# MAXUM II

## Online monitoring of polysilicon production in photovoltaic industry

## Case Study · January 2009

**Boom in Photovoltaics**

Global demand for solar energy is booming as a cost competitive reliable source of clean energy. Because cost of electricity is increasing rapidly, solar energy is gradually becoming cost competitive when compared to conventional energy. Since the source of solar energy is nearly unlimited, solar energy has a tremendous potential to dominate the energy mix in the future.

Photovoltaics (PV) is the technology of using solar cells for energy generation by converting sunlight into electricity. Solar cells are typically covered by a glass sheet (fig. 3) and electrically connected together to form photovoltaic modules. Due to the growing demand in solar energy, the manufacture of solar cells and photovoltaic arrays has expanded dramatically in recent years. After the first solar cell has been produced in 1954, the market started to grow continuously with a 40 % rate per annum, in average, over the last decade. Production capacities are concentrated in the USA (50 %), Japan (24 %) and Germany (18 %) but currently numerous new plants are planned or under construction in many other countries.

**Solar Grade Polysilicon**

The raw material for photovoltaic cells is silicon (Si) and has historically come from off-spec and waste silicon, produced either during the polysilicon purification process or during ingot and wafer production. But the requirements for so-called „solar grade" silicon are different from the silicon used for semiconductor industry. On the one hand it has not to be as pure as for semiconductor, but the quality has to be reproducible for large quantities. Therefore, the industry is asking for process analytics, mainly process gas chromatographs, to monitor the production process, to ensure the purity requirements and to optimize the quality and quantity for polysilicon production.

Siemens Process Analytics is very likely the analytical solution provider with the greatest experience and the best analytical solution to control and optimize this demanding process.

Process Analytics

Answers for industry.

SIEMENS

# Production of Polysilicon

### Semiconductor Grade silicon

Silicon is the second most common element in the earth's crust and occuring as oxide (sand and quartz) or as silicate (granite, clay, and mica). For use as semiconductor material, silicon must be highly purified. For solar cells, it must be 99.9999 percent pure (often referred to as "six nines" or 6N pure). The silicon grade used in electronics is even more pure, typically 9N to 11N. In order to reach semiconductor grade, whether for solar cells or integrated circuits, silicon must be processed extensively.

### Metallurgical Grade Silicon (MG-Si)

Quartz obtained from a silica mine is put into a furnace with a carbon source such as coal, coke, woodchips, or charcoal. The mixture is heated and the silicon chemically reduced forming liquid silicon, carbon dioxide, and silica fumes. The liquid silicon is poured out of the furnace and further purified. The resulting silicon material is referred to as metallurgical grade silicon (MG-Si).

### Polysilicon

Several processes are known to produce polysilicon. The majority of polysilicon that is used by the semiconductor and Photovoltaic industry is produced via *chemical vapor deposition*. In that process Trichlorosilane (TCS, $HSiCl_3$) is thermally decomposed at 1 100 °C whereby highly pure silicon is deposited onto heated rods. In order to get Trichlorosilane HCl (generated by $H_2$ and $Cl_2$) is reacted with MG-Si. This forms a liquid that, after temporary storage, is purified by distillation and fed back to the storage tank. In the next step TCS is vaporized, mixed with hydrogen and fed into the so-called Siemens-Reactor (Siemens has originally developed that process) where the chemical deposition of silicon takes place at high temperatures. TCS has many advantages such as high deposition rates and high volatility which makes it easier to remove impurities like boron and phosphorus. One of the disadvantages of using TCS is the high electricity requirement to maintain the high process temperatures. Finally the silicon is removed from the rods in the form of chunks (fig. 2). Process by-products are recycled and recovered in a vent gas recovery and a converter unit, e.g. $SiCl_4$ from the reactor is converted with $H_2$ to $HSiCl_3$ and HCl.

Another process for getting polysilicon further refines TCS to produce gaseous monosilane ($SiH_4$), which is then deposited on heated silicon rods. Monosilane is a higher purity starting material which leads to more pure polysilicon. A third process for polysilicon production uses a fluidized bed reactor resulting in granular silicon as final product.

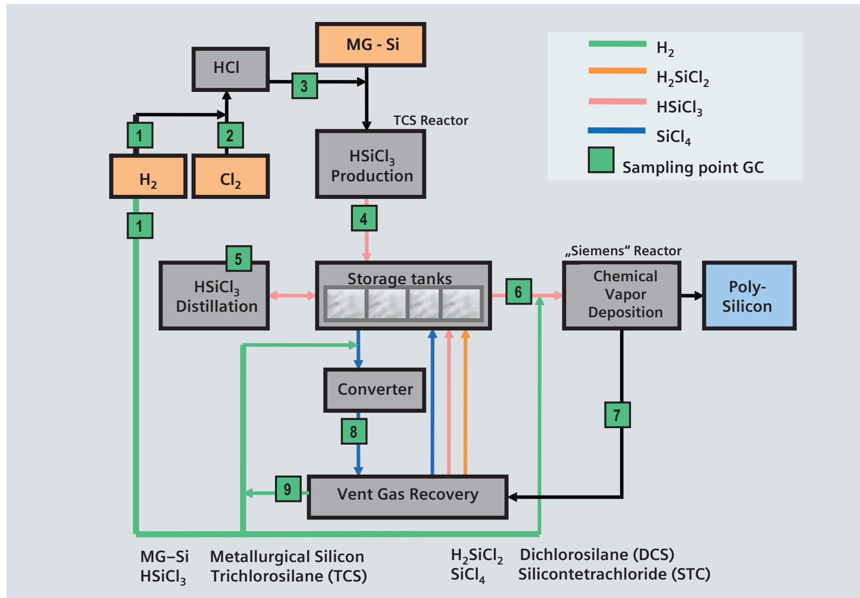


Fig. 1: Polysilicon production via the Siemens process

| Sampling point Sampling stream | | Measuring purpose | Measuring components | Measuring ranges | Siemens Analyzer |
|---|---|---|---|---|---|
| 1 | $H_2$ make up gas | $H_2$ purity | $H_2O$<br>$O_2$, $N_2$, CO, $CO_2$, HC | 0 ... 100 ppm<br>0 ... 50 ppm | TPA<br>MAXUM II |
| 2 | $Cl_2$ supply | $Cl_2$ purity | $H_2O$<br>$N_2$, $O_2$, $H_2$ | 0 ... 2 %<br>0 ... 5 % | TPA<br>MAXUM II |
| 3 | HCl | HCl purity | $H_2O$<br>$O_2$, $N_2$, CO,$CO_2$, HC | 0 ... 100 ppm<br>0 ... 10 ppm | TPA<br>MAXUM II |
| 4 | Crude TCS reactor outlet | Process control | $HSiCl_3$, $SiCl_4$<br>$H_2SiCl_2$, HCl | 0 ... 100 %<br>0 ... 1 % | MAXUM II |
| 5 | TCS distillation column outlet | Process control | $HSiCl_3$<br>$H_2SiCl_2$, $SiCl_4$, $N_2$ | 0 ... 100 %<br>0 ... 30 % | MAXUM II |
| 6 | Feed gas to Siemens reactor | Process control | $HSiCl_3$, $SiCl_4$<br>$H_2SiCl_2$, HCl, $H_2$ | 0 ... 100 %<br>0 ... 30 % | MAXUM II |
| 7 | Vent gas from Siemens reactor | Process control | $HSiCl_3$, $SiCl_4$<br>$H_2SiCl_2$, HCl, $H_2$ | 0 ... 100 %<br>0 ... 30 % | MAXUM II |
| 8 | Vent gas from converter | Process control | $HSiCl_3$, $SiCl_4$<br>$H_2SiCl_2$, HCl, $H_2$ | 0 ... 100 %<br>0 ... 30 % | MAXUM II |
| 9 | $H_2$ from vent gas recovery | $H_2$ purity<br>Process control | $HSiCl_3$, $SiCl_4$<br>$H_2SiCl_2$, $N_2$ | 0 ... 50 ppm | MAXUM II |

Table 1: Polysilicon production, analysis details, corresponing to fig. 1 (TPA: Third Party Analyzer)

### Analysis tasks

Analysis tasks include feed gas purity monitoring as well as by-product composition measurements. Other measurements provide data for process control. Typical sampling points are shown in fig. 1 with more details in table 1. Though typically offline laboratory analyzers are used for this application, Siemens established successfully a reliable online solution.

## Challenge

### Advanced analysis technique

The challenging polysilicon production process with its extremely high product quality requirements along with the difficult-to-handle TCS substance (see below) require advanced analysis technique to reliably control safe and correct operation of the process as well as product quality. Siemens is probably the only supplier of analytical instrumentation that disposes of suitable process-oriented analyzers (Process Gas Chromatography) along with long-time experience in this specific application.

### TCS, a very harmful substance

The main component in the polysilicon process is a harmful substance, which require special sample conditioning and special analyzer configuration. Trichlorosilane (TCS) is a colorless, fuming liquid with pungent odor and a boiling point of 32 °C. It is extremely flammable with a flammability range in air from 1.2 to 90.6 %. Mixtures with air are heavier than air spreading on the ground. Moreover, TCS is highly corrosive, forming $H_2$ on reaction with metals, and shows violent reaction with water and moist air resulting in the formation of corrosive, toxic HCl and of solid $SiO_2$ (plugging and damage of analyzer hardware). TCS is harmful to eyes, skin, and respiratory tract.

# Siemens Solution

### Process-suitable online analysis

Typically, offline laboratory gas chromatographs are used to perform this application which causes the need of sample transportation to the laboratory and a time delay between sampling and availability of the measurement data. Siemens Process Analytics, however, has long standing experience with the Chlorosilane application and has designed a solution, that is based on process gas chromatography using MAXUM II PGC along with a specific sample conditioning system. This also eliminates the need for disconnecting and connectiing sample cylinders , exposing it to ambient air and risk of contamination. The installed base for such online Chlorosilane analyzers exceeds 100 units.

### Dedicated analysis method and special MAXUM II configuration

The MAXUM II PGC is well known for its modular design and high flexibility in designing an optimized analysis configuration. To realize the different measurement tasks in the polysilicon process the versatility of MAXUM II is utilized extensively:

- Air bath oven with anti-corrosive purging
- Isothermal oven configuration or temperature programming
- Separation column type especially selected regarding reactivity and performance
- Special mechanical and chemical drying of carrier gases
- Drying of purging gases
- Use of a special injection and column switching technology (valveless, see below)
- Use of non-corroding materials and special sealings
- Use of different detector types

### Special sample conditioning

Based on extensive experience at former installations the sample conditioning system considers the following (fig. 5):

- Highly leak-proof design
- Use of non-corroding materials for all sample wetted parts, such as piping, valves, pressure regulators & flow meters
- Use of special sealing materials and special fitting techniques
- Special design for additional pipe purging procedures for maintenance purposes, exchange of calibration gas bottles, etc.
- Additional purging of cabinets & shelters with dried purge gas
- Anti-corrosive surface treatment of hardware components

### Valveless column switching

For chromatography with high resolution capillary columns, MAXUM II offers valveless column switching providing the best in low volume high performance column switching and long-term stability and reliability. It performs backflush, heartcut or distribution to two different columns without any switching valves or moving parts in direct contact with the sample. This is done by a unique coupling module (fig. 4) based on pressure differential, controlled by precision Electronic Pressure Controllers. Due to its zero dead volume it is perfectly suited for the low flow rates used with capillary columns. This also eliminates maintenance of the column switching device, increases separation power and simplifies complicated separations. Backflush technology provides very short analysis times especially compared to laboratory GC operation.

### Trace level analysis

Analysis of trace impurities is very important to ensure reproducible product quality of Solar Grade Polysilicon (99.99 to 99.999 %) with Boron and Phosphorus being of special importance as dopants. Common trace components at ppb levels such as Methyldichlorosilane ($MeHSiCl_2$) cannot be analyzed by using conventional detectors such as TCD or FID.
The Siemens solution applies a Pulsed Discharge Helium Ionization Detector (PDHID, supplied by VICI, adapted to MAXUM II) which provides universal detection of organic and inorganic components. Under appropriate separation conditions, a PDHID shows a sensitivity that is over an order of magnitude better compared to FID or TCD.

Fig. 2: Polysilicon (chunks)

Fig. 3: Solar panel

Fig. 4: Valveless column switching module

# User Benefits

### Turn-key measurement solutions
Based on many years experience with silane analytic. From sample extraction, sample conditioning to analyzer and installation infrastructure, all sections together are tuned to be a coherent measurement system.

### Continuous measurement
Without intervention of laboratory or process technicians, repeatable and stable over long periods of time.

### Accurate, fast and reliable analysis
- Special sample conditioning system well proved in numerous installations worldwide
- Highly leak proof design using non-corroding materials for all sample wetted parts
- Superior analytic performance with valveless column switching and highly sensitive detectors (fig. 6)

### Direct process control capabilities
- Process optimization through closed-loop control
- Automatic control of sample conditioning through stream switching and automatic calibration

### Field installation
- MAXUM II certified for use in hazardous areas (ATEX, CSA, NEC, NEPSI)
- MAXUM II suited for ambient temperature range of -18 to +50 °C: No shelter with sluice gate needed, cabinet is sufficient
- MAXUM II installed near sampling point: Reduced costs by less piping and fast analysis by short fast loop

### Comprehensive control and communication capabilities
- Direct connection to DCS
- Integration into communication networks (Modbus, Ethernet TCP/IP)
- Remote access and maintenance
- Easy hook-up of other analyzer via hubs and gateways
- Compatible with SIMATIC Scalance components

### Conclusion of benefits
- Cost reduction and yield increase by use of processs gas chromatographs
- Online measurement with possibility to use data for process control and optimization
- Entire system adapted for operation in harsh, corrosive environment
- Increased reproducibility of batch quality over high product quantities
- Improved sample quality by direct measurement at the process

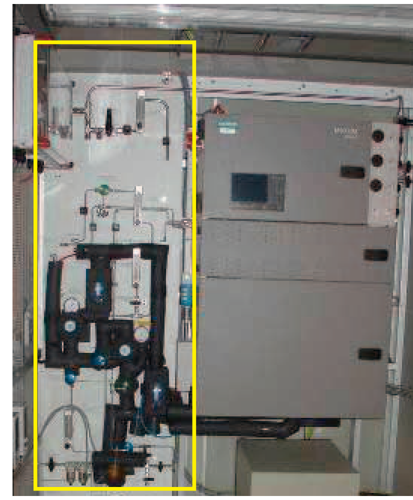

Fig. 5: Sample conditioning system

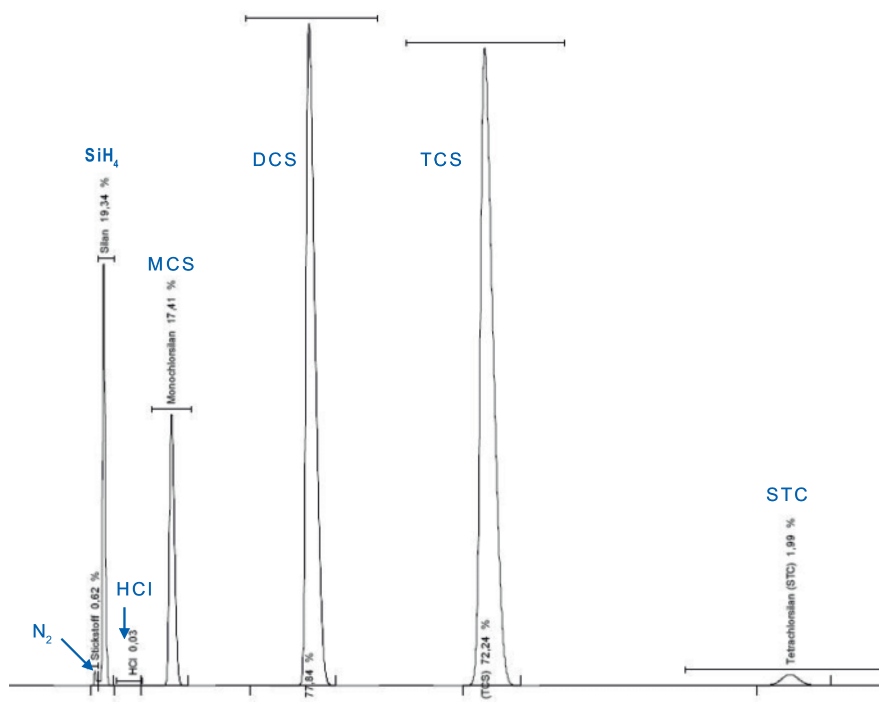


Fig. 6: Typical chromatogram

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