Research Article

Methods of trichlorosilane synthesis for polycrystalline silicon production. Part 2: Hydrochlorination and redistribution

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Abstract

Novel technical solutions and ideas for increasing the yield of solar and semiconductor grade polycrystalline silicon processes have been analyzed. The predominant polycrystalline silicon technology is currently still the Siemens process including the conversion of technical grade silicon (synthesized by carbon-thermal reduction of quartzites) to trichlorosilane followed by rectification and hydrogen reduction. The cost of product silicon can be cut down by reducing the trichlorosilane synthesis costs through process and equipment improvement. Advantages, drawbacks and production cost reduction methods have been considered with respect to four common trichlorosilane synthesis processes: hydrogen chloride exposure of technical grade silicon (direct chlorination, DC), homogeneous hydration of tetrachlorosilane (conversion), tetrachlorosilane and hydrogen exposure of silicon (hydro chlorination silicon, HC), and catalyzed tetrachlorosilane and dichlorosilane reaction (redistribution of anti-disproportioning reaction). These processes remain in use and are permanently improved. Catalytic processes play an important role on silicon surface, and understanding their mechanisms can help find novel applications and obtain new results. It has been noted that indispensable components of various equipment and process designs are recycling steps and combined processes including active distillation. They provide for the most complete utilization of raw trichlorosilane, increase the process yield and cut down silicon cost.

Keywords

trichlorosilane synthesis, polycrystalline silicon.

2.3. Trichlorosilane synthesis by hydrochlorination

The production of polycrystalline silicon using the Siemens method or the silane method involves the formation of large amounts of tetrachlorosilane ($SiCl_4$). The amounts of $SiCl_4$ obtained at different process stages depend on the process route used. The following tetrachlorosilane production amounts per 1 kg of polycrystalline silicon have been reported [1]:

1. 2–5 kg at the direct trichlorosilane synthesis stage;
2. 11–14 at the stage of polycrystalline silicon synthesis from trichlorosilane;
3. 22–27 during trichlorosilane disproportioning (the silane technology).

Tetrachlorosilane can be used for the production of aerosil, quartz crucibles, ethyl silicate in epitaxy processes and quartz fiber light guides. It is technically and econo-

Table 4. Approximate market prices for silicon and some silicon based compounds

Compound	Chemical formula	Purity (wt.%)	Price ($/kg)	Information source
Technical grade silicon	Si	98–99	1.75–2.07	www.metal.com
Trichlorosilane	$SiHCl_3$	99.9	6.3	http:/original.metal.com
Tetrachlorosilane	$SiCl_4$	99.9	1.2–1.86	www.zauba.com
Aerosil	SiO_2	99.8	0.5–0.8	www.china.com
Ethyl silicate	$Si(OC_2H_5)_4$	99.3	1.5–2.2	www.china.com
Dichlorosilane	SiH_2Cl_2	99.9–99.99	23.26–46.5	www.china.com
Silane	SiH_4	99.9999	55–90	alibaba.com
Solar grade silicon	Si	99.9999	12–19.2	www.metal.com

mically viable to recycle tetrachlorosilane in the silicon production route (Table 4).

From economic and technical standpoints tetrachlorosilane recycling after conversion to trichlorosilane is more appropriate. These methods will be addressed below.

2.3.1. Homogeneous tetrachlorosilane hydration (tetrachlorosilane conversion)

Homogeneous tetrachlorosilane hydration is based on the following reaction:

$$SiCl_4 + H_2 \rightleftarrows SiHCl_3 + HCl, \tag{3}$$

occurring at high temperatures (700–1400 °C) followed by rapid cooling (quenching) of the mixture. Hydration of organic compounds by hydrogen was first described in 1929 [2]. Motorola's patent (US, [3], 1979) taught passing a tetrachlorosilane and hydrogen mixture with a 1 : 1–1 : 3 molar ratio through the reaction chamber at 900–1200 °C. The mixture exposure duration should be several seconds. The trichlorosilane yield attained was 12–13 %. A higher trichlorosilane yield was achieved [4]. Tetrachlorosilane was hydrated in a graphite tube at 600 to 1200 °C with a $SiCl_4 : H_2 = 1 : 1–1 : 50$ molar ratio in equilibrium with trichlorosilane and hydrogen and rapid mixture cooling to 300 °C for 50 ms using a cooling liquid. This method proved to be power consuming due to the use of cooling liquid. Further development of the method was widely described in literature[1–5]. Other works suggested different process equipment[1], critical pressure exposure[2], and cooling at different rates after mixture output from the reaction zone[3]. It was recommended to achieve higher conversion efficiency by using different cooling methods[4] and different types of reaction mixture mass exchange[5].

Thermodynamical calculations of the $SiCl_4 - H_2$ system during $SiCl_4$ to $SiHCl_3$ conversion was carried out [5]. The best results {25%} in comparison with conventional one {20%} can be achieved at $T = 1100$ °C, 0.3 MPa pressure and a $H_2 : SiCl_4 = 4 : 1$ molar ratio.

Process simulation in an ideal replacement flow-type reactor [6] taking into account 63 possible reactions and 26 reaction products showed that the highest conversion efficiency (39,34%) is achieved at a $SiCl_4 : H_2 = 1 : 4$ molar ratio, $T = 1200$ °C and a $50,92$ K·s^{-1} cooling rate.

Tetrachlorosilane to trichlorosilane converters

The design of tetrachlorosilane to trichlorosilane converters is similar to that of silicon deposition reactors. A cooled reaction chamber contains electrically heated graphite rods or tubes (1200–1400 °C). On average one converter is intended for 2–5 silicon deposition reactors [7].

The growth of silicon production and the construction of new factories capable of more than 10,000 tpy silicon output required a number of modifications to tetrachlorosilane conversion process design. It was required to reduce the number of recirculation flows and the number of converters, cut down service costs and increase safety. Polycrystalline silicon equipment developers announced a single-flow 7500 tpy $SiCl_4$ converter [8]. The converter unit power growth trend persisted. Recently Silicon Products GmbH, Germany, designed a new converter type based on thermodynamical simulation of converter processes and tetrachlorosilane to trichlorosilane conversion kinetic model (Fig. 4).

This converter type has an up to 15000 kg/h $SiCl_4$ output and provides for a 16.5 wt.% (20.7 mol.%) conversion efficiency. If a company producing up to 10,000 tpy Si with a power cost of 0.05 $/kWh uses this converter its specific power consumption will decrease from 3 kWh/kg $SiHCl_3$ to 0.7 kWh/kg $SiHCl_3$. This will provide for an annual power cost saving of 230 mln. $/y.

There also was a converter design comprising a number of ring-shaped units and same-shaped heaters [9]. The heaters are coated with silicon carbide (SiC), niobium (NbC), hafnium or tantalum carbides or aluminum, tantalum (T_2O_5), zirconium (ZrO_2) or yttrium (Y_2O_3) oxides. This converter design provides for intense convective heat transfer optimizes heater temperature and increases converter service life.

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[1] Pat. DE 102005046703, 2007; Pat. US 5906799, 1999.
[2] Pat. US 2010/0008842A1, 2010.
[3] Pat. US 2012/0308465A1, 2012; Pat. WO 2006/081980, 2006.
[4] Pat. WO 2011/098064, 2011.
[5] Pat. US 8663573, 2014; Pat. US 9776878, 2017.

Figure 4. Tetrachlorosilane to trichlorosilane converter: (*a*) converter general appearance: (*1*) heater, (*2*) heated heat exchanger; (*b*) evaporator to converter reactant flow diagram: (*1*) evaporator, (*2*) converter, (*3*, *4*) liquid $SiCl_4$, and H_2 directed from evaporator to converter, (*5*) vapor/gas $SiCl_4$ and H_2 mixture at converter input, (*6*) heated converted vapor/gas $SiHCl_3$, $SiCl_4$, SiH_2Cl_2 and HCl mixture at converter output, (*7*) evaporator-cooled $SiHCl_3$, $SiCl_4$, SiH_2Cl_2 and HCl mixture, (*8*, *9*) converter enclosure water coolant input and output, (*10*, *11*) converter electrode water coolant input and output; (*c*) graphite heater.

Source: http://www.silicon-products-GmbH.com
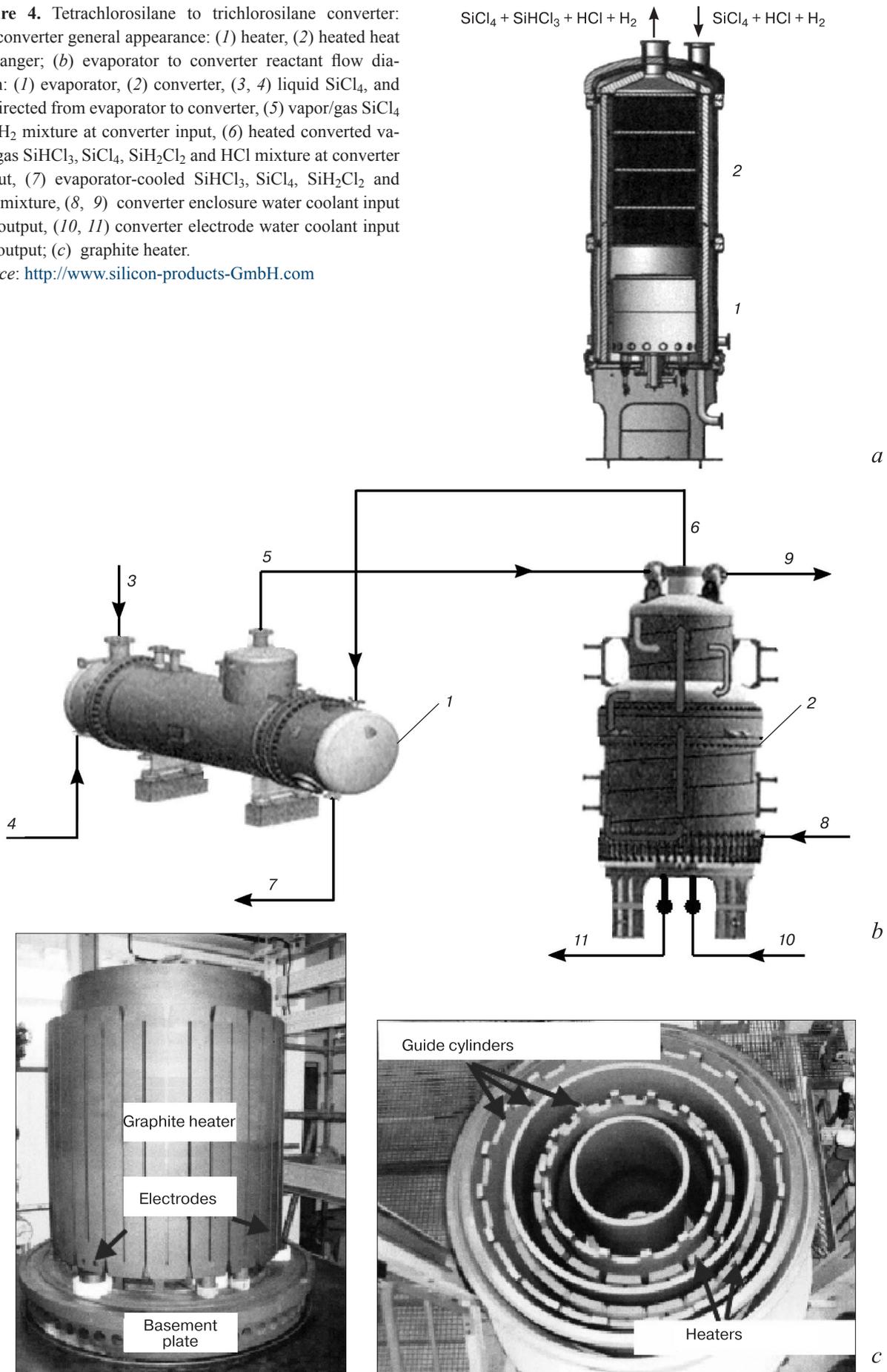
2.3.2. Production of trichlorosilane by silicon hydrochlorination (HC)

This method is alternatively referred to as tetrachloride hydration in the presence of silicon or cold hydration. The process is based on the following reaction:

$$3SiCl_4 + Si + 2H_2 \rightleftarrows 4SiHCl_3. \tag{4}$$

This reaction is weakly endothermic, the byproducts being dichlorosilane and hydrogen chloride in small quantities. It was reported [10] with reference to unpublished research data from Union Carbide (1948) that reaction (4) at atmospheric pressure and apparent equilibrium provided for a trichlorosilane yield of 16 mol.% which increased with pressure. Wagner and Ericsson (1952) patented a process in which hydrochlorination is carried out at 400–525 °C and ~35 MPa in the presence of copper, nickel or their compounds [11]. Depending on process temperature, pressure, $H_2 : SiCl_4$ molar ratio, contact duration and silicon powder coarseness, the authors could achieve a trichlorosilane yield of 14 to 38 mol.%.

Later on this reaction was studied in laboratory reactors with an immobilized silicon layer [12–16] and in laboratory fluidized bed reactors [17, 18].

According to the conclusions made by the authors of the above patent, $SiCl_4$ conversion to $SiHCl_3$ in the presence of silicon and hydrogen has thermodynamic restrictions. At normal atmospheric pressure and 500–600 °C, the trichlorosilane yield is within 20 mol.%. Higher trichlorosilane yields can be achieved by raising the process pressure to 30 MPa, but still a large portion of $SiCl_4$ is not converted. Catalyst addition increases the trichlorosilane yield and reduces the duration of the reaction initiation phase which is typically 30 min to 2 h. Increasing the $H_2 : SiCl_4$ molar ratio increases the trichlorosilane yield but reduces the specific yield of the reactor. In the absence of copper catalyst the process is mostly catalyzed by iron.

Studies of silicon particles by scanning electron microscopy, optical emission spectroscopy, energy dispersion X-ray spectroscopy (EDX) and other methods [15, 17] showed that the hydrochlorination reaction occurs in iron-rich surface regions.

The interaction of silicides with the $SiCl_4 + H_2$ was also studied [19–21]. The experimental data suggest that hydrochlorination may occur with the participation of silicides. Initially metal silicide forms in the $SiCl_4 + H_2$ mixture:

$$xSiCl_4 + 2xH_2 + yM \rightarrow M_ySi_x + 4xHCl, \tag{5}$$
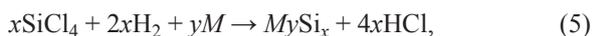
accompanied by the trichlorosilane formation reaction due to silicide destruction:

$$M_ySi_x + 3HCl \rightarrow M_ySi_{x-1} + SiHCl_3 + H_2, \tag{6}$$
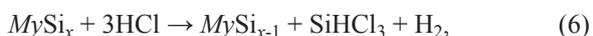
and further trichlorosilane formation occurs by the following reaction:

$$SiCl_4 + H_2 \rightleftarrows SiHCl_3 + HCl. \tag{7}$$

According to earlier data [20] the overall reaction includes adsorption of $SiCl_4$ molecules and transport of electrons to them from metal silicide atoms acting as a catalyst. The intermediate compound, silyl ($SiCl_2$) forms on the catalyst surface from adsorbed $SiCl_4$ molecules. Hydrogen molecules inject electrons into the solid phase whereby hydrogen chloride is generated on the surface. Trichlorosilane is formed as a result of sequential HCl addition to adsorbed $SiCl_2$.

It should also be taken into account that other silicide forming metals (Co > Re > Ni = Pd > Cu > Fe > Mo) affect the process rate ($T = 660$ °C, $H_2 : SiCl_4$ ratio from 4) to different extents [15].

If copper is used as a catalyst at $P = 30$ MPa the hydrochlorination process rate is 6 times higher than if Fe is used. However copper catalyst has a number of disadvantages: Cu powder is pyrophoric, just like the dust coming with copper, copper contaminated dumps are difficult for disposal or recycling, copper is relatively expensive etc. Therefore there are a large number of studies proving that Fe is preferable as a catalyst (Table 3, Part 1). To achieve a uniform distribution it was suggested to crush iron together with silicon and granulate [22, 23].

The surface of silicon particles that is free from metals does not participate in the reaction. Fluidized bed reactor studies showed that the highest trichlorosilane yield of ~31% can be achieved at 525–575 °C temperature, 0.1 MPa pressure and exposure time of > 5 s. Thermodynamical calculations taking into account the main reaction (4) and six side reactions [24] show that the tetrachlorosilane conversion rate reaches 0.41 at $SiCl_4 : H_2 = 1 : 5$, 5 MPa pressure and 200 °C temperature. To increase the $SiCl_4$ conversion rate and the trichlorosilane yield it was suggested [25] to mix silicon particles with copper or iron catalyst. The materials were mixed in the presence of hydrogen for up to 60 min at 100–400 °C. As copper and iron sources once can alternatively use either their oxides. For the hydrochlorination reaction silicon should contain iron silicides (~1–5 wt.%) and be preferably in granulated form [26]. The $SiCl_4 : H_2$ ratio in the reaction mixture is maintained at $0.25 : 1$–$4 : 1$, the process temperature was maintained at 400–800 °C and pressure at up to 40 MPa. The average silicon grain size should be within 10–1000 μm and the catalyst grains should be 30–100 times smaller [27].

It was also reported [28] that a binary catalyst consisting of nickel and copper can be used. This catalyst is produced by co-deposition of copper and nickel hydroxides. Due to a synergetic effect the catalyst noticeably affects the $SiCl_4$ conversion rate.

The hydrochlorination reaction is preferably conducted in a fluidized bed reactor. An important advantage of this reactor type is the absence of temperature gradi-

ents due to intense mixing of solid particles and gaseous phase. Furthermore silicon and/or catalyst particles can easily be loaded into this reactor type and used materials can be easily withdrawn from it.

Since the process is carried out at high pressures and relatively high temperatures, the reactor should be made from Ni–Cr–Mo alloys with a chromium content of at least 5 wt.%, iron content of less than 4 wt.% and other alloying additions 0–10 wt.%, balance nickel. The most advantageous are Inconel 617, Inconel 625 and Alloy 59 alloys [29].

Hydrochlorination reactor operation was simulated on the basis of laboratory tests [30], the hydrodynamics of the occurring processes being interpreted adequately well by the Kunii and Levenspiel model.

A homogeneous temperature field can be developed in the reactor by means of microwave heating [31]. A hydrochlorination process was described in which $SiCl_4$ + H_2 vapor and gas mixture before feeding to the reactor is preheated in a special heater to 525–575 °C [32].

The construction materials for the heater and the hydrochlorination reactor, Inkolloy 800 alloy is used (C ≤ 0,12%, Si – 1,0%, Mn ≤ 2,0%, P ≤ 0,3%, S – 0,015%, Cr ~ 19–23%, Ni – 30–34%, Ti – 0,15–0,60%, Al – 0,15–0,60%, Fe ≥ 38,63%).

Patent literature contains disclosures of various hydrochlorination reactor designs[6]. Schematic of one hydrochlorination reactor in which the process is conducted at a constant temperature (without heat supply) is shown in Fig. 5 [33].

The temperature is maintained at a constant level by means of periodical supply of hydrogen chloride to the chamber. Heat is regularly released as a result of interaction between HCl and Si.

To increase the trichlorosilane yield the hydrochlorination process is implemented in two sequentially connected fluidized bed reactors [34]. For the same purpose it was suggested to add a catalyst of the lits comprising Cu, Ni, Co, Pt, Au, Rh, Pd, into metallurgical grade silicon during melting. Then another type of catalyst of the above list is feed to the silicon surface in the course of hydrochlorination. This approach allows increasing the trichlorosilane yield by 11% as compared with the base method [35].

2.4. Trichlorosilane synthesis by tetrachlorosilane redistribution or anti-disproportioning

This method (otherwise referred to as redistribution or anti-disproportioning method) is based on the tetrachlorosilane redistribution reaction. Dichlorosilane is formed during silicon production along with trichloprosilane. Dichlorosilane is produced during direct trichloprosilane synthesis, especially if catalysts are used, and during silicon deposition. Thermodynamical studies of SiH_2Cl_2 be-

havior in the Siemens process showed [36, 37] that at a 1–5 MPa pressure, a $H_2 : SiHCl_3$ = 2–50 molar ratio and a 727–1227 °C temperature, it is pressure that has the greatest effect on the dichlorosilane yield. The temperature and molar ratio of this $H_2 : SiHCl_3$ mixture have no strong influence on SiH_2Cl_2 yield. Dichlorosilane that is released from silicon deposition process abgases can be used after additional cleaning as a source product for silicon nitride or tungsten silicide epitaxial layers and films [38]. The difficulty of dichlorosilane cleaning is caused by the proximity of the boiling points of SiH_2Cl_2 (8.4 °C) and boron chloride BCl_3 (12.6 °C). One should therefore use cooled high pressure rectifying columns. The possibility of using dichlorosilane as a component for the production of polycrystalline silicon was studied in the 1980s within a NASA project by Hemlock Semiconductor [39] and by one USSR enterprises [40]. It was assumed that lower silicon deposition temperature from dichlorosilane would lead to lower energy consumption and hence cut down production costs. Preliminary tests yielded silicon rods with a homogeneous polycrystalline structure [39–41] and achieved a high (up to 40%) yield recovery. However the rod growth rate differed but slightly from that for trichlorosilane processes. Process control was complicated by the formation of "mist" in the reactor and amorphous silicon powder settlement onto the basement plate and on the top of the reactor.

Small dichlorosilane additions to trichlorosilane compromised the technical and economical parameters of silicon deposition process. Additionally, process control should in this case take into account the dichlorosilane
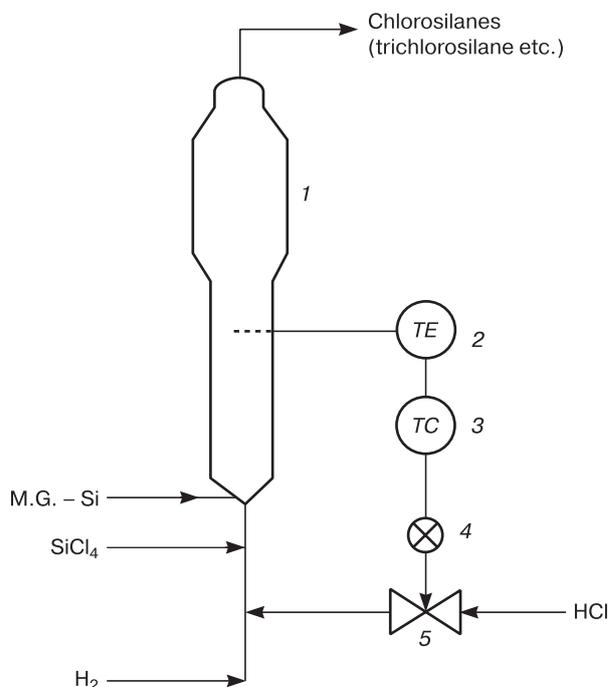

Figure 5. Schematic hydrochlorination reactor with zero heat supply [33]: (*1*) fluidized bed reactor, (*2*) temperature gage, (*3*) control unit, (*4*) valve drive, (*5*) valve.

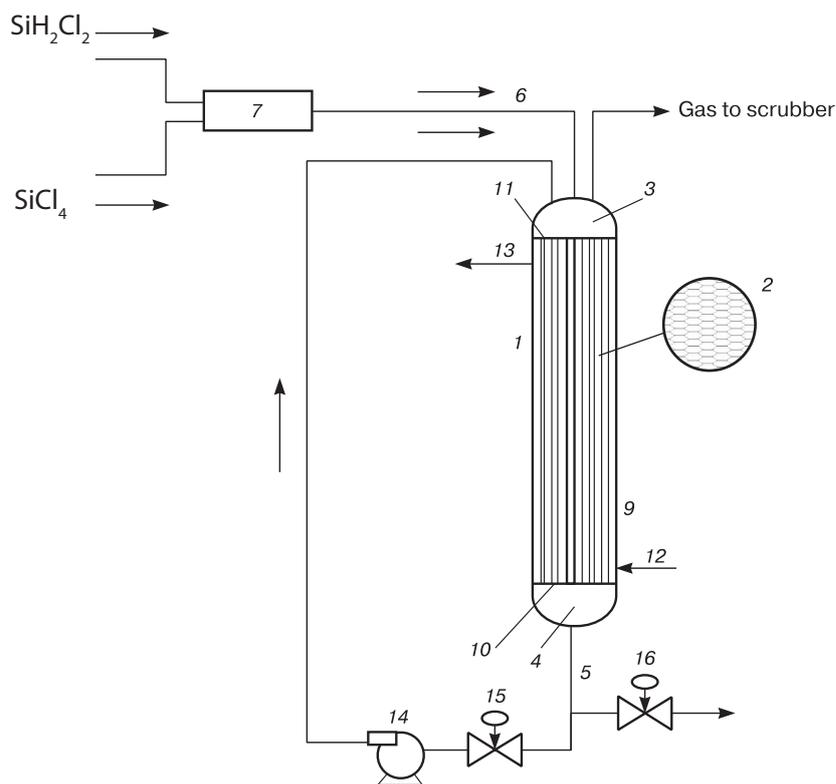[6] Pat. WO 2010/028878, 2010; Pat. WO 2011/150642, 2011; Pat. CN 102674369, 2012

Figure 6. Basic schematic of SiH_2Cl_2–$SiCl_4$ mixture conversion reactor [43]: (*1*) disproportioning reactor, (*2*) reactor cross-section and reaction pipes, (*3*, *4*) top and bottom reactor heads, (*5*) input, (*6*) SiH_2Cl_2 + $SiCl_4$ reaction mixture pipeline, (*7*) static mixer, (*8*) recirculation pipe, (*9*) reaction piping cooling enclosure, (*10*, *11*) top and bottom sieves, (*12*, *13*) cooling mixture input and output, (*14*) recirculation pump, (*15*, *16*) control valves.

content in the mixture, rod temperature, rod diameter and quantity of mixture fed to the reactor [42]. Because of its instability, fire and explosion hazard, dichlorosilane did not find application as a key source component for silicon deposition and beginning from the 1990s is has not been used for polycrystalline silicon production [43, 44]. Dichlorosilane disposal is a complex problem in industrial scale silicon production and leads to significant abgas and sewage water neutralization costs.

Dynamic Ingineering Co. announced a new method for dichlorosilane and tetrachlorosilane disposal [43, 45]. The method is based on the following reaction

$$SiH_2Cl_2 + SiCl_4 \rightleftarrows 2SiHCl_3. \qquad (8)$$
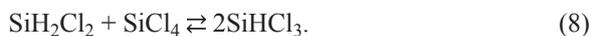
This reaction is exothermic (+11 kCal/mole SiH_2Cl_2) and shifts to its right-hand side with decreasing temperature. the process is catalyzed with a macroporous anion-exchange resin made from styrene and divinylbenzene with a tertiary anion function group (Dowex M43 anionite). The basic schematic of the reactor is shown in Fig. 6.

This reactor type was presented by Dynamic Ingineering for GCL Solar's 1000 tpy polycrystalline silicon factory [46, 47]. This allowed for the production of 2295 tpy trichlorosilane from 1000 tpy recycled tetrachlo-

rosilane and 1700 tpy dichlorosilane. Low equipment and power costs and cutdown of caustic soda costs for abgas and sewage water neutralization allowed a 3,825 mln. \$/y saving [48].

Later on the process was intensely studied by Chinese researchers and they called it trichlorosilane anti-disproportioning of the GCL process. The dichlorosilane and tetrachlorosilane interaction operation is carried out in reaction and rectifying columns [49–51]. Basic schematic of one of method embodiment is shown in Fig. 7 [51]. Part of $SiCl_4$ is fed to the column *10* in the form of vapor from its bottom (stripper section) and the liquid portion of $SiCl_4$ and possible high boiling point impurities are passed through two heat exchangers (*17*, *18*). The liquid $SiCl_4$ flow is fed through pipeline *11* to the rectifying column for spraying. The $SiCl_4$ flow enriched with high boiling point impurities is regularly output from the system (flow *9*).

Process simulation and optimization [52] with the AspenPlus software provided preferable process parameters. At 55 °C, 0.7 MPa and 250 kg/h flow the conversion rate achieved was 98–99%. An advantage of this method is the absence of $SiCl_4$ and SiH_2Cl_2 byproducts. The process is distinguished by low equipment and power costs and increases the $SiHCl_3$ yield by 2–4% at the direct synthesis stage and by 3–6% at the product recycling stage
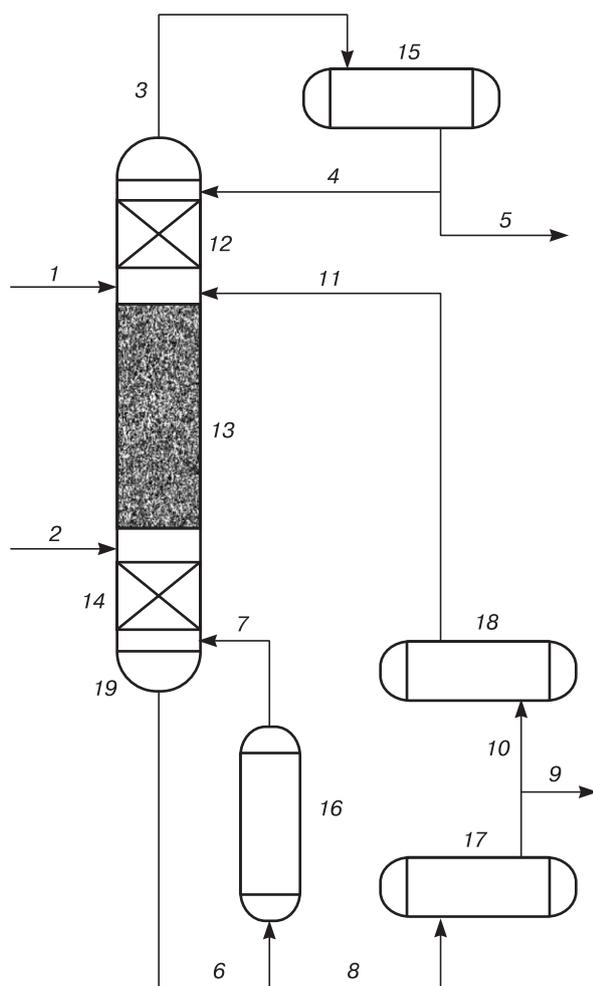
Figure 7. Basic schematic of trichlorosilane anti-disproportioning process [51]: (*1*) tetrachlorsilan (SiCl$_4$) flow; (*2*) dichlorosilane (SiH$_2$Cl$_2$) flow; (*3*) gaseous trichlorosilane flow; (*4*) reflux liquid (mainly trichlorosilane), (*5*) final product (pure trichlorosilane), (*6*, *8*) product pipelines (mainly tetrachlorosilane), (*7*) evaporated tetrachlorosilane pipeline, (*9*) high boiling point residual fraction output, (*10*) aberage boiling point product, (*11*) cooled tetrachlorosilane, (*12*) top rectifying section, (*13*) middle section (reaction zone) with a catalyst head, (*14*) stripper column section, (*15*) reflux column, (*16*) reboiler, (*17*) separating refrigerator, (*18*) low-temperature refrigerator, (*19*) reactive distillation column.

in the Siemens process [45]. However the method does not allow complete conversion of all tetrachlorosilane produced and is therefore considered as an auxiliary process.

Joint dichlorosilane and tetrachlorosilane to trichlorosilane conversion methods based on carbon-containing catalysts[7] at 50–1000 °C were described [53, 54]. Somewhat different approach was suggested elsewhere [55]. The SiH$_2$Cl$_2$ and SiCl$_4$ mixture with methane CH$_4$ in the (SiH$_2$Cl$_2$ + SiCl$_4$) : CH$_4$ = 1 : 1–1 : 10 ratio is heated to 1100 °C and then cooled to < 200 °C. The

reaction produces methylchlorosilane which can be used for the production of silicon polymers, hydrophobization of various materials, production of corrosion proof concrete etc.

Patent [56] taught using dichlorosilane diverted from trichlorosilane hydrogen reduction for silane production. Pure dichlorosilane or its mixtures with other reaction products are directed to the bottom section of the four-section catalytic reactor heated to 30–100 °C. The reactor pressure is 2.5–3.5 MPa, the catalyst being anion exchange resin based on polystyrene with quaternary amine groups and *n*-butyls. The reactor gas (SiH$_4$) is directed to the bottom section of the reboiler-heated rectifying column and the vapor-liquid phase from the top reactor section is fed to the middle column section. Cleaned silane is taken off from the top column section for use as a final product or for silicon production. The method allows dichlorosilane as a waste of silicon production from trichlorosilane to be used for the production of a more valuable product, i.e., silane, thus increasing the efficiency of silane and silicon production. This option also reduces sewage water emission, wastes and abgases.

3. Trichlorosilane production methods in polycrystalline silicon processes

The efficiency of polycrystalline silicon production depends directly on the technology and equipment, trichlorosilane flowrate and power parameters. The cost breakdown is also determined by production volume and current polycrystalline silicon market price.

A 3000 tpy polycrystalline silicon factory that uses the Siemens process (direct trichlorosilane synthesis, rectifying and separation columns, silicon deposition reactors, vapor/gas mixture regeneration and tetrachlorosilane conversion) consumes as much power as a town with a 50,000 population [45].

Chinese polycrystalline silicon companies achieve competitive advantage due to efficient State support including lower power prices. Whereas electricity rates for industry in Germany are at 4 c per 1 kWh, those in China are within 2 c per kWh [57].

The use of tetrachlorosilane conversion or silicon hydrochlorination methods in polycrystalline silicon processes reduces power consumption by 20–30 kWh/kg silicon [58]. Comparison between silicon hydrochlorination and tetrachlorosilane hydration methods is given in Table 5 [59].

Although the tetrachlorosilane conversion process provide for pure trichlorosilane and as a result more pure silicon, the hydrochlorination process is more economically viable.

Start up of 5000+ tpy factories and the wide use of the hydrochlorination process (with SiCl$_4$ as the raw mate-

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[7] Pat. WO 2012 098069, 2012.

Table 5. Comparison of technical parameters of silicon hydrochlorination and tetrachlorosilane hydration methods [59]

No.	Cost Item & Parameter	Silicon hydrochlorination	Tetrachlorosilane hydration
1	$SiCl_4$ output (kg/h)	12500	500–1500
2	Conversion rate (%)	23–28	17–22
3	Reaction temperature (°C)	400–600	1200–1300
4	Power consumption (kWh/kg $SiHCl_3$)	0.4–0.7	2.0–3.5
5	Continuous service period (days)	150–330	~120
6	Working mode features	Difficulty of silicon powder supply to reaction volume due to air-tightness conditions. Specific requirements to dimensions and air tightness due to high pressure used	Graphite electrodes and carbon parts require regular replacement. Carbon is involved in high-temperature reaction and reduces product quality

rial) has revealed the following drawbacks of these processes:

Hydrochlorination reactors allow limited scalability;

10,000 tpy factories require large tetrachlorosilane recycling quantities. This entails high production costs and large capital investments;

Production requires highly skilled and experienced personel.

Compromise solution for 10,000+ tpy factories is the joint use of direct trichlorosilane synthesis reactors and hydrochlorination reactors, i.e, the so-called hybrid method [60, 61]. This methods is also distinguished by direct trichlorosilane synthesis with turbo loading of the fluidized bed reactor, i.e., additional feeding of an inert material with particle sizes, specific weight and bulk weight close to those of silicon particles. This material can consist of quartz powder, glass beads, oxides or metal helogenides (except iron) and zircon. Turbo loading provides for quite a uniform temperature profile in the fluidized bed, the trichlorosilane selectivity being above 95%. The power saving is 220 ths. kWh/year.

Three process routes were analyzed using the Aspen Plus software [62]:

– the classical Siemens process where trichlorosilane is produced by direct chlorination (DC);

– the Union Carbide process where trichlorosilane is produced by hydrochlorination (HC) and then disproportionated for silane production;

– according to the Author's definition, "hybrid process" in which trichlorosilane is produced by hydrochlorination (HC) and used for siicon deposition in the Siemens reactor.

All processes were simulated for a 2000 tpy production.

The calculations show that optimization of the processes will reduce yearly costs by 53 to 88%. The Siemens process showed the lowest costs and the best economic parameters but the smallest output. The "hybrid process" showed the best results with the highest silicon recovery rate and the highest income while being inferior to the Siemens process in environmental parameters. The Union Carbide process proved to be the most expensive one of the three above listed processes.

Thus the Siemens process and its modifications remain attractive and useful for polycrystalline silicon production. New silicon factories in Russia and China use upgraded Siemens process options. They combine advanced direct trichlorosilane synthesis and silicon hydrochlorination processes in one unit or their combinations [59–63].

4. Conclusion

According to recent information [64–66], Chinese and other renowned silicon companies increase their silicon production volumes thanks to demand revival and favorable silicon price drop increasing predictions in 2021. Therefore the trichlorosilane demand of silicon companies grows. For example, Hemlock Semiconductor, US, bought trichlorosilane production premises from Du Pont de Nemours Inc., US, [67]. Other companies seek cutting down their consumption rates, including trichlorosilane consumption, by using strategies towards increasing process efficiency and equipment improvement.

The predominant polyscrystalline silicon technology is still the Siemens process, and direct trichlorosilane synthesis, tetrachlorosilane hydration and silicon hydrochlorination remain vital and permanently improved approaches. Special attention is paid to processes on silicon surface [68] including catalytic reactions. Understanding the mechanisms of these processes will show efficient ways to new worthwhile applications, reduce power consumption, solve environmental problems and improve the quality of semiconductor grade silicon. Necessary components of equipment and process solutions are recycling and joint processes, e.g. reactive distillation. They provide for a more complete use of raw reactants, retrieving valuable byproducts and reducing final silicon product costs.

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