomposition has been carried out on silicon wire at 750 °C [192], on a quartz plate at 500 °C [193], or on quartz crucibles [194].

Hydrogen as a reducing agent has been used to make bulk polycrystalline silicon above 250 °C [195] or to produce atomic layers of silicon by homoepitaxy [196]. A viscous oil obtained by reacting hexachlorodisilane with tetrabutylphosphonium chloride at 200 °C can be pyrolyzed to give finely divided amorphous silicon [197]. The reaction of hexachlorodisilane with propane on graphite surfaces at 700 °C [198] gives β-silicon carbide. On a cobalt-containing substrate, silicon carbide whiskers are obtained [199]. Mixed carbides of silicon and titanium are made by hydrogenation of a mixture of hexachlorodisilane, titanium tetrachloride, and alkyl halide [200].

Optical fibers can be made by direct surface coating of preforms by flame hydrolysis of hexachlorodisilane [201], [202]. Ultrafine silica particles are formed by thermal decomposition of hexachlorodisilane in an oxygen atmosphere [203]. The method is suitable for the manufacture of quartz glass as a substrate for wave guides [204].
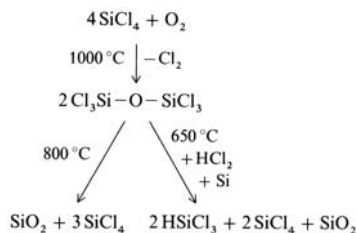
3.4. Other Silicon Chlorides

Hexachlorodisiloxane, intermediate or byproduct in oxidation or hydrolysis reaction, can be obtained as the chief product by reacting tetrachlorosilane with sulfur trioxide 500 °C.

$$2\, SiCl_4 + SO_3 \rightarrow (Cl_3Si)_2O + SO_2 + Cl_2$$
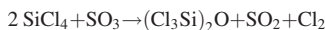
By comparison, other monosilanes react differently. The bromide and hydride at room temperature give silicon dioxide, the fluoride, not at all even at 600 °C [205]. Formation and degradation of hexachlorodisiloxane can be shown by high-temperature reactions. It is formed from tetrachlorosilane and oxygen [206] together with other oligomeric siloxanes but with mono- and polycyclic siloxanes also. Thermodynamic stud-

ies indicate a certain metastability of halosiloxanes in general. No direct use has been made of hexachlorodisiloxane, conversion to chlorosilanes, i.e., recycling, is practised [207]:

$$4\,SiCl_4 + O_2$$
$$1000\,°C \downarrow -Cl_2$$
$$2\,Cl_3Si-O-SiCl_3$$
$$800\,°C \swarrow \qquad \searrow \begin{array}{l} 650\,°C \\ +HCl_2 \\ +\,Si \end{array}$$
$$SiO_2 + 3\,SiCl_4 \qquad 2\,HSiCl_3 + 2\,SiCl_4 + SiO_2$$

An important intermediate is dichlorosilylene, the first reaction product of the attack of chlorine on silicon. Dichlorosilylene can be obtained directly in high-vacuum apparatus from the elements at 1250 °C [208], [209], and 1100 °C [210]; it is a transparent, amber-like solid.

3.5. Silicon Fluorides (Silicon Tetrafluoride, see → Fluorine Compounds, Inorganic, Section 5.1.)

Difluorosilylene. Silicon tetrafluoride and silicon react at 1200 °C in a high vacuum, yielding a condensate with the composition $(SiF_2)_x$]. This turns yellow on cooling with liquid air and ignites on contact with atmospheric oxygen. It loses its color on heating to -78 °C and becomes highly polymeric [211].

A plasma flame in an argon atmosphere [212], [213] can also be used as a reaction medium. A molar ratio of tetrafluorosilane to silicon of 0.8 : 1 gives a SiF_2 yield of 70 %.

Difluorosilylene can be used to produce silicon difluoride filaments [214]. The production of amorphous silicon films from SiF_2 by chemical vapor deposition leads to material with residual Si – F groups [215], which is claimed to afford a higher doping efficiency [216] for boron and phosphorus.

Reacting SiF_2 with methane and hydrogen in a glow discharge [217] gives a photoconductive amorphous silicon carbide. Silicides can be prepared by reacting hexafluorides of tungsten or molybdenum with difluorosilylene in a hydrogen atmosphere at 300 – 600 °C [218]. Oxidation of SiF_2 with oxygen, nitrous oxide, or nitrogen dioxide [219] gives silicon dioxide with residual Si – F groups, suitable for the manufacture of optical fibers.

3.6. Silicon Bromides

Silicon tetrabromide, tetrabromosilane, $SiBr_4$, M_r 347.7, is produced from silicon and bromine vapor at >600 °C. It is a colorless liquid, with *mp* 5 °C and *bp* 153 °C.

With ferrosilicon powder a 70 % yield of $SiBr_4$ is obtained. Crude tetrabromosilane is heated with zinc to remove residual bromine [220].

The main use for silicon tetrabromide is as a raw material for the production of silicon and its compounds. The reaction used is the reverse of the preparation method, i.e., it is pyrolytically decomposed [221], [222], usually together with silanes, using fluidized-bed processes [223], or crystal growth techniques [224]. These techniques are also used in the manufacture of optical fibers [225–228] and photoconductive silicon [229].

In a plasma, tetrabromosilane is readily cleaved to the elements, and the deposition of the silicon layer is much faster than with tetrachlorosilane [230]. Tribromosilane can be produced by reacting metallurgical-grade silicon with tetrabromosilane at 600 – 800 °C in hydrogen atmosphere [231].

Other processes include the electrolytic deposition of silicon from solutions of silicon tetrabromide in aprotic organic solvents [232–234].

Silicon tetrabromide is also used to produce silicon nitride itself [235–238], as a coating, or to seal porous solids by exposing them to $SiBr_4$ vapor followed by reaction with ammonia [239]. Boron – silicon phases have been obtained by the copyrolysis of halogenated silanes and boranes [240].
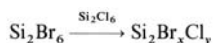
Silicon tetrabromide is used as an auxiliary in the production of SnO_2 whiskers [241], the etching of aluminum and its alloys [242], and the copolymerization of dienes and vinyl compounds [243].

The entire series of bromosilicon hydrides are obtained by disproportionation [244]. With Amberlite A 21 as catalyst at 135 °C the major product is dibromosilane. Fluorobromosilanes are made by reacting tetrabromosilane with antimony trifluoride [245].

Fluorobromosilicon hydrides are made by reaction with alkyltin hydrides [246] at room temperature under reduced pressure:

$$SiBr_4 \xrightarrow{SbF_3} SiF_2Br_2 \xrightarrow{R_3SnH} HSiF_2Br$$
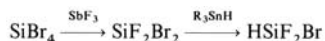
Comproportionation can be extended to the disilanes:

$$Si_2Br_6 \xrightarrow{Si_2Cl_6} Si_2Br_xCl_y$$

Separation of the products by distillation is difficult due to continuing halogen redistribution [247]. Since aryl groups on silicon can be cleaved by hydrogen halides in the presence of aluminum halide catalysts, this method can be used to prepare higher silicon bromides:

$$Ph_3Si-SiCl_3 \xrightarrow{HBr/AlBr_3} Br_3Si-SiCl_3$$

A well-defined, very reactive subhalide with the composition $[(SiBr_2)_x]$ is obtained by the reaction of $SiBr_4$ and silicon at 1150 – 1200 °C in a high vacuum. It is a transparent, almost colorless, amber-like solid, soluble in benzene, xylene, and CCl_4 [15], [248], [249].

3.7. Silicon Iodides

Silicon iodide, SiI_4, M_r 535.7, mp 121 °C, is a crystalline substance that is very sensitive to hydrolysis, decomposes into its elements on heating or on exposure to light, and reacts with oxygen at elevated temperature with liberation of iodine. SiI_4 is produced in 70 % yield by passing a carrier gas saturated with iodine vapor over silicon containing 4 % copper at 600 – 700 °C [15]. Silicon tetraiodide can be obtained on the kilogram scale in quantitative yield by passing nitrogen saturated with iodine vapor at ca. 200 °C over granulated silicon at 1150 – 1200 °C. Approximately 1.5 kg SiI_4 can be produced in 5 h by this method [250].

Other methods include the reaction of mixtures of iodine with bromine or chlorine with silicon at 600 – 800 °C [251], and heating alkali metal fluorosilicates with alkaline-earth iodides at 500 – 1000 °C [252] or with aluminum iodide at 300 °C [253].

Like the tetrachloride, tetraiodide can be used for the production of high-purity silicon by thermal decomposition (sometimes in the presence of hydrogen). The silicon tetraiodide can be purified beforehand by repeated sublimation and zone melting [254], [255].

Silicon tetraiodide has some value as an additional reactant in the pyrolysis of silicon hydrides for the production of high-purity silicon [135], in the reduction of other silicon halides in a fluidized bed [256], and for the purification of silicon by zone melting [222].

Silicon tetraiodide is used as a starting material for the preparation of high-purity silicon films for solar cells by electrolyzing a solution of SiI_4 in aprotic organic solvents [232], [233].

Special applications of silicon tetraiodide as a raw material include the manufacture of cermets [230], and of optical fibers with a germanium core and an outer coating of SiO_2 [257].

A subhalide having the composition of diiodosilylene has been reported [3].

## 4. Silicon Oxides (Silicon Dioxide, → Silica)

With the oxides, more so than with the halides, the growth of interest in use and production, i.e., formation, is brought about by the same driving forces as for the halides, i.e., electronics manufacture and environment protection.

Sources of silicon oxides are chiefly high-temperature processes in heavy industry like blast furnaces, carbide manufacture, coke making, and silicate processing. Main uses are found in high-tech precision preparation of chips, wafers, integrated circuits, layers, and coatings.

4.1. Silicon Monoxide

Silicon monoxide, SiO, M_r 44.06, is formed initially as a gas when SiO_2 and silicon, or SiO_2 and an amount of carbon insufficient for complete reduction, are heated to >1250 °C. It therefore plays a part in the industrial production of silicon and silicon carbide from SiO_2 and carbon, and in the production of ferrosilicon [258], [259].

At lower temperature (ca. 600 – 1000 °C), SiO disproportionates into silicon and silicon dioxide:

$$2\,SiO \rightleftharpoons SiO_2 + Si$$
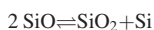
There has, therefore, been prolonged controversy over the question whether SiO should be considered a true compound. Nevertheless, rapid chilling of the gas to room temperature enables the monoxide to be obtained in a solid metastable state. It has a wide range of uses as an additive in applied solid-state physics, and as a raw material in the production of other silicon compounds.

4.1.1. Production

A stoichiometric mixture of finely powdered SiO_2 and silicon in a reaction tube closed at one end is heated at its lowest point in a high vacuum for ca. 4 h at 1250 °C. A brown mixture of SiO_2 and Si, formed by disproportionation, collects in a short transition zone in the part of the tube that just protrudes from the furnace, and the SiO collects as black, compact, shellac-like masses in the parts further away from the furnace.

If an intimate mixture of SiO_2 and silicon is heated for 9 h to 1300 °C and rapidly chilled, cubic crystals of SiO are formed [15]. On an industrial scale, the monoxide can be produced by heating SiO_2 with silica, carbon, or silicon carbide to 1500 – 1800 °C in a resistance furnace [260], [261].

Heating the vapors of the reaction

$$SiO_2 + Si \xrightarrow{1500\,°C} 2\,SiO$$
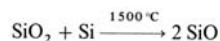
to 1800 °C in an ammonia atmosphere gives amorphous silicon monoxide powders [262].

Silicon monoxide can be made directly in the form of fibers by reducing sand flour with methane at 2500 °C in a fluid-wall reactor [263].

The formation of silicon monoxide by side reactions or as a byproduct of the main process takes place in the course of a number of industrial production streams. In terms of chemical categories these production steps are based on reductions as well as oxidations.

$$\begin{array}{ccc} +\,Si & & Si \\ SiO_2 + SiC \longrightarrow SiO \longleftarrow & SiC & +\,O_2 \\ +\,C & & SiMe \end{array}$$
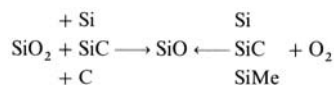
4.1.2. Properties

At room temperature, silicon monoxide is a light brown, finely divided powder, or, if it has been produced by slow condensation, it is a black or very dark brown, shellac-like, glassy mass. The lower limit of stability for gaseous SiO is not below 1025 °C, and is very probably >1175 °C [264]. The best temperature range for its production from SiO_2 and Si is 1200 – 1400 °C [265–267].

At 600 °C, SiO decomposes in several hours, at 700 – 900 °C in ca. two hours, and at 1000 – 1200 °C almost instantaneously into SiO_2 and silicon [266], [268]. Oxygen causes surface oxidation to SiO_2 even at room temperature, and complete oxidation takes place at ca. 500 °C. Finely divided SiO is pyrophoric and burns with flame formation if there is rapid access of air.

With the increase in the number of possible uses for SiO, the silicon – oxygen system has been the subject of extensive investigations [269], particularly with regard to suppressing the formation of SiO during the production of high-purity silicon [270], and of Si – O – N mixed phases in atmospheres containing O_2 and N_2 [271].

4.1.3. Uses

Silicon monoxide is used in small quantities to produce protective films on semiconductors [272–274], vidicon targets [275], and in antireflective coatings on optical glass and plastics [276–279]. Silicon monoxide prevents the formation of anatase in rutile coatings on glass [280]. In entertainments electronics and data processing, silicon monoxide is used in recording tape, other types of data storage media, data transfer heads [281], [282], and in the alignment of liquid crystals for digital displays [283], [284]. Other applications include the coloring of glass surfaces by the simultaneous or sequential deposition of metals and silicon monoxide [285].

Another application of silicon monoxide electronics is the manufacture of heat-resistant films and devices in which corrosion resistance is required. It can be used as a heat-resistant protective layer in laser recording media [286], and in multilayer thermal heads for thermographic printers [287]. Multilayer devices consisting of aluminum, germanium, and silicon monoxide are selective solar absorbers for thermal conversion [288]. Ceramics consisting of silicon carbide whiskers in a graphite matrix can be reinforced

by decreasing the porosity by filling the voids with silicon prepared in situ [289].

Silicon monoxide is used as a raw material, a construction material, and as an auxiliary. The best known application is the oxidation of gaseous silicon monoxide to amorphous finely divided silica [290], (see → Silica). Other uses include the production of silicon carbide [291], [292], silicon nitride [293–295], Si – O – N mixed phases [296], and cermets [297], [298]. Silica can be removed from silica-containing materials (e.g., kaolin) by adding silicon and heating the mixture at 1450 °C in a vacuum [299–301]:

$$Al_2O_3 \cdot 2\,SiO_2 + 2\,Si \rightarrow Al_2O_3 + 4\,SiO_{Gas}$$
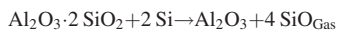
Silicon monoxide can be used to remove phosphorus from blast furnace slag, allowing it to be recycled [302].

Hard coatings of SiO_2 on metals, especially on metallic mirrors, can be produced by deposition of SiO from the vapor state (→ Thin Films). The SiO is then oxidized by atmospheric oxygen to form SiO_2.

In the production of silicon nitride ceramic powders, silicon monoxide is reacted with a reducing atmosphere consisting of a mixture of ammonia and hydrocarbons at 1000 °C. When methane is used as sole reductant, the product is cubic β-silicon carbide [303].

A convenient method to prepare members of the halosilane family is the reaction of silicon monoxide with hydrogen halides [304].

Low-silicon metals are produced by effecting silicon depletion of the melt by limited oxidation. In the production of high-purity vanadium, vanadium pentoxide is added to the melt and the silicon monoxide formed is evaporated [305]. Silicon in molten indium is oxidized with water in a hydrogen atmosphere at 800 °C; ca. 90 % of the initial silicon content is converted to SiO [306].
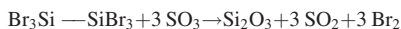
4.2. Silicon Sesquioxides

Depending on temperature and pressure, the following disproportionation steps can take place:

$$4\,SiO \rightleftarrows Si_2O + Si_2O_3$$

$$Si_2O_3 \rightleftarrows SiO + SiO_2$$
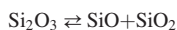
When the monoxide is evaporated at reduced pressure the vapor invariably condenses as the sesquioxide, Si_2O_3 [307].

The reaction of sulfur trioxide with hexabromodisilane at room temperature affords an almost quantitative yield of the sesquioxide; no cleavage of the Si – Si bond takes place [308]:

$$Br_3Si \text{—} SiBr_3 + 3\,SO_3 \rightarrow Si_2O_3 + 3\,SO_2 + 3\,Br_2$$

The sesquioxide can be prepared from hexachlorosidilane by hydrolysis via a sol – gel route [309].

Polymeric silicon sesquioxide can be prepared by thermal dehydrogenation of silicon oxyhydride in high vacuum [310].

$$2\,HSiO_{1.5} \xrightarrow{1000\,°C} Si_2O_3 + H_2$$
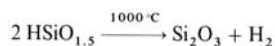
Silicon sesquioxide can be prepared in situ on surfaces. Plasma – vapor deposition from a mixture of monosilane and nitrous oxide [311] gives a moisture-resistant film of silicon sesquioxide, used as a protective layer for p-Si substrates. On polycarbonate sheets, Si_2O_3 layers are prepared by electric discharge [312] or vacuum deposition [313]. On polyethylene [314] a Si_2O_3 layer has been applied by sputtering with an oxygen plasma, using silicon monoxide as the silicon source.

The suboxides, the sesquioxide being the predominant species, are present in semiinsulating films of polycrystalline silicon [315]. Annealing at 1100 °C converts the other suboxides to the sesquioxide only. The suboxides are also formed on etched surfaces of silicon [316] and in layers obtained by silicon implantation oxidation [317]. Thermal annealing leads to a composition corresponding to that of the sesquioxide when carried out at 600 °C.

Less for effects in high-tech physics than essentially in basic chemical processes, the sesquioxide has found quite different applications. Cleaning and purification spans from that of arsenic vapors [318] to the treatment of waste fluid from sweet potato processing [319]. Highly permeable membrane separation elements are made from a ceramic material based on alumina and silicon sesquioxide [320]. The material is stable in aqueous environment having a water penetration rate of 4.2 m³/h. In ceramic material the sesquioxide has been used as an oxidizing agent during manufacture [321] and as bits for

welldrilling [322]. Wear resistance is much lower though, than for tungsten carbide.

4.3. Other Silicon – Oxygen Compounds

Oxyhydrides of the composition $(HSiO_{1.5})_x]$ are obtained by the hydrolysis of trichlorosilane [323–325]. In organic solvents the product is formed as an amorphous powder or as transparent mica-like flakes [310], depending on the type of solvent. Well-defined, low molecular oligomers – the smallest [326], [327] being a cage of 8 silicon atoms arranged at the corners of a cube with 12 oxygen atoms forming the bridges along the edges – can be prepared by hydrolysis in a two-phase system [328–330]. Oligomers with x an even number ranging from 8 to 16 are obtained.

The Si_8-cube is also the smallest cage in zeolite structures; it is the 4 – 4 secondary building unit in zeolite A. Since the silver zeolite reacts with water evolving oxygen, ligand-to-metal charge transfers in the Si_8-cube are of interest in the context of processes involving photolysis of water by visible light [331]. By photochemical oxidation of tetrachlorosilane the trichlorosilanol is produced, a compound existing only in equilibria with others [332]. Utilizing structural possibilities new silicon – oxygen compounds were prepared, the oxygen taking part as the donor atom in penta-coordinate silicon alkoxide complexes. Alkoxysilanes react with metal hydrides to trialkoxy anions which then rearrange to the tetraalkoxy anion [333]

$$4 \, H \, Si(OR)_3 + 4 \, KH \rightarrow 4 \& H_2Si(OR)_3]^- K^+$$
$$\rightarrow 3 \& H \, Si(OR)_4]^- K^+ + SiH_4 + KH$$
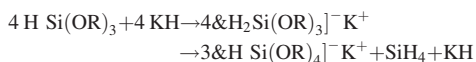
Likewise the reaction of silica with glycol is made possible through penta-coordinate complex formation around the silicon atom [334].
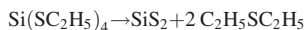
5. Silicon Sulfides

Silicon sulfide, SiS_2, M_r 92.18, mp 1090 °C, sublimation point 1130 °C, forms white, asbestos-like needles, which readily hydrolyze. It is formed from silicon and sulfur at 1100 – 1300 °C [335], but preferably at >1400 °C [336], [337]. Silicides react with sulfur at >700 °C,

hydrogen sulfide at 1100 – 1200 °C, or sulfur chlorides (e.g., S_2Cl_2, at its boiling point of 135 °C). The SiS_2 formed must be recovered from the other reaction products (e.g., MgS) by sublimation.

The simplest laboratory method consists of a combination of these two processes. The reaction of Mg_2Si with S_2Cl_2 is used to start the reaction of silicon with sulfur. A mixture of 3 parts by weight of Si, 0.5 parts by weight of Mg_2Si, and 8 parts by weight of sulfur is impregnated with 1 part by weight of S_2Cl_2 in a glass tube and heated at one point with a small flame. The reaction starts with a glow. The SiS_2 formed is sublimed off in a vacuum [336].

On a large scale, SiS_2 can be produced by the thermal decomposition of esters of thiosilicic acid. The ethyl ester decomposes at 300 °C:

$$Si(SC_2H_5)_4 \rightarrow SiS_2 + 2 \, C_2H_5SC_2H_5$$

The reaction temperature can be lowered to 200 °C by adding sulfur [336], [338].

The formation of silicon – sulfur compounds, including SiS_2, has also been observed during the drilling of holes in crystalline silicon plates by laser beams in an atmosphere of sulfur hexafluoride [339].

Direct synthesis from the elements is still being carried out and improved. Continuous feeding into reactors [340] allows a lower reaction temperature of 800 °C to be used. Under a pressure of 2.5 – 6.0 GPa and 1000 – 1200 °C the conversion to the sulfide is almost complete, yielding four different polymorphic modifications of silicon sulfide [341].

Silicon disulfide can be conveniently obtained from silica, carbon, and sulfur vapors in an atmosphere of hydrogen sulfide above 1130 °C [342]. The product consists of glassy solid and needle-like crystals.

Silicon disulfide reacts with ammonia to give silicon nitride, Si_3N_4. Between 800 and 1400 °C the nitride is obtained as an amorphous powder. If a lower temperature and silicon disulfide in the form of whiskers are used, the product retains the morphological characteristics and consists of silicon nitride whiskers [343].

Because of their volatility, the formation of silicon sulfides at high temperature is utilized for desiliconization in purification processes. For example, pure zirconium oxide is obtained by

conversion of silica impurities followed by vaporization at 1300 °C [344]:

$$SiO_2 + C + 2\,S \rightarrow SiS_2 + CO_2$$
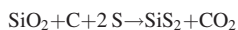
Glassy phases containing silicon disulfide can be used as solid electrolytes in conducting glasses for batteries, especially microbatteries. A system consisting of a $Li_2S - SiS_2(P_2S_5)$ phase between a $Li/V_2O_5 - TeO_2$ couple has an open circuit voltage of 2.8 – 3.1 V [345], [346].

From a melt of equimolar amounts of silicon disulfide and lithium sulfide, lithium silicon sulfide is obtained in three phases: equilibrium, metastable crystalline, and glassy Li_2SiS_3 [347]. The conductivity is greatly enhanced by the addition of lithium bromide [348], [349], iodide [350], [351], or chloride [349]. The highest conductivity reported [333] is 1.8 s/cm at 25 °C, measured in a glass consisting of the phase $0.24\,SiS_2 - 0.36\,Li_2S - 0.4\,LiI$.

Glassy phases containing silicon disulfide are also obtained by the action of elemental silicon on arsenic sulfide [352]

$$5\,Si + 2\,As_2S_3 \rightarrow 2\,SiS_2 + 2\,As_2Si$$
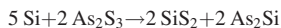
6. Silicon Nitrogen Compounds

The prevailing chemical of this class is the silicon nitride, Si_3N_4, a solid of regular valence composition that has found commercial use in high-temperature engineering ceramics and in the form of whiskers as reinforcing material in cermets. A number of processes are now available to produce the nitride as a powder, a film, or as needles.

For nitride production, choice of process is largely influenced by the material, of having it at disposal or having to dispose of it. Byproducts and wastes from other production lines of silicon chemistry manufacturing decide on availability and necessity.

The direct synthesis from the elements has been carried out only to study the effects on silicon surfaces. Between 1350 and 1450 °C the nitride is formed [353]. Nitridation is enhanced by the presence of iron in silicon and by hydrogen in the nitrogen atmosphere, the latter also increasing the ratio of α-/β-silicon nitride [354]. Gas-phase reactions of monosilane and ammonia [355] can be used for deposition of silicon nitride.

Of the silicon halides, the tetrachlorosilane can be reacted with a nitrogen – hydrogen mixture giving amorphous nitride [356]

$$3\,SiCl_4 + 2\,N_2 + 12\,H \rightarrow Si_3N_4 + 12\,HCl$$

Hexachlorodisilane is useful to obtain silicon nitride whiskers [357] by chemical vapor deposition in the course of the reaction with ammonia. Between 950 and 1700 °C the resulting whiskers are coiled in shape; they exhibit good dispersibility [358]. The reaction can be extended to include other halide derivatives of disilane [357]. Finely divided nitride is obtained using silicon fluorides as the silicon source [359]. Making silicon nitride from the disulfide can result in needles [343], [360]. By reacting evaporated silicon disulfide with ammonia above 1130 °C [361] or in a two-step process first at 800 °C, then at 1400 °C [362] the product is a powder of α-Si_3N_4. During the synthesis of silicon carbide the nitride is formed through contact of the carbide with nitrogen at temperatures below 2050 K [363]. For a variety of silicon or nitrogen sources the reaction temperature of 900 to 1100 °C seems practical, the energy furnished by a plasma induced by radio frequency discharge [364]. A critical review of thermal plasma reactions leading to silicon nitride from different silicon sources presents data on the thermodynamics and nucleation kinetics [365]; i.e., a high supersaturation of silicon should always be avoided.

7. Silicon Borides

The long-known binary silicon borides, SiB_3 and SiB_6, are produced simultaneously when the constituent elements are heated between carbon electrodes in an electric furnace [366]. Phases with the composition SiB_4 have since been produced and evaluated for a large number of application areas.

The compound SiB_4 is produced from its elements at 1090 – 1370 °C by resistance heating and is purified by treatment with a mixture of nitric and hydrofluoric acids. It can also be produced from boron trioxide and silicon [367]. It is used as a refractory material in blast furnaces. Its use as a catalyst for the liquid-phase oxidation of alkenes with organic hydroperoxides to form oxiranes has also been reported

[368]. Mixed phases of silicon borides and molybdenum silicides resistant to oxygen up to 1600 °C are prepared by sintering a pasty mixture of these materials with colloidal silica at 1300 – 1500 °C. They can be used as abrasives and as highly refractory materials [369].

References

1 A. Stock: *Hydrides of Boron and Silicon*, Ithaca, New York 1933; Z. Elektrochem. 32 (1926) 341.

2 A. G. McDiarmid, *Quart. Rev.* **10** (1956) 208.

3 *Gmelin*, System. no. 15, part B, 227 ff.

4 A. Stock, C. Somieski, *Ber. Dtsch. Chem. Ges.* **49** (1916) 125, 155.

5 H. J. Emeleus, A. F. Maddock, *J. Am. Chem. Soc.* (1946) 1131.

6 H. Clasen, *Angew. Chem.* **70** (1958) 179.

7 W. C. Johnson, S. Isenberg, *J. Am. Chem. Soc.* **57** (1935) 1349.

8 A. E. Finholt, A. C. Brown, K. E. Wilzbach, H. I. Schlesinger, *J. Am. Chem. Soc.* **69** (1947) 2692.

9 Internat. Standard Electric Corp., US 2 888 328, 1956.

10 Kali-Chemie, DT 1 034 159, 1956; DE-AS 1 049 835, 1956.

11 Allied Chem. Corp., DT 1 080 531, 1959.

12 Standard Telephone & Cables, GB 832 333 and 832 334, 1956.

13 W. Sundermeyer, O. Glemser, *Angew. Chem.* **70** (1958) 625.

14 Ethyl Corp., EP 300 320, 1989 (J. A. Bossier, D. M. Richards, L. T. Crasto).

15 Ethyl Corp., US 4 778 668, 1988 (E. M. Marlett, R. N. DePriest).

16 Union Carbide, CA 1 151 305, 1983 (W. C. Breneman).

17 Tokuyama Soda, JP 59 174 516, 1984.

18 Union Carbide, CA 1 184 017, 1985 (W. C. Breneman, L. M. Coleman).

19 Tokuyama Soda, JP 60 060 917, 1985.

20 Solavolt International, US 4 542 004, 1985 (K. R. Sarma, C. S. Chanley).

21 J. Moriyama: "Production of High-Purity Silicon. A Review, " *Suiyokaishi* **20** (1988) no. 10, 671 – 679.

22 Mitsui Toatsu Chemicals, JP 58 156 522, 1983.

23 Toa Gosei Chemical, JP 01 234 316, 1989 (S. Watanabe, T. Hattori).

24 Toa Gosei Chemical, JP 61 191 512, 1986 (O. Hirano *et al.*).

25 Bell Téléphone, BE 566 348, 1960.

26 Licentia Patentverwertung, DT 1 073 460, 1958.

27 V. V. Balabanov *et al.*, *Vysokochist. Veshchestva* **6** (1990) 60 – 66.

28 Toshiba Corp., JP 58 048 417, 1983.

29 Seiko Instruments and Electronics, JP 63 132 420, 1988 (N. Shimizu, M. Shinho).

30 Canon, DE 3 208 494, 1982 (I. Shimizu, K. Ogawa, E. Inoue).

31 S. W. Depp, W. E. Howard, *Spektrum der Wissenschaft* 1993, 547.

32 Bell Laboratories, US 4 579 752, 1986 (L. H. Dubois, R. G. Nuzzo).

33 J. R. Hartmann, J. Famil-Ghiriha, M. A. Ring, H. E. O'Neal, *Combust. Flame* **68** (1987) no. 1, 43 – 56.

34 Pioneer Electric Corp., JP 61 090 726, 1986 (K. Kitahara, T. Shimada).

35 A. Y. Adamova *et al.*, *Kim. Vys. Energ.* **15** (1981) no. 4, 365 – 369.

36 C. B. Moore, J. Biedrzycki, F. W. Lampe, *J. Am. Chem. Soc.* **106** (1984) no. 25, 7761 – 7765.

37 T. N. Bell, K. A. Perkins, P. G. Perkins, *J. Chem. Soc. Chem. Commun.* 1980, no. 22, 1046 – 1047.

38 H. Buff, F. Wöhler, *Liebigs Ann. Chem.* **104** (1857) 94.

39 G. Braver: *Handbuch der präparativen anorganischen Chemie,* vol. 1, F. Enke, Stuttgart 1960.

40 Wacker, DT 1 067 010, 1951; BASF, DT 1 105 389, 1960.

41 Linde, US 2 499 009, 1947.

42 Union Carbide, US 2 595 620, 1948.

43 Dynamit Nobel, BE 856 480, 1977.

44 Wacker, DT 623 290, 1977.

45 Telecomunicações Brasileiras, BR 8 006 892, 1980 (J. W. C. Carvalho *et al.*).

46 A. C. F. de Arruda, L. C. Barbosda, *Congr. Ann. ABM, 35th*, vol. 3, Assoc. Brasileira Metais, Sao Paulo 1980, pp. 375 – 390.

47 V. F. Popenko *et al.*, SU 833 494, 1981.

48 General Electric, DE 3 303 903, 1983 (A. Ritzer, N. B. Shah, E. Daniel).

49 Toa Nenryo, JP 63 170 210, 1988 (H. Yamada, H. Ogawa, T. Hosokawa, M. Tachikawa).

50 Hüls, DE 3 809 784, 1989 (K. Ruff).

51 Elkem, DE 3 938 897, 1990 (K. Forwald, G. Schüssler, O. Soerli).

52 High Pure Silicon Co., JP 02 145 413, 1990 (M. Takaguchi, N. Moriika).

53 T. C. Hwang, H. H. Hsieh, *Energy Res. Abstr.* **24** (1984) no. 24.

54 K. X. Li, S. H. Peng, T. C. Ho, *AIChE Symp. Ser.* **84** (1988) 114 – 125.

55 Nippon Aerosil Co., DE 3 230 590, 1983 (T. Ito, H. Hori).

56 Mitsubishi Kakoki Kaisha, JP 02 172 811, 1990 (K. Akaike).

57 C. Zhang, CN 87 100 535, 1987.

58 Shin-Etsu Chemical Ind., JP 58 161 915, 1983.

59 Osaka Titanium Co., JP 56 073 617, 1981.

60 Mitsui Toatsu Chemicals, JP 63 100 014, 1988 (K. Inoe *et al.*).

61 General Electric, US 4 390 510, 1983 (A. Ritzer, B. Shah, D. E. Silva).

62 Mitsubishi Metal Corp., JP 57 003 711, 1982.

63 Council of Sci. and Ind. Research, IN 166 734, 1990 (V. G. Neurgaonkar *et al.*).

64 Denki Kagaku Kogyo, JP 60 081 010, 1985.

65 Motorola, EP 133 209, 1985 (W. M. Ingle, S. M. Peffley, H. S. N. Setty).

66 High Pure Silicon Co., JP 51 118 017, 1982.

67 Wacker, DE 3 024 319, 1982 (A. Goeppinger *et al.*).

68 Nippon Steel Corp., JP 63 112 410, 1988 (M. Onozawa).

69 Shin-Etsu Chemical Ind., JP 57 140 309, 1982.

70 Mitsubishi Kakoki Kaisha, JP 63 008 207, 1988 (K. Akaike).

71 Nippon Steel Corp., JP 62 021 707, 1987 (M. Onozawa).

72 Mitsubishi Metal Corp., JP 62 288 109, 1987 (E. Kimura, K. Ogi, T. Kurashige).

73 Wacker, DE 3 341 340, 1985 (A. Schnegg, R. Rurlaender).

74 J. Y. P. Mui, D. Seyferth, *Sci. Tech. Aerosp. Rep.* **19** (1981) no. 18.

75 J. Y. P. Mui, D. Seyferth, *Energy Res. Abstr.* **6** (1981) no. 6.

76 Rhône-Poulenc, EP 100 266, 1984 (J. L. Lepage, G. Simon).

77 Osaka Titanium, JP 57 140 312, 1982.

78 Osaka Titanium, JP 57 140 311, 1982.

79 Osaka Titanium, JP 57 129 817, 1982.

80 Denki Kagaku Kogyo, JP 59 035 017, 1984.

81 Denki Kagaku Kogyo, JP 55 045 919, 1984.

82 W. M. Ingle, M. S. Peffley, *J. Electrochem. Soc.* **132** (1985) no. 5, 1236 – 1240.

83 Mitsui Toatsu, JP 01 313 317, 1989 (K. Inoue *et al.*).

84 Mitsui Toatsu, JP 63 095 107, 1988 (K. Inoue *et al.*).

85 Mitsui Toatsu, JP 63 095 108, 1988 (K. Inoue *et al.*).

86 Mitsui Toatsu, JP 63 100 015, 1988 (K. Inoue *et al.*).

87 Mitsui Toatsu, JP 63 095 109, 1988 (K. Inoue *et al.*).

88 Mitsui Toatsu, JP 63 100 016, 1988 (K. Inoue *et al.*).

89 Mitsui Toatsu, JP 63 095 110, 1988 (K. Inoue *et al.*).

90 Osaka Titanium, JP 57 156 319, 1982.

91 Osaka Titanium, JP 58 011 042, 1983.

92 Z. Shen, J. Wang, CN 85 107 465, 1987.

93 Mitsui Toatsu, JP 63 095 111, 1988 (K. Inoue *et al.*).

94 Nippon Kokan, EP 255 877, 1988 (N. Yoneda *et al.*).

95 Nippon Kokan, JP 01 100 011, 1989 (K. Ozaki *et al.*).

96 Mitsubishi Metal Corp., JP 62 256 713, 1987 (E. Kimura, K. Ogi, T. Kurashige).

97 Idemitsu Kosan, JP 62 270 413, 1987 (N. Tanaka).

98 High Pure Silicon Co., JP 57 156 318, 1982.

99 V. F. Kochubei, *Otkrytiya, Izobret., Prom. Obraztoy, Tovarnye, Znaki* 1981, no. 45, 122.

100 Osaka Titanium, JP 62 235 205, 1987 (S. Morimoto).

101 Mitsui Toatsu, JP 63 250 484, 1988 (M. Murakami *et al.*).

102 Wacker, GB 906 617, 1960.

103 Siemens & Halske, DT 955 415, 1955.

104 Wacker, DT 1 134 973, 1958.

105 Union Carbide, DT 2 507 864, 1975.

106 Smiel, DT 2 852 598, 1979.

107 Bochkarev, SU 504 699, 1976.

108 Dynamit Nobel, DT 1 767 667, 1976.

109 Wacker, DT 2 546 957, 1977.

110 Akademie der Wissenschaft, DL 135 613, 1979.

111 Akademie der Wissenschaft, DL 136 493, 1979.

112 A. A. Efremov, Y. D. Zel'venskii, *Tr. Mosk. Khim. Tsuetn. Inst. im. D. J. Mendeleeva* **96** (1977) 4 – 10.

113 Z. A. Elunika, V. J. Lobov, J. P. Polokhina, *Tovetn. Met.* 1980, no. 3, 72 – 73.

114 Wacker, DT 2 558 183, 1977.

115 B. Koehler et al., DD 158 322, 1983.

116 L. Y. Shvartsman *et al.*, *Vysokochist, Veshchestva* 1989, no. 5, 136 – 140.

117 Dow Corning, EP 107 784, 1984 (R. S. Doornbos).

118 General Electric, DE 3 423 611, 1986 (W. D. Kray).

119 General Electric, JP 59 097 519, 1984.

120 General Electric, JP 59 097 518, 1984.

121 Motorola, US 4 409 19, 1983 (R. D. Darnell, W. M. Ingle).

122 Union Carbide, DE 3 709 577, 1987 (W. C. Breneman, C. C. Yang, G. Henningsen).

123 Hüls Troisdorf, DE 3 642 285, 1988 (B. Falk, W. Graetz, K. Ruff).

124 Osaka Titanium, JP 73 047 500, 1973.

125 Mitsubishi Metal, JA 78 097 996, 1978.

126 Texas Instruments, US 3 963 838, 1976.

127 Pennish, US 4 176 166, 1979.

128 Mitsubishi Paper Mill, JA 77 144 959, 1978.

129 Wacker, BE 857 689, 1978.

130 Harris-Intertype, US 3 935 040, 1976.

131 Siemens, DT 2 535 813, 1976.

132 Hitachi, JA 77 044 166, 1977.

133 Dow Corning, US 3 961 003, 1976.

134 Kuratomi, JA 74 076 721, 1974.

135 Kuratomi, JA 74 059 729, 1974.

136 Union Carbide, US 3 900 660, 1975.

137 Motorola, NL 75 008 684, 1976.

138 Siemens, DT 2 508 802, 1976.

139 Hitachi, JA 76 027 077, 1976.

140 Nippon Electric, JA 76 086 080, 1976.

141 Siemens, BE 841 241, 1976.

142 Osaka Titanium, JP 02 279 512, 1990 (M. Kuramoto, T. Nakai).

143 Cabot, BE 850 891, 1977.

144 IBM, US 3 974 003, 1976.

145 Siemens, DT 2 519 572, 1976.

146 UKR Agric Acad. ZAP, SU 660 968, 1980.

147 Hiratsuka Resin, JA 76 033 149, 1976.

148 Dow Corning, US 2 571 884, 1950.

149 BASF, FR 1 009 837, 1948.

150 Monsanto, GB 815 276, 1950.

151 Th. Goldschmidt, DT 685 728, 1936. Union Carbide Belge, BE 562 868, 1956.

152 Carborundum, US 1 271 713, 1918.

153 Stauffer Chem. Co., US 2 739 041, 1953.

154 Cabot, US 2 843 458, 1955.

155 E. Grunder, J. Elöd, *Z. Anorg. Allg. Chem.* **195** (1931) 269.

156 Konsort. für Elektrochem. Ind., GB 176 811, 1922.

157 Degussa, DT 1 079 015, 1960.

158 Stauffer Chem. Co., GB 865 939, 1959.

159 Stauffer Chem. Co., *Chem. Eng.* **69** (1962) 71.

160 L. V. Laine, SU 108 316, 1957.
161 Kali-Chemie, DT 901 412, 1954.
162 Horizons, GB 735 617, 1953.
163 Union Carbide, EP 26 860, 1979.
164 Mitsui Toatsu Chemicals, JP 59 195 519, 1984.
165 Mitsui Toatsu Chemicals, JP 59 184 720, 1984.
166 Wacker, DE 3 503 262, 1986 (R. Standigl, R. Griesshammer).
167 Int. Standard Electric, DAS 1 074 560, 1958.
168 Du Pont, US 2 820 698, 1954.
169 Bell Telephone Lab., US 2 812 235, 1955.
170 Westinghouse Electric, DT 1 088 473, 1957.
171 Western Electric, DT 1 029 811, 1956.
172 G. A. Wolff, US 2 877 097, 1958.
173 H. C. Theuerer, *J. Electrochem. Soc.* **107** (1960) 29.
174 G. G. Deryatykh, N. Kh. Agliulov, A. E. Wikolaev, E. M. Shcheplyagin, *Zh. Prikl. Khim. (Leningrad)* **53** (1980) no. 8, 1845 – 1848.
175 Denki Kagaku Kokyo, JP 02 196 014, 1990 (M. Fujimoto, M. Shinoyama, H. Matsumura).
176 Bell Telephone Lab., US 4 282 196, 1981 (T. Kometani, D. L. Wood).
177 General Electric, GB 309 393, 1928.
178 Union Chimique Belge, GB 1 042 076, 1951.
179 Faustel Metallurgie, US 2 665 997, 2 665 998, 1950.
180 E. Fitzer, DE 178 779, 1952.
181 Mitsui Toatsu Chemicals, JP 59 162 121, 1984.
182 Mitsui Toatsu Chemicals, JP 59 232 910, 1984.
183 Mitsui Toatsu Chemicals, JP 59 207 829, 1984.
184 Toa Gosei Chemical, DE 3 623 493, 1987 (M. Ito, T. Hattori, Y. Miwa).
185 Toa Gosei Chemical Industry, JP 63 021 211, 1988 (M. Ito, T. Hatsutori, Y. Miwa).
186 Mitsui Toatsu Chemicals, JP 61 205 614, 1986 (A. Hiai, K. Wakimura, T. Use).
187 Mitsui Toatsu Chemicals, JP 59 207 830, 1984.
188 Mitsubishi Metal Corp., JP 62 070 425, 1987 (H. Ikeda).
189 Mitsubishi Metal Corp., JP 63 089 414, 1988 (H. Ikeda, M. Tsunashima).
190 Mitsubishi Metal Corp., JP 62 036 014, 1987 (Y. Kuroda, K. Yamakawa).
191 Mitsubishi Metal Corp., JP 63 091 138, 1988 (H. Ikeda, M. Tsunashima, M. Sato).
192 Mitsubishi Metal Corp., EP 282 037, 1988 (H. Ikeda, M. Tsunashima).
193 Mitsubishi Metal Corp., EP 264 722, 1988 (H. Ikeda, M. Tsunashima, M. Sato).
194 Mitsubishi Metal Corp., JP 63 210 015, 1988 (H. Ikeda, M. Tsunashima, M. Sato).
195 Mitsubishi Metal Corp., JP 01 192 716, 1989 (K. Ogi, T. Kurashige, E. Kimura).
196 NEC Corp., JP 62 296 511, 1987 (A. Ishitani).
197 Dow Corning, FR 2 486 057, 1982 (J. H. Gaul, D. R. Weyenberg).
198 Toa Gosei Chemical, JP 61 295 372, 1986 (S. Motojima, T. Hattori, N. Ishikawa).
199 Toa Gosei Chemical, JP 63 277 599, 1988 (S. Motojima, T. Hattori, N. Ishikawa).
200 Mitsubishi Metal Corp., JP 01 301 507, 1989 (T. Hirai, H. Ikeda).
201 Mitsui Toatsu Chemicals, JP 62 143 839, 1987 (T. Iwao, K. Morii, Y. Tajima).
202 Mitsui Toatsu Chemicals, JP 62 143 840, 1987 (T. Iwao, K. Morii, Y. Tajima).
203 Mitsui Toatsu Chemicals, JP 61 227 914, 1986 (T. Iwao, K. Morii, Y. Tajima).
204 Wacker, DE 3 518 620, 1986 (R. Griesshammer, H. Herrmann, R. Standigl).
205 B. S. Suresh, D. K. Padma, *Polyhedron* **5** (1986) no. 10, 1579 – 1579.
206 A. Kornick, M. Binnewies, *Z. Anorg. Anal. Chem.* **587** (1990) 157 – 166.
207 Dynamit Nobel, DE 3 615 509, 1987 (B. Falk, K. Ruff, K. Schrage).
208 P. Voss, Ph.D. thesis, Aachen 1961.
209 P. Voss, Dissertation, Aachen 1962.
210 H. Bloching, Dissertation, Freie Universität Berlin 1961.
211 Du Pont, US 2 840 588, 1956.
212 Kemira Oy, FI 822 32, 1990 (V. P. Judin, A. Hayha, P. Koukkari).
213 Kemira Oy, US 5 077 027, 1991 (V. P. Judin, A. Hayha, P. Koukkari).
214 Semiconductor Energy Laboratory Co., JP 60 054 913, 1985.
215 M. Janai *et al.*, *J. Appl. Phys.* **52** (1981) no. 5, 3622 – 3624.
216 H. Matsumura, H. Ihara, T. Uesugi, *J. Appl. Phys.* **57** (1985) no. 12, 5483 – 5485.
217 H. Matsumura, T. Uesugi, H. Ihara, *Mater. Res. Soc. Symp. Proc.*, **49** (1985) 175 – 180.
218 État Français, FR 2 620 736, 1989 (Y. Pauleau, P. Lami, J. Pelletier).
219 Semiconductor Energy Laboratory Co., JP 60 144 940, 1985 (S. Yamazaki).
220 K. Zhang, Q. Yuan, *Huaxue Shijie* **23** (1982) no. 12, 353 – 354.
221 Schumacher, GB 2 028 289, 1980.
222 Ceres Corp., WP 8 001 489, 1980.
223 Schumacher, US 4 084 024, 1978.
224 Siemens, JA 77 035 605, 1977.
225 Western Electric, US 3 932 160, 1976.
226 Nippon Teleg. & Tel., JA 77 088 348, 1977.
227 Nippon Teleg. & Tel. and Furukawa Electric, JA 77 104 936, 1977.
228 Nippon Teleg. & Tel., JA 79 127 914, 1979.
229 Fuji Photo Film, JA 80 167 119, 1981.
230 Micron Technology Inc., US 5 082 524, 1992 (D. A. Cathey).
231 Schumacher, US 4 318 942, 1982 (L. M. Woerner, E. B. Moore).
232 Battelle Dev., US 3 990 953, 1976.
233 Exxon Res. & Eng., US 4 192 720, 1980.
234 Licentia Patentverwertung, DT 2 929 669, 1981.
235 Tokyo Shibaura Electric, JA 78 140 311, 1979.
236 UBE Industries, GB 2 020 264, 1979.
237 Asahi Glass, JA 79 134 098, 1979.

238 Asahi Glass, JA 79 160 600, 1980.

239 Rosenthal, DT 2 635 167, 1977.

240 B. Armas, C. Combescure, G. Male, M. Morales, *Less-Common Met.* **67** (1979) no. 2, 449 – 453.

241 Toyota Cent. Res. & Dev., JA 75 108 183, 1977.

242 Hitachi, GB 19 915, 1980.

243 Phillips Petroleum, BE 858 462, 1978.

244 Asahi Glass, JP 62 070 219, 1987 (K. Sato *et al.*).

245 K. Zhang *et al.*, *Huaxue Shiji* **5** (1983) no. 4, 251 –253.

246 Dow Corning, EP 301 678, 1989 (K. G. Sharp, J. J. D'Errico).

247 H. Schmaelzer, E. Hengge, *J. Organomet. Chem.* **225** (1982) no. 1, 171 – 176.

248 M. Schmeisser, M. Schwarzmann, *Z. Naturforsch.* B 116 (1956) 278.

249 Kali-Chemie, DT 955 414, 1954.

250 K. Friedrich, Thesis, RWTH-Aachen 1964.

251 Licentia Patentverwertung, DT 1 045 381, 1957.

252 Morrizons, GB 735 617, 1953.

253 Kali-Chemie, DT 901 412, 1954.

254 B. Rubin, G. H. Moates, J. R. Wenier, *J. Electrochem. Soc.* **104** (1957) 656.

255 Japan Telegram & Telephone, JA 13 669, 1988.

256 Texas Instruments, US 4 154 870, 1979.

257 Int. Telephone & Telegraphe, US 3 961 926, 1976.

258 H. Schäfer, *Chem.-Ztg.* **75** (1951) 48.

259 E. Zintl *et al.*, *Z. Anorg. Chem.* **245** (1940) 1.

260 Goodrich, DT 1 079 608, 1956.

261 O. K. Botoinkin, SU 139 657, 1960.

262 Fumio Hori, JP 59 008 613, 1984.

263 J. M. Huber, EP 176 770, 1986 (D. E. Schramm).

264 L. Brewer, *Chem. Rev.* **52** (1953) 39.

265 W. Blitz, P. Ehrlich, *Naturwissenschaften* **26** (1938) 188.

266 G. Grube, H. Speidel, *Z. Elektrochem.* **53** (1949) 339.

267 H. v. Wartenberg, *Z. Elektrochem.* **53** (1949) 343.

268 H. Schäfer, R. Hörnle, *Z. Anorg. Allg. Chem.* **263** (1959) 261.

269 J. Berak, D. Grzeskowiak, *Zesz. Nauk. Politech. Slask. Vhem.* **88** (1979) 154 – 155.

270 Kemanord, RD 199 058, 1980.

271 A. Marcks, H. Hausner, *Therm. Anal. Proc. Int. Conf. 6th* **2** (1980) 223 – 228.

272 Hammatsu, NL 74 006 827, 1975.

273 Hitachi, DT 2 365 056, 1975.

274 Fujitsu, JA 79 018 689, 1979.

275 Stepanov, SU 423 203, 1975.

276 Hoya Glass Works, DT 2 443 718, 1975.

277 Unitika, JA 74 041 469, 1975.

278 Richter, DL 120 190, 1976.

279 Teijin Lens, JA 80 110 127, 1980.

280 BFG Glassgroup, BE 859 428, 1978.

281 AS Phys. Metall. Inst., SU 609 121, 1979.

282 Sony Corp., JA 79 031 721, 1979.

283 ITT Industries, FR 2 362 089, 1978.

284 Matsushita Elec. Ind., JA 79 024 866, 1979.

285 M. Schmitt, FR 2 369 103, 1978.

286 Matsushita Elec. Ind., JP 63 276 724, 1988 (K. Kimura *et al.*).

287 NHK Spring Co., JP 62 071 665, 1987 (T. Ebihara, T. Yokoo).

288 S. Yoshida, S. Misawa, *Denshi Gijutsu Sogo Kenkyusho Iho.*, **44** (1980) no. 1/2, 14 – 22.

289 United States Dept. of Energy, US 389 802, 1983 (J. V. Milewski).

290 Lonza, DT 2 531 481, 1976.

291 Osaka Titanium, JA 74 098 807, 1975.

292 Suzuki, DT 2 909 104, 1979.

293 Toyota Chuv Kenkyusho, JA 76 048 799, 1976.

294 Lucas J. Industries, GB 1 470 171, 1977.

295 N. Azuma, T. Yamada, S. Kuwabare, *Yogyo Kyokaishi* **86** (1978) no. 9, 418 – 424.

296 Ceraver, BE 858 704, 1978.

297 Bludov, SU 438 050, 1975.

298 Victor Co. of Japan, JA 75 038 200, 1976.

299 E. Zintl *et al.*, *Z. Anorg. Allg. Chem.* **245** (1940) 1.

300 I.G. Farbenind., CH 215 137, 1939.

301 Duisberg, US 2 242 497, 1939.

302 Kawasaki Steel, JA 78 134 794, 1979.

303 Toyota Motor Co., DE 3 602 647, 1986 (S. Abe, M. Ogawa).

304 Dow Corning, US 5 051 248, 1991 (G. N. Bokerman, J. P. Canady, C. S. Kuivida).

305 O. N. Carlson, F. A. Schmidt, *Proc. Vac. Metall. Conf. Spec. Met. Melting Process* 1985, 129 – 136.

306 L. M Ericsson, SE 450 391, 1987 (T. S. Ganev, M. Jansson).

307 K. L. Day, B. Donn, *Science* **4365** (1978) 307 – 308.

308 B. S. Suresh, D. Krishnamurth Padma, *J. Chem. Soc. Dalton Trans.*, 1984, no. 8, 1779 – 1780.

309 V. Belot *et al.*, *J. Non-Cryst. Solids* **127** (1991) no. 2, 207 – 214.

310 E. Wilberg, W. Simmler, *Z. Anorg. Allg. Chem.* **283** (1956) 401.

311 Hitachi, JP 59 074 637, 1984.

312 Asahi Glass, JP 55 058 230, 1980.

313 Asahi Glass, JP 55 145 739, 1980.

314 Toppan Printing Co., JP 02 122 924, 1990 (M. Sekiguchi *et al.*).

315 Y. Wang, C. Jiang, *Bandaoti Xvebao*, **7** (1986) no. 6, 596 – 601.

316 N. A. Takasaki, E. Ikawa, Y. Kurogi, *J. Vac. Sci. Technol. B* **4** (1986) no. 4, 806 – 811.

317 R. E. Stahlbush, W. E. Carlos, S. M. Prokes, *IEEE Trans. Nucl. Sci., NS-34* **6** (1987) part I, 1680 – 1685.

318 E. P. Bochkarev *et al.*, *Vysokochist. Veshchestva* **1** (1989) 73 – 77.

319 Ei Shokusan K. K., JP 62 183 899, 1987 (F. Baba, K. Kozono, T. Hashiguchi, K. Maemura).

320 Kubota Ltd., JP 62 250 910, 1987 (Y. Okumura, Y. Okamoto, K. Yanai).

321 Unisearch Ltd., WO 8 906 222, 1989 (J. A. Bourdillon *et al.*).

322 I. N. Buyanovskii *et al.*, *Trenie Iznos* **6** (1985) no. 1, 119 – 124.

323 A. Stock, F. Zeidler, *Ber. dtsch. chem. Ges.* **56** (1923) 986.

324 R. Müller, *Chem. Techn.* **2** (1950) 1.
325 G. H. Wagner, A. N. Pines, *Ind. Eng. Chem.* **44** (1952) 321.
326 R. Müller, R. Kohne, S. Sliwinski, *J. prakt. Chem.* **9** (1959) 71.
327 K. Larssow, *Ak. Kemi* **16** (1960) 215.
328 C. L. Frye, W. T. Collins, *J. Am. Chem. Soc.* **92** (1970) 5586.
329 H. Bürgi, G. Calzaferri, *J. Chromatography* **507** (1990) 481.
330 P. A. Agaskar, *Inorg. Chem.* **30** (1991) 2707.
331 G. Calzaferri, *Nachr. Chem. Tech. Lab.* **40** (1992) 1106.
332 R. Gooden, J. W. Mitchell, *J. Electrochem. Soc.* **129** no. 7, 1619.
333 R. J. P. Corrir, *Organometallics* **10** (1991) 3574.
334 M. Laine, *Nature* **353** (1991) 642.
335 W. Humpel, V. Haasy, *Z. Anorg. Allg. Chem.* **23** (1900) 32.
336 M. Schmeisser, H. Müller, W. Burgermeister, *Angew. Chem.* **69** (1957) 781.
337 L. E. Gorsh, G. N. Dolenko, ZZV, *Akad. Nauk. SSSR Neorg. Mater.* **15** (1979) no. 9, 1521 – 1523.
338 Kali-Chemie, DT 1 008 265, 1955, 1 029 810, 1957.
339 Mitsubishi Electric, JA 77 070 498, 1977.
340 Toyota Motor Corp., JP 63 079 716, 1988 (S. Abe, O. Kazuaki, M. Ogawa).
341 N. V. Tolstoguzov, *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.* 1991, no. 4, 22 – 25.
342 Asahi Chemical Industry, JP 62 252 310, 1987 (Y. Yamada, N. Tamura, K. Makita).
343 Rockwell International Corp., US 4 552 740, 1985 (P. E. D. Morgan, E. A. Pugar).
344 Asahi Chemical Industry, JP 62 252 321, 1987 (Y. Yamada, N. Tamura, K. Makita).
345 R. Creus *et al.*, *Mater. Sci. Eng. B* B 3 (1989) no. 1/2, 109 – 112.
346 J. H. Kennedy, Z. Zhang, *J. Electrochem. Soc.* **136** (1989) no. 9, 2441 – 2443.
347 B. T. Ahn, R. A. Huggins, *Mater. Res. Bull.* **25** (1990) no. 3, 381 – 389.
348 S. Sahami, S. W. Shea, J. H. Kennedy, *J. Electrochem. Soc.* **132** (1985) no. 4, 985 – 986.
349 J. H. Kennedy *et al.*, *Solid State Ionics* 18 – 19 (1986) no. 1, 368 – 371.
350 Matsushita Electric Industrial Co., JP 04 133 209, 1992 (K. Yamamura, K. Takada, S. Kondo).
351 J. H. Kennedy, Y. Yang, *J. Electrochem. Soc.* **133** (1986) no. 11, 2437 – 2438.
352 A. A. Godovikov, R. G. Kuryaeva, *Fiz. Khim. Skekla* **9** (1983) no. 4, 502 – 509.
353 P. Barlier, J. P. Torre, *Ann. Chim. (Paris)* **5** (1989) no. 8, 701 – 709.
354 N. J. Shaw, *Sci. Tech. Aerosp. Rep.* **20** (1982) no. 6, 113.
355 J. F. Lartigue, M. Ducarroir, B. Armas, *J. Mater. Sci.* **19** (1984) no. 9, 3079 – 3089.
356 P. M. Jeffers, S. H. Bauer, *J. Non-Cryst. Solids* **57** (1983) no. 1, 189 – 193.
357 Toa Gosei Chemical, JP 02 034 598, 1990 (S. Motojima, T. Hattori, N. Ishikawa).
358 Toa Gosei Chemical, JP 02 034 599, 1990 (S. Motojima, T. Hattori, N. Ishikawa).
359 Kemira Oy, DE 3 939 048, 1990 (V. P. Judin, A. Hayha, P. Koukkari).
360 P. E. D. Morgan, E. A. Pugar, *J. Am. Chem. Soc.* **68** (1985) no. 12, 699 – 703.
361 Asahi Chemical Industry, JP 62 252 304, 1987 (Y. Yamada, N. Tamura, K. Makita).
362 Asahi Chemical Industry, JP 62 252 303, 1987 (Y. Yamada, N. Tamura, K. Makita).
363 V. D. Pershin *et al.*, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **24** (1981) no. 11, 1323 – 1326.
364 Unión Explosives Río Tinto, ES 2 006 119, 1989 (F. Gómez Aleixandre *et al.*).
365 Y. Chang, R. M. Young, E. Pfender, *Plasma Chem. Plasma Processes* **7** (1987) no. 3, 299 – 316.
366 H. Moissan, A. Stock, *Ber. Dtsch. Chem. Ges.* **33** (1990) 2125.
367 Allis-Chalmers, US 3 427 131, 1969.
368 Texaco Dev., US 4 038 292, 1977.
369 Aktiebolag Kauthal, SW 201 850, 1966.

Further Reading

B. Arkles: *Silicon Compounds, Silanes*, "Kirk Othmer Encyclopedia of Chemical Technology", 5th edition, John Wiley & Sons, Hoboken, NJ, online DOI: 10.1002/0471238961.1909120101181112.a01.

M. Butts *et al.*: *Silicones*, "Kirk Othmer Encyclopedia of Chemical Technology", 5th edition, John Wiley & Sons, Hoboken, NJ, online DOI: 10.1002/0471238961.1909120918090308.a01.pub2.

R. de Jaeger, M. Gleria (eds.): *Silicon-Based Inorganic Polymers*, Nova Science Publishers, New York 2008.

P. R. Dvornic, M. J. Owen (eds.): *Silicon-Containing Dendritic Polymers*, vol. 2, Springer, Dordrecht 2009.