There was no lack of warnings. The Eurosolar president and SPD member of parliament Hermann Scheer, speaking in May 2000 at the European Photovoltaic Solar Energy Conference in Glasgow, had forecasted a worldwide delivery bottleneck in solar modules due to a shortage of silicon. But this was not the only voice of warning. As early as 1999, a study conducted on behalf of the European Commission had concluded that towards 2005 the photovoltaic industry would be faced with a feedstock crisis.

But then the semiconductor industry suffered a strong dip, and the manufacturers of electronic-grade polysilicon were happy and relieved that at least part of their unused capacity could be taken up with deliveries to the photovoltaic sector. Up to 1998, the solar sector had still been able to live exclusively from the off-spec silicon it obtained from the semiconductor industry. But since then the production of solar cells from mono- and polycrystalline silicon, which accounts for over 90% of the total market, has quintupled. Despite thinner cells and other efficiency gains, the corresponding silicon consumption has quadrupled, according to the latest solar energy study by the Swiss Bank Sarasin (see table 1).

It was only because several manufacturers of polysilicon are now able to produce slightly less pure material for the photovoltaic industry that annual growth rates of between 34% and 54% were possible. However, the continuing good availability of solar-grade silicon meant that the efforts of the photovoltaic industry to establish a feedstock supply independent of the semiconductor industry “were pursued with insufficient intensity,” as Sarasin summarized in its study.

As late as April 2004, Karl Hesse, the director of process development at the polysilicon producer Wacker-Chemie, complained at the first Solar Silicon Conference in Munich that hardly any customers in the PV industry had entered into long-term contractual commitments, but instead were trying to meet their needs on the spot market. In July 2003, Wacker had announced that it would expand its production capacity for solar-grade silicon according to the classical Siemens process (see text box on page 83) up to 2,600 tons by mid-2004. In fact, this first resulted in a little less than 2,000 tons. “The solar industry didn’t fully accept our offer,” explains Reimund Huber, marketing director of the Wacker Polysilicon business division in the Upper Bavarian town of Burghausen. The “big push” first came in November 2003 with the German EEG preliminary legislation regulating higher feed-in-tariffs for solar electricity.
As it will take about 18 months to expand the production capacity for polysilicon, people are now feeling the consequences: the prophesied feedstock crisis is now a fact. »The sector has missed the boat. No one listened to the prophets,« is the clear verdict of Peter Woditsch, the chief executive officer of Deutsche Solar AG in the town of Freiberg in Saxony, one of the leading manufacturers of silicon wafers. It seems likely that the amount of solar-grade silicon available in 2005 will be not much more than in the previous year – about 8,000 tons worldwide, estimates Woditsch. According to Rob Bushman, president of the Californian company Silicon Recycling Services, this was augmented in 2004 by another 2,600 tons or so of off-spec silicon from the semiconductor industry – making a total of around 10,600 tons (see table 1).

Some 20,000 tons of polysilicon will be produced this year for the semiconductor industry itself, says Woditsch. So relief for the market cannot be expected from this quarter. On the one hand, industry experts expect a stagnation in the semiconductor market for 2005, following a strong growth of 28% in the previous year. But the trend towards thicker wafers and the attempt to top up stocks will keep the demand for silicon at a high level. This view is supported by the fact that the Japanese polysilicon manufacturer Tokuyama, which has increased its production capacity by 400 tons up to 5,200 tons per year, intends to supply this additional amount almost exclusively to the semiconductor industry. »The demand is very strong right now,« says Tokuyama spokesman Osamu Yokota, assistant manager in the corporate communications centre of Tokuyama. Yokota reports that about 20% of the production capacity will be going to the PV industry, i.e. some 1,000 tons a year.

Besides Wacker and Tokuyama there are two other large suppliers of solar-grade silicon, both based in the USA: the Hemlock Semiconductor Corporation (HSC), named after its home town of Hemlock in the state of Michigan, is the world’s biggest manufacturer of polysilicon with an annual capacity of 7,000 tons. In 2004, according to its product and market specialist Hitoshi Takahashi, the company supplied about 2,500 tons to the photovoltaic industry, Solar Grade Silicon LLC (SGS), a joint venture between the American polysilicon producer Advanced Silicon Materials LLC (Asimi) and the Norwegian Renewable Energy Corporation (REC) which was set up in 2002, achieved a figure of 2,100 tons, reports the SGS president and COO Tor Hartmann. The joint venture, operating from the Asimi base of Moses Lake in the US state of Washington, has specialized exclusively in the production of solar-grade silicon since 2003.

Over 5,000 tons more from 2007 onwards

With a consortium of companies, REC covers the entire value chain from solar-grade silicon through to the sale of photovoltaic systems and holds a 70% participation in Solar Grade Silicon. Now the enterprise also plans to acquire 75% percent of the shares in Asimi from the current owner, the Japanese construction and industrial machinery corporation Komatsu. To this end, REC and Komatsu published a corresponding letter of intent on 10 February; the transaction should be concluded in the first half of 2005.

Based in Butte (State of Montana), Asimi has been producing extremely pure polysilicon for the semiconductor industry, as well as silane for semiconductor and LCD applications, since 1998. In 2004, it manufactured some 2,800 tons of polysilicon, and by the end of 2005, the annual capacity should rise to about 3,400 tons. While observing existing supply agreements, after the takeover REC aims to gradually shift the polysilicon production from semiconductor applications to photovoltaic applications. Reidar Langmo, REC senior vice-president for business de-
PHOTOVOLTAICS

The feed material is melted down again and then, with the help of a seed crystal, extracted from the melt as a cylindrical single crystal.

For 2006 one can expect a degree of relaxation on the supply side of the silicon market. This will be due mainly to the market leader Hemlock, which according to Hitoshi Takahashi will get 2,000 tons of new production capacity for the photovoltaic industry up and running in the first quarter of the year, followed by another 1,000 tons in the fourth quarter. Wacker is following suit, with an increase in annual production of 500 tons in 2006 and a further 1,000 tons in 2007.

According to the marketing director Huber, this capacity growth is intended mainly for the photovoltaic industry. Together with the moderate capacity expansion at Solar Grade Silicon, this means that an additional 2,700 tons of solar-grade silicon will be available to the market in 2006, with another 2,100 tons in 2007 (see table 2), thus making a total of 4,800 tons. Following the changes at Asimi, it is highly probable that the growth will even exceed 5,000 tons.

**Fluidised bed reactors under development**

In the medium term, the major silicon manufacturers plan to increase their production not only by way of the comparatively expensive Siemens process (see text box on page 83). Like a few other companies, they are also working in parallel on alternative manufacturing processes (see table 3). Wacker, Hemlock and Solar Grade Silicon are pinning their hopes on the fluidised bed reactor. This consists of a quartz tube into which trichlorosilane (Wacker, Hemlock) or silane (Solar Grade Silicon) is blown from below together with hydrogen. The gas stream blends with small particles of silicon which are pored into the reactor from above (Wacker) or which are created by the collision of larger silicon granules in the reactor (Solar Grade Silicon). Silicon separates from the trichlorosilane or silane onto the particles and thus forms larger granules. This requires process temperatures of 700 °C for silane or 1,000 °C for trichlorosilane. At a certain point, the silicon grains become so heavy that they precipitate out of the gas stream onto the floor and can be removed from the reactor.

This process not only uses significantly less energy than the Siemens process, but in contrast to rod deposition it can also be operated continually. The figure of 25 €/kg of produced silicon granulate is a price we can do investment with, commented Wacker’s development director Karl Hesse at the Solar Silicon Conference last year. In October 2004, the company started operations with two pilot reactors in Burghausen, Germany, each with an annual capacity of 50 tons. According to the marketing director Reimund Huber, it will be decided in mid-2005 whether Wacker will then set up one or several production reactors, each with an annual capacity of 500 tons. Following a construction period of 18 months, production could then be commenced in early 2007.

Solar Grade Silicon has made similar progress in Moses Lake, where a pilot plant with an annual capacity of 200 tons started operation in mid-December 2004. The initial results are very promising, reports the president and COO Tor Hartmann. By the end of 2007, the fluidised bed reactor is to be upscaled to an industrial-scale plant. This should go hand-in-hand with an expansion of the silane production at the site from 3,000 to 5,000 tons per year, which would correspond to an additional silicon capacity of some 2,600 to 4,300 tons. Hemlock has plans on a similar scale for its fluidised bed process which should be ready for the market in mid-2008: Hitoshi Takahashi cites 3,000 to 5,000 tons per year as production goal. The capacity of the experimental reactor, which the company plans to start up in the second quarter of 2005, is just a modest 20 tons per year. But Takahashi points out that Hemlock was the first company to develop silicon granulate from trichlorosilane back in the 1980s. At that time, the technique failed to be adopted only due to the high purity requirements of the semiconductor industry. The case is different for solar-grade silicon: »We are quite confident that we can meet the requirements.«

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**Table 2: Solar-grade silicon production capacities until 2007 (Siemens process)**

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar-grade silicon</td>
<td>silicon overall</td>
<td>solar-grade silicon</td>
<td>silicon overall</td>
<td>solar-grade silicon</td>
</tr>
<tr>
<td>Hemlock</td>
<td>2,500</td>
<td>7,000</td>
<td>2,500</td>
<td>7,000</td>
</tr>
<tr>
<td>Wacker</td>
<td>2,000</td>
<td>5,000</td>
<td>2,000</td>
<td>5,000</td>
</tr>
<tr>
<td>SGS</td>
<td>2,100</td>
<td>2,100</td>
<td>2,100</td>
<td>2,100</td>
</tr>
<tr>
<td>Tokuyama</td>
<td>1,000</td>
<td>4,800</td>
<td>1,000</td>
<td>5,200</td>
</tr>
<tr>
<td>Asimi</td>
<td>0</td>
<td>2,800</td>
<td>&lt; 500</td>
<td>&gt; 2,800</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>7,600</td>
<td>21,700</td>
<td>&lt; 8,100</td>
<td>&gt; 22,100</td>
</tr>
<tr>
<td><strong>Increase</strong></td>
<td>&lt; 500</td>
<td>&gt; 400</td>
<td>&gt; 2,700</td>
<td>3,300</td>
</tr>
</tbody>
</table>

Source: Manufacturer’s instructions, REC
New ideas from Japan

In contrast, the tube reactor currently being developed by the Joint Solar Silicon GmbH & Co. KG (JSSI) – a joint venture set up by Solarworld AG and the chemical corporation Degussa in 2003 – is very close to the conventional Siemens process. The silicon is separated onto a hollow silicon cylinder instead of onto slim rods. Since silane is used as feed material, the process temperature can be limited to 800 °C. «All in all we expect a significantly better use of energy,» says Raymund Sonnenschein of Degussa, who together with Armin Müller of the Solarworld subsidiary Deutsche Solar is managing director of the joint venture.

According to Sonnenschein, the process design «features a trick»; the company will not reveal details until the experimental reactor, located in the Upper Rhine town of Rheinfelden and with an annual capacity of 100 tons, has successfully started operation in the second quarter of 2005. This year, it will be decided where a pilot plant with an annual capacity of 800 tons will commence production in early 2007. Sonnenschein has four locations to choose from. Like most developers of alternative manufacturing processes, JSSI hoped to commence the pilot phase much earlier – in 2005. But Sonnenschein explains that the initial plan «was too ambitious».

The Japanese Tokuyama Corporation has developed a totally new procedure for manufacturing solar-grade silicon. This is known as «Vapour to Liquid Deposition» (VLD), involves separation from the vapour phase to the liquid phase and represents a radicalisation of the Siemens process. Here too, trichlorosilane and hydrogen are fed into a reactor, but from above, not from below, and things get considerably hotter: instead of silicon rods which in the Siemens reactor reach a temperature of 1,100 to 1,200 °C, a graphite tube is heated up to 1,500 °C and thus above the melting point of silicon, which lies between 1,410 and 1,420 °C. This means that silicon separates from the trichlorosilane in liquid form on the hot graphite wall. It drips onto the reactor floor and solidifies there to granulate. The energy investment for the higher temperature is considerably hotter: instead of onto slim rods. Since silane is used as feed material, the process temperature can be limited to 800 °C. «All in all we expect a significantly better use of energy,» says Raymund Sonnenschein of Degussa, who together with Armin Müller of the Solarworld subsidiary Deutsche Solar is managing director of the joint venture.

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Following a small pilot reactor with an annual production of ten tons, Tokuyama has now commenced construction of a verification plant in Shunan (Yamaguchi Prefecture) which has an annual capacity of 200 tons and should be completed by the end of 2005. The company has cited a commercial production of «several thousand tons» as its goal. Project director Oda estimates that this phase could start in 2008.

Tokuyama’s project is being supported by Japan’s New Energy and Industrial Technology Development Organisation (NEDO); this organisation is also funding a project being conducted by the Japanese chemical company Chisso Corporation since 2002 in its research centre in Minimata (Kumamoto Prefecture) on the southern island of Kyushu. Chisso plans to produce solar-grade silicon through the reduction of silicon tetrachloride (SiCl4) with zinc vapour, whereby the chlorine atoms are bonded to zinc chloride (ZnCl2) – an approach that had already been pursued in the 1980s by such companies as Bayer AG, but without commercial success. The problem lies in removing traces of residual metals. A high number of process steps are necessary in order to obtain high-grade silicon, says Wolfgang Koch, who has researched solar-grade silicon for Bayer for many years.

Chisso seems to have cracked the nut: according to an interim report by the project director Masatsugu Yamaguchi, the zinc content of the silicon extracted in a pilot plant was under 10 ppm, while the proportion of each heavy metal was under 0.1 ppm.

Table 3: State of development of alternative manufacturing processes

<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
<th>Based in</th>
<th>Feed material</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wacker</td>
<td>Germany</td>
<td>Burghausen</td>
<td>trichlorosilane</td>
<td>fluidised bed reactor</td>
</tr>
<tr>
<td>JSSI</td>
<td>Germany</td>
<td>Rheinfelden</td>
<td>silane</td>
<td>tube reactor</td>
</tr>
<tr>
<td>SGS</td>
<td>USA</td>
<td>Moses Lake</td>
<td>silane</td>
<td>fluidised bed reactor</td>
</tr>
<tr>
<td>Hemlock</td>
<td>USA</td>
<td>Hemlock</td>
<td>trichlorosilane</td>
<td>fluidised bed reactor</td>
</tr>
<tr>
<td>Tokuyama</td>
<td>Japan</td>
<td>Shunan</td>
<td>trichlorosilane</td>
<td>Vapour to Liquid Deposition</td>
</tr>
<tr>
<td>Chisso</td>
<td>Japan</td>
<td>Minamata</td>
<td>silicon tetrachloride</td>
<td>reduction with zinc</td>
</tr>
<tr>
<td>Elkem</td>
<td>Norway</td>
<td>n/a</td>
<td>metallurg. grade silicon</td>
<td>slagg/etching/refining</td>
</tr>
<tr>
<td>Inversil</td>
<td>France</td>
<td>Chambéry</td>
<td>metallurg. grade silicon</td>
<td>plasma purification</td>
</tr>
<tr>
<td>Sunergy/ECN/Sintef Scanarc</td>
<td>Netherl./Norw./Sweden</td>
<td>Trondheim/Hofors</td>
<td>high-grade quartz / carbon black</td>
<td>carbothermic reduction</td>
</tr>
</tbody>
</table>
The report states that there is »no specific difference in performance between solar cells made out of conventional polysilicon and those made out of the silicon by our process«. Electrolysis is then used to extract zinc and chlorine from the by-product zinc chloride. The company declined to provide further details of its work. NEDO cites a cost target of maximally 2,000 yen (just under 15 €) per kilogramme of silicon for an annual production of 1,000 tons.

**Metallurgical alternatives**

Efforts have long been underway to manufacture solar-grade silicon without the energy-intensive chemical detour through trichlorosilane, silane or silicon tetrachloride. The Norwegian company Elkem, the world’s biggest supplier of metallurgical-grade silicon, thus starts right away with the feed material: the liquid metallurgical-grade silicon is first slagged, making it easier to crack open when, after solidifying, it is etched in the second phase. In a third step, the material is then further refined; the company declines to reveal further details.

Christian Dethloff, the director of the corporate division Elkem Solar, confirms that a pilot plant with an annual production of between 100 and 250 tons will be completed during late summer 2005. »After this we will move on to industrial production as soon as possible,« says Dethloff. But this depends on the results of the pilot phase; 2007 or 2008 are »certainly not off the mark« as regards the start-up year. An annual production of between 2,000 and 5,000 tons is then planned.

The Faculty of Applied Solid State Physics at the University of Konstanz, Germany, has already produced polycrystalline solar cells from Elkem material, with an average efficiency level of just half a percentage point below that of commercial cells. Process adjustments during the cell manufacture will allow further increases in quality. »I am convinced by the material,« says Kristian Peter, director of the feedstock group at the faculty in Konstanz.

Meanwhile, the number 2 behind Elkem, the French silicon manufacturer Invensil, has also started developing a metallurgical process for solar-grade silicon. Invensil, a subsidiary of the French aluminium and packaging concern Pechiney which is run by the former Photowatt manager Robert de Francieu, now under the umbrella of JFE Steel, also developed a metallurgical purification process at the end of the 1990s which, among other methods, utilised a plasma torch. For reasons...
of cost, however, JFE Steel so far does not use metallurgical-grade silicon for casting solar-grade ingots, but instead a mixture of 60 to 70% polysilicon and 30 to 40% off-spec silicon. «We can get hold of scrap silicon very easily,» explains Hisashi Osanai, general manager for production at the Kurashiki plant. But in view of the fairly dramatic rise in the prices of silicon, the original process is still in with a chance. «We are reconsidering that process,» comments Osanai.

Perhaps in the end, it will be the most radical approach that proves to have the best future prospects: producing metallurgical-grade silicon with such pure feed materials that it hardly needs to be purified in order to achieve the solar grade. A consortium that essentially consists of the Dutch project development company Sunergy, the Energy Research Centre of the Netherlands (ECN), the Norwegian research company Sintef and the Swedish company ScanArc Plasma Technologies is firmly focussed on this goal. A rotary plasma furnace operated by Sintef in Trondheim is first used to produce silicon carbide from very pure pellets of quartz and carbon black. In a second step, further quartz pellets are reduced with the silicon carbide to silicon; this takes place in an electrical arc furnace operated by ScanArc in Hofors. In order to reduce the high carbon content, the produced silicon is melted and then heated to above the melting point and then slowly cooled again. As a result, the carbon is precipitated on the form of silicon carbide. The best solar cells made of the purified silicon had an efficiency level about 15% below that of commercial cells.

The purification and subsequent crystallisation of silicon are to be optimised right now. While the annual capacity of the furnaces until now has been between 50 and 100 tons, the consortium aims to set up a pilot production of 500 to 1,000 tons per year in 2007. Advanced discussions with a candidate are already underway, says Bart Geerligs, the responsible project supervisor at ECN. Geerligs is convinced that the process has a rosy future. «It looks good. I really believe that it can work out techno-economically.» The direct route from quartz to silicon promises a particularly low energy consumption and moderate manufacturing costs, while the feed materials are available in large quantities. Geerligs points out that the photovoltaic industry is heading for an annual silicon requirement of 50,000 tons after 2010 and concludes: «Metallurgical routes are really necessary for the growth of the photovoltaic industry.»

Information:
Apollon Solar: www.apollonsolar.com
CNRS: www.cnrs.fr
Electronic Materials Division of Mitsubishi Materials Corporation (MMC): www.mmc.co.jp/adv/ele/english
JFE Steel: www.jfe-steel.co.jp
MEMC Electronic Materials: www.memec.com
New Energy and Industrial Technology Development Organisation: www.nedo.go.jp
Sumitomo Mitsubishi Silicon Corporation (Sumco): www.sumcasi.com
From quartz to solar-grade silicon (the Siemens process)

Silicon is literally as plentiful as sand on the seashore: after oxygen it is the second most common element in the earth’s crust. But it doesn’t occur in a pure form in nature, but is bonded to oxygen in the form of silicon dioxide (SiO$_2$) – above all in quartz and sand. In order to crack open the oxygen bond the process of «carbothermic reduction» is used. This requires a large amount of energy: an electrical arc furnace is filled not only with quartz but also with carbon-containing materials such as charcoal, coal and coke. A strong electrical current jumps as an electrical arc between carbon electrodes and heats the material to over 1,800 °C. Through several intermediate reactions the oxygen atoms from the quartz bond with carbon to form carbon monoxide (CO), and silicon can be tapped as melt from the floor of the furnace.

But this metallurgical-grade silicon is not pure enough for either the semiconductor or the photovoltaic industry, because it contains between 0.5 and 1.5 % foreign materials such as iron, aluminium, calcium, magnesium, carbon, phosphorus and boron. However, in a microchip a maximum of just one foreign atom for every billion silicon atoms is permissible. Therefore manufacturers of electronic-grade silicon, mostly large chemical companies, further process the silvery grey metal: it is ground up and converted with hydrogen chloride (HCl) to trichlorosilane (SiHCl$_3$), a highly volatile liquid. Impurities can then be separated out relatively easily by distillation in house-sized fractionating columns.

But now the silicon has to be regained, and this too is only possible with a high energy expenditure. The Siemens process, as it is known, has become the industrial standard. In this process, the trichlorosilane or silane is fed together with hydrogen into a reactor in which slim rods of electronic-grade silicon (diameter about 8 to 10 mm) are heated with an electrical current to over 1,100 °C. Silicon from the trichlorosilane or silane separates onto the slim, hot rods. Several days are needed before the rods, with a length of about 1.50 m, have reached a diameter of 15 to 20 cm.

The extracted silicon is now electronic-grade, but still polycrystalline – thus the description «polysilicon» or in industry jargon just «poly». For manufacturing a single crystal, the Czochralski process is the most frequent solution: the silicon rods are broken into fist-sized chunks, filled in a quartz crucible and melted there at a temperature of about 1,420 °C. A seed crystal is dipped into the melt and moves slowly upwards with a rotating motion, while silicon solidifies onto it. In this way a cylindrical single crystal grows upwards.

The wafers, which the semiconductor industry uses to make microchips, are then sawn from this crystal. The photovoltaic industry uses the same process to produce monocrystalline solar cells from slightly less high-quality (solar-grade) polysilicon or from off-spec silicon from the semiconductor industry. In order to produce polycrystalline cells, the industry allows the silicon melt to cool evenly in one direction inside a large casting block. This process of «directional solidification» leads to the formation of fewer grain boundaries which limit the efficiency of the solar cells.

Johannes Bernreuter