

Innovation meets experience

The new converter technology and the silver-plated CVD-reactors from Silicon Products Bitterfeld GmbH & Co.KG (SPB), lead to a substantial contribution regarding reduced production costs and higher quality of silicon produced by standard Siemens process.

This article presents the latest development and technology in the production and purification of trichlorosilane (TCS) and converter technology developed by SPB and first operating results. Further on production experiences are shown by using silver-plated reactors in comparison to stainless steel CVD-reactors.

Chlorosilanes (Silicontetrachloride (STC), Trichlorosilane (TCS)) are generally used for decomposition to polysilicon in Siemens-reactors and this technology is also applied in Bitterfeld.

2. Market development

The overall photovoltaic market will continue to increase strongly in volume in the next few years. Nevertheless in all stages of the value-added chain cost reductions and efficiency improvements are required so as to further increase the economic efficiency and competitiveness of solar power compared to fossil energy sources.

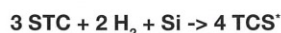
Market research shows that the worldwide demand for high-purity and competitive solar-grade silicon for photovoltaic applications is going to increase annually into double-figures. In 2015 the worldwide production capacity of silicon for solar stood at approximately 350,000 MT and various forecasts show a possible increase in demand to over 800,000 MT in 2025.

In regards to this improved technological solutions for process optimisation and the resulting cost reductions are of the utmost importance.

3. TCS-Production Processes

Mainly two different processes are in use to produce TCS:

STC Hydrogenation (Hydrochlorination, cold conversion):



Requirements and reaction conditions:

- Special Incoloy Fluidised Bed Reactor (pressure: 20-32 BARg, ca. 550°C)
- Definite need for Cu catalyst
- Mildly endothermic
- Reactor internals are properly designed distributor plate and bubble breakers
- Moderate degree of fluidization to prevent the larger particles from separating
- Expanded heads are not feasible and carry-over of MG-Si is experienced, even with internal cyclones
- 25-30% conversion to TCS

Disadvantage of this method is the necessary mixture of the already cleaned high purity chlorosilanes with the low purity mg-silicon. This results in complex purification methods and leads to higher investment and operating costs.

Thermal STC hydrogenation:



Requirements and reaction conditions:

Special robust reactor design: Converters or hydrogenation-reactors (low pressure: 6 BARg, ca. 1300°C conversion temperature/ reactor bell jar temperature < 300°C)

- Easy to operate
- Due to the optimized gas flow the TCS yield is maximized under consideration of a minimal power demand. This is reached by the use of special designed heat exchanger integrated in the reactor.
- Reactor internals made out of special graphite, reactor body: Carbon or stainless steel.
- Yield of TCS: > 16.5 ma%

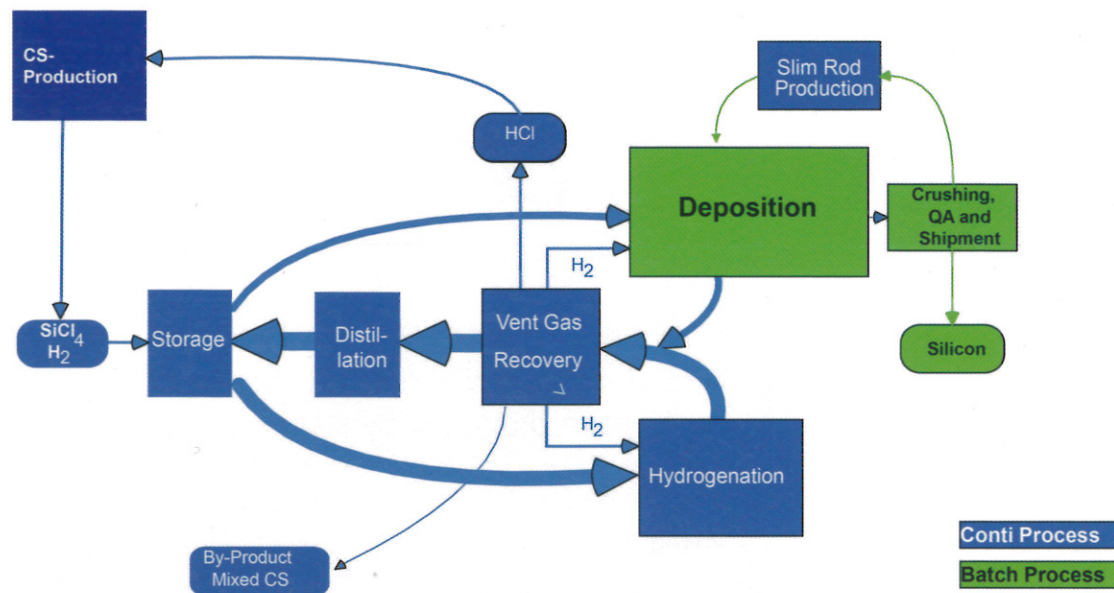
Development and in operation by SPB: more details and results see below.

4. Siemens process

The Siemens process for the production of high-purity silicon is a thermal-chemical process at temperatures between 1,000 and 1,300 degrees centigrade. The typical process consists of the following stages (picture 1 and picture 2):

- Tank farm
- Silicon slim rod production facility for mounting in Siemens reactors
- Chlorosilane production made of mg-silicon
- Hydrogenation of silicon tetrachloride using hydrogenation-reactors (converters)
- Process gas treatment and purification (vent gas recovery)
- Multi-stage distillation facility
- Silicon deposition in deposition reactors – Siemens reactors – for the production of high-purity silicon

* "Advances in Impurity Removal for TCS Production" Randall Jurisch, Krista Hanna, Larry Coleman; Silicon for the Chemical and Solar Industry XI, Bergen, Norway, 2012.



Picture 1 shows schematically the mass flows of chlorosilanes and silicon between the different units of the Siemens-process. The thickness of the arrows illustrates the quantity of the throughput. Especially the throughputs between the deposition reactors and converters (hydrogenation) and the vent gas recovery plant are tremendous in comparison to the relative "thin" silicon output.



Picture 2 shows the Silicon Production Plant in Bitterfeld near Leipzig, Germany

"It is obvious how important an increase of yield in converters and Siemens-reactors are and what potential this has regarding reducing investment and operating costs."

- Auxiliary facilities for the generation of compressed air, exhaust gas and waste water treatment

It is obvious how important an increase of yield in converters and Siemens-reactors are and what potential this has regarding reducing investment and operating costs. Despite the longstanding and worldwide production experience with the Siemens process and the developments that have

been made, the individual process stages still offer considerable potential for further cost reductions.

5. Innovations by Silicon Products

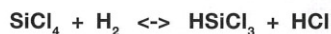
The following 2 innovative developments of the silicon production plant will be presented:

- Converter type 16.5 (best-in class) and
- Deposition reactor (silver-plated)

5.1 Thermal hydrogenation process and the second generation of hydrogenation reactors (converter type 16.5)

In addition to the deposition of silicon in CVD-reactors (Siemens reactors) the thermal hydrogenation of chlorosilanes is the central stage in which considerable energy and cost savings – regarding production as well as investment – will still be possible in the future. This reaction takes place in converters.

The thermal conversion is the transformation of silicon tetrachloride (SiCl₄) into trichlorosilane (HSiCl₃) at high temperatures, medium pressures and in a hydrogen atmosphere based on the following molecular reaction:



This reaction is an equilibrium reaction with fast establishment of the equilibrium concentrations which crucially determines the yield of the process and correspondingly the geometry of the reactor. With our innovative design of the converter the equilibrium is shifted towards higher yields (picture 3).

Based on the longstanding production experience of Silicon Products developments were pushed ahead and successfully implemented in the second generation of converters in 2013. The bases of the developments were existing Computational Fluid Dynamics (CFD) simulations of the converter combined with a kinetic model of the TCS formation. This model respects amongst others temperature, molar ratio, pressure, flow rate, heat exchange and is generated and validated with operational results.

This new type of converter was successfully tested and operated. The significant increase of the conversion yield by more than 30% – from 12.5% by mass (15.7 mol%) to 16.5% TCS by mass (20.7 mol%) referred to STC-feed – results in considerable economic advantages in the operation of the existing production facility (energy savings of 12%) and for new investments.

Mass balance (typical values) are shown below:



In the table opposite the cost savings due to reduced power consumption of the new converter type 16.5 in comparison to competition are listed:

Because of these high savings the ROI of this technology has advantages in comparison to the other technologies.

A change of existing older systems is well spent money to reach lowest production costs.

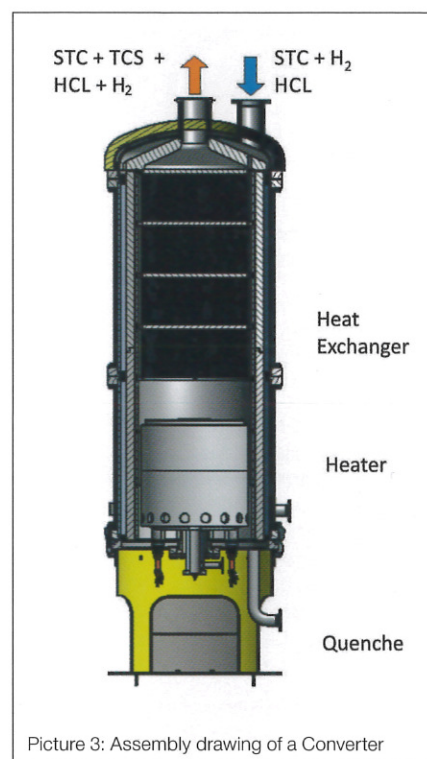
Additional savings due to less investment costs of the vent gas recovery unit have not been taken into account.

Advantages of the new Converter type 16.5 (2nd generation):

- Latest developed hydrogenation reactor already successfully tested in production
- High yield: > 16.5 ma. %
- Longer lifetime of internals due to special graphite > 6 months (approx. 9 months)
- Best in class power consumption: <0.70 kWh/kg TCS
- Throughput: up to 15,000 kg/h STC
- High energy recuperation
- Equipment proven by TÜV
- Tailor-made design according to customer needs

5.2 Siemens-reactor (deposition reactor): stainless steel versus silver-lining

This part of the plant comprises the heart of the system where silicon is deposited on hot silicon slim rods from SiHCl₃.



Picture 3: Assembly drawing of a Converter

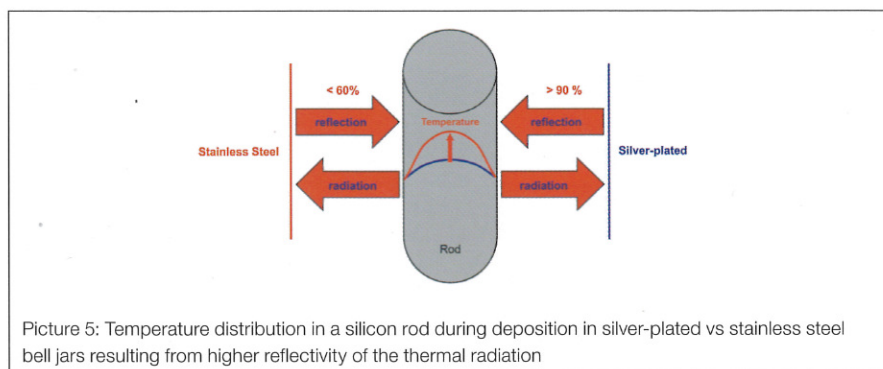
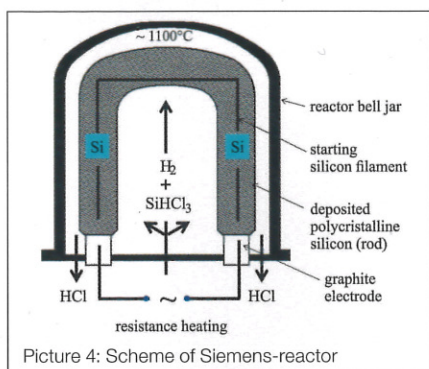
Power consumption of converter 16.5	0.70	kWh/kg TCS
Power consumption of competition	3	kWh/kg TCS
Power costs	0.05	US\$ / kWh
Cost savings per kg Si	2.3	US\$ / kg Si
Throughput of large scale plant	10,000	t/year Silicon
Savings of power costs	23,000,000	US\$/year



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In the Siemens-reactors gaseous TCS and hydrogen is converted to polysilicon by chemical vapor deposition. The polysilicon deposits on the surface of hot silicon slim rods at temperatures of approx. 1,100 °C. The silicon rods grow continuously to a thickness of 150 mm-180 mm. Electric resistance heating is used to heat the rods. The deposition process takes about 4 days to produce solar silicon.

Advantages of silver-plated Siemens-reactors are (picture 5):

Cost advantages

- 50% electric power savings in comparison to stainless steel
- Thicker silicon rods (up to 180 mm) corresponding also with energy savings. Less temperature in the centre of the rods allows thicker diameter without silicon melting.
- Easier and less cleaning of the bell jar

Quality advantages

- Less popcorn surface on the rods
- Less fallen rods before harvesting caused by lower thermal-mechanical stress inside the rods
- Less contamination of stainless steel in silicon
- Homogeneous distribution of radiation inside the bell jar due to a higher reflexion of the silver-lining leads to a higher

homogenization of the rod geometry (picture 6)

Because of these advantages regarding costs and quality silver-plated CVD-reactors are an interesting alternative to stainless steel reactor bell jars even to produce solar-grade silicon. For the production of semi-conductor grade silicon silver-plated reactors are the technology of choice.

6. Summary

The silicon production industry faces a variety of challenges. Silicon Products supports customers to decide which technology or manufacturing process is the best. Silicon products also makes improvements to existing operations. Our own manufacturing experience and know-how, German engineering, continuous research & development are the basis for delivering success to our customers.



Picture 6: Silicon (solar-grade) rods before harvesting

Our goal is to bring manufacturers up to world class standards as quickly as possible to be successful in this competitive market. ■

Silicon Products Group is active in the following fields:

Production of silicon for photovoltaic and semi-conductor purposes and other related products using the existing plant in Bitterfeld-Wolfen. SPB has several years' experience in silicon production.

Sale of know-how and engineering services on silicon production, chlorosilane processing and photovoltaics.

Research and development on the Siemens process for the production of low-cost silicon, with a particular focus on cost reduction and improvement in the silicon quality.

Further R&D projects in cooperation with universities and institutes are in progress.

Silicon Products Bitterfeld GmbH & Co. KG (SPB) is a wholly owned subsidiary of Silicon Products Group located in Bitterfeld-Wolfen, Germany.

www.silicon-products-gmbh.com/en/