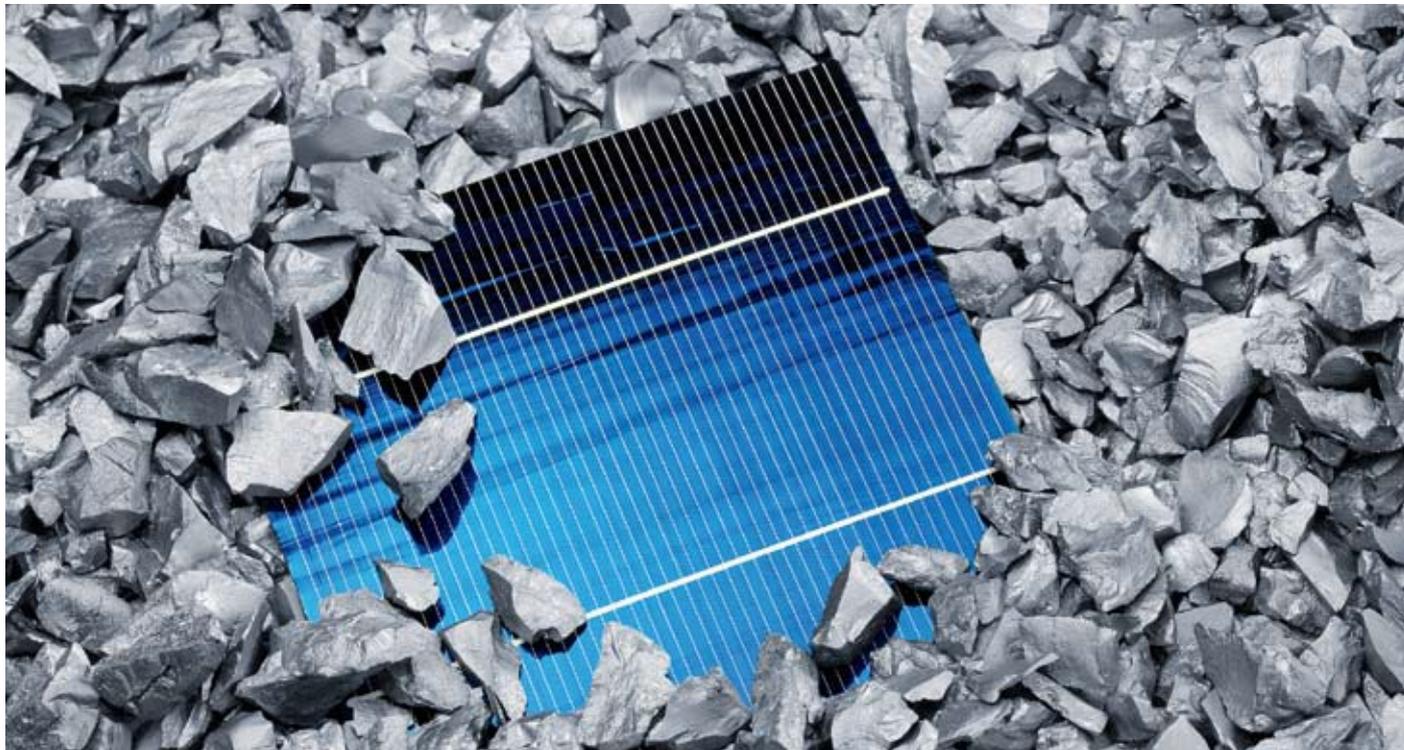


Polysilicon production drives prices down



Polycrystalline silicon chips from Wacker: polysilicon is the raw material for the manufacture of both computer chips and solar cells. The solar industry has since become the main buyer. It consumes 5 times more silicon than the semiconductor industry.

Photos (3): Wacker

Global polysilicon production has increased significantly in recent years. The classic Siemens procedure was optimised, but now there are other procedures ripe for industrial production.

According to studies by the bank Sarasin & Cie, the Si industry produced around 105,000 t in 2009, 160,000 t in the following year and an estimated 210,000 t in 2011. The Swiss bank reckons production will level off at 240,000 t this year. Consequently, photovoltaics has now overtaken the semiconductor industry as a sales channel. In 2011, photovoltaics consumed about four times more polysilicon than the semiconductor industry. The main producing countries are the USA and China: together they supply more than half of the total production.

Market shake-up in full flow

The study determined that temporary delivery bottlenecks in 2010 caused prices to rise to 75 US\$/kg. Now the situation has calmed down. During the study in November 2011, contract prices were at 40 to 50 US\$/kg, dealers were getting 35 US\$/kg on the spot market. The decline in prices is not solely due to market mechanisms. Producers have achieved substantial cost benefits from new reactor types and improved processes. The main focus here is on energy

consumption. It is the largest proportion of the cost structure with 22 % to 32 %, depending on the layout of the factory. But Si producers are turning the screws. German producer Wacker claims to have lowered specific energy consumption in silicon production by 50 % over the last ten years. Not everyone can keep up with this level of innovation. It is foreseeable that with prices at their current levels around 60 smaller manufacturers, mainly from China, will have to leave the market – their production costs are at least 40 US\$/kg. Silicon producers do not believe they are in a difficult situation solely due to falling prices. In addition to the greater levels of efficiency that cell manufacturers have been focussing on, demands on the quality and purity of the polysilicon have also increased.

Siemens – the mother of all procedures

The market demands cost reductions and, at the same time, increases in quality. There are a series of approaches to meet this double challenge. But only a

few of them have been able to take hold in major industry. The actual starting point for the various developments, however, is not in current market conditions but can be traced much further back. In order to get silicon at the beginning of the millennium, the photovoltaic industry drew on the semiconductor industry. That was not a particularly economical practice as silicon specialist Johannes Bernreuter points out, "The demands of the semiconductor industry on the purity of the silicon were much too high for the photovoltaics industry." In short, there was more demand for solar-grade and not electronic-grade silicon. As a result, developers set their sights on the dominant procedure for producing polysilicon, the so-called Siemens procedure. The Siemens procedure uses trichlorosilane (TCS) to take the last 0.5 to 1 % of impurities out of the metallurgical silicon. In order to manufacture TCS, small pieces of metallurgical silicon are placed in a reactor with hydrogen chloride and heated to 300 to 400 °C. So TCS makes up between 80 % and 90 % of the reaction product. The by-products silicon tetrachloride (STC) and unused hydrogen chloride are separated and recycled by distillation.

Criticism of energy consumption

The TCS cleaned in this way is mixed with hydrogen and added to the actual Siemens reactor. This reactor contains U-shaped rods of pure silicon electrically heated to 1,100 °C. When it comes into contact with



the rods at these temperatures, the TCS breaks down into its component parts. Pure silicon is then deposited on the rods. The whole process takes place at an excess pressure of 6 bar. The remaining gas consists of hydrogen, dichlorosilane and STC and is fed back into the production cycle again. Only about one fifth of the silicon contained in the TCS is deposited on the rods. In order to prevent the reactor walls becoming encrusted with a layer of pure silicon, they are cooled from the outside.

Polysilicon deposition at the Nünchritz plant. These state-of-the-art production plants are designed for an annual capacity of 15,000 t.



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Gas circulation system for polysilicon production at the plant in Nünchritz. Resulting by-products are recycled in the system to be added back into the manufacturing process.

The procedure attracts criticism due to its relatively high investment costs and the use of chlorine chemistry. But the main criticism against the Siemens procedure is the cooling of the walls. "This means the procedure consumes a lot of energy," says Johannes Bernreuter who regularly publishes studies on silicon production. However, he does point out that this argument does not have the same impact it did ten years ago. In recent years, the procedure has been optimised so much that total energy consumption is limited to 80 kWh/kg for the best-in-class companies. Average energy consumption is 150 kWh/kg. Small production plants in China, however, have a consumption level of more than 300 kWh/kg. They are the ones perpetuating the Siemens procedure's reputation as an energy guzzler.

Obviously this is still decisive in the search for alternatives, although there are other options to reduce costs further. For example, recycling STC would lead to significant cost savings. In the traditional procedure, a converter converts STC into TCS. The obtained yield is 20 % – that figure could be increased. Manufacturers also promise efficiency gains through monosilane.

Schmid starts monosilane procedure

The latest advancements in this technology have come from Southern Germany. Schmid Silicon Technology (SST), founded in 2006 by entrepreneur Christian Schmid, produced the first silicon at its own production plant in mid-June 2011. According to company data, the 9N specification was achieved in its first production run. This means the silicon produced was 99.999999 % pure. Just two months after the "first silicon out", SST was even able to manufacture silicon corresponding to an 11N specification and

thereby meeting the high demands of the electronics industry. According to SST, only very few top producers can achieve these levels of quality using traditional technology. In some cases, certain companies mix these high quality products with their own to obtain a marketable product. According to Jochem Hahn, COO of SST, the quality achieved was not surprising but proof that this cleaning effect can easily and reliably be achieved with the disproportionation of trichlorosilane to monosilane. Jochem Hahn also points out other milestones: the deposition rate of 1 mm on the silicon rods and the low energy consumption. Both help reduce production costs.

The procedure: TCS is made from STC and a metallurgic grade TCS in a hydrochlorination reactor which is then converted to monosilane in another reactor. The ultra pure silicon is then deposited on hot silicon rods in a CVD (chemical vapour deposition) reactor. The process is a chemical-thermal decomposition in which large molecules break down into small ones due to the high temperatures. As a result, ultra pure silicon (Si) and hydrogen ($2 \times H_2$) are produced from SiH_4 . The hydrogen is then added back to the hydrochlorination process. Here it is needed to generate the required TCS from the STC.

Production costs below 10 €/kg

"A process based on monosilane opens up the possibility of producing a second marketable product with this same monosilane," says Johannes Bernreuter, explaining the advantage of the technology. The second advantage is the relatively low production costs. Conventional monosilane production requires an energy expenditure of 40 kWh/kg, 60 kWh/kg for the Si deposition and 57 kWh for the infrastructure of the process – a total of 157 kWh/kg. Production costs at a 10,000 t factory would be around 18 €/kg, if you base these figures on an electricity tariff of 0,02 €/kWh.

SST claims they can do even better now. Schmid Polysilicon Production has optimised the process significantly. Using their own procedure, they can now produce silicon with an electrical energy expenditure of about 55 kWh/kg, including the necessary infrastructure. 30 kWh/kg of which is used for the deposition. 30 kWh/kg in the form of steam is not included in that figure. But it is used again in a heat recovery process so it doesn't have to be included in the balance. With an assumed electricity tariff of 0,02 €/kWh, this results in current SST production costs of less than 10 €/kg – even at a capacity of 6,000 t/year.

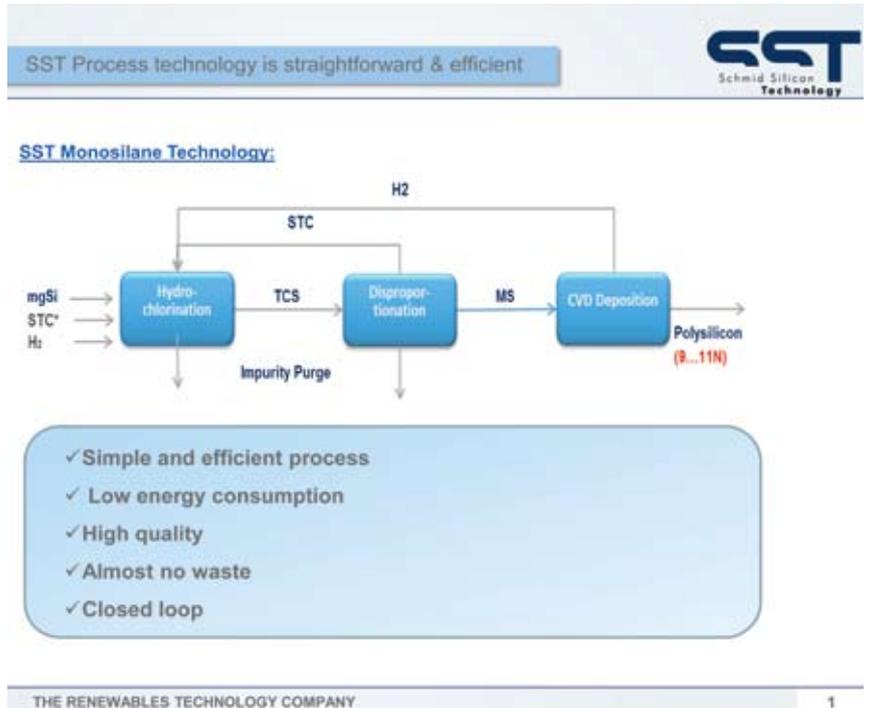
The expansion party continues

In the meantime, factories of this size are now seen as small. Obviously there is an unshakable faith in the future of photovoltaics prevalent among silicon producers. Companies are currently planning capacities in individual factories that, even just a decade ago, would be enough to supply the entire German

solar industry. LDK Solar, for example, announced the construction of a silicon production plant in Inner Mongolia with an annual capacity of 30,000 t. The company expects a significant increase in demand from 2014 and intends to prepare for it by expanding the factory.

LDK Solar currently has two plants in Xinyu (Jiangxi province) with an annual capacity of 17,000 t. The LDK board wants to expand this capacity to 25,000 t by mid-2012. By the end of 2013, final capacity should reach at least 55,000 t. As a result, LDK will be among the top group of silicon producers. A group which also includes a German firm, Wacker Chemie AG. Just days before LDK Solar's announcement, the company began producing ultra pure silicon at its new plant in Nünchritz, Eastern Germany. It should reach its full rated capacity of 15,000 t by the second quarter of 2012. According to initial estimates, Wacker produced around 33,000 t of ultra pure silicon in 2011 using the traditional Siemens procedure. After the expansions in Burghausen and Nünchritz, the German chemical group will have a nominal capacity of 52,000 t. 15,000 t will be added a year later from a plant in Cleveland, USA. Wacker will then claim its place in the top group of producers with an annual capacity of 67,000 t. Wacker comments this with remarkable understatement, "Others are expanding as well."

Jörn Iken



The Schmid procedure: TCS is made from STC and metallurgic grade silicon in a hydro-chlorination reactor which is then converted to monosilane in another reactor. The ultra pure silicon is then deposited on heated silicon rods in a CVD (chemical vapour deposition) reactor.

Graphic: Schmid Group

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