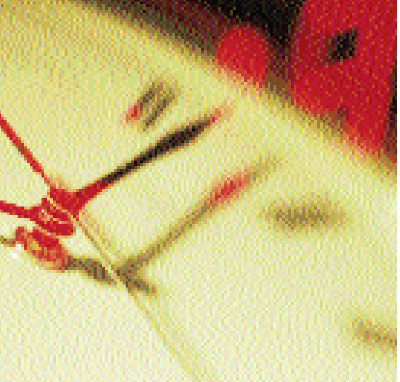

Update

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Polysilicon Business Shines Brightly

To meet growing demand for solar energy, new polysilicon plants are being built at an unprecedented rate, and several new technologies will play a role in the capacity expansion.

In the 1980s, John Schumacher was busy working on a fluidized-bed process to produce polysilicon for semiconductors. Many others were engaged in similar projects as part of a push by the U.S. Dept. of Energy (DOE; Washington DC; www.doe.gov) to develop less-energy-intensive alternatives to the popular Siemens process — a chemical vapor deposition (CVD) technology named for the company that developed it. Most of the projects were abandoned when DOE pulled the plug on the program, and the polysilicon business subsequently fell on hard times because of overcapacity and a slump in semiconductor production.

Today, the veteran semiconductor-industry entrepreneur is back on track with his fluidized-bed process. Schumacher's company, Peak Sun Silicon Corp. (Salem, OR; www.peaksunsilicon.com) is building a pilot plant to test his upgraded process, prior to commercializing it in 2011.

He is not alone. Driven mainly by the strong worldwide demand for solar energy, polysilicon manufacturers are adding capacity at an unprecedented rate (see sidebar). While most of the new capacity uses the Siemens method, several companies are commercializing or developing fluidized-bed (FB) processes, and others are working with so-called upgraded metallurgical routes as lower-cost alternatives to both Siemens and FB technologies. (DOE is supporting photovoltaics (PV) development as part of its Solar Energy Technologies Program, but most of the funding is aimed at reducing PV cell and system fabrication costs and increasing solar conversion efficiencies, which are beyond the scope of this article.)

The Siemens process has been the workhorse of the semiconductor industry for decades. It starts with the reaction of metallurgical-grade silicon (of about 99% purity) and hydrogen chloride at around 600°F and 500 psi to form a mixture of chlorosilanes. Trichlorosilane is obtained from the mix by distillation (other compounds are recycled) and introduced with excess hydrogen into a bell jar containing pure silicon filaments, which are heated to about 1,100°C. At this temperature and a pressure of a few bars, polycrystalline silicon deposits on the filaments to form rods. The role of the H_2 is to prevent homogeneous nucleation of silicon, which would create dust in the reactor.

An alternative to trichlorosilane for silicon deposition is silane (SiH_4), which saves energy because the Si deposition temperature is about two-thirds that of $SiHCl_3$. So far, silane has not found widespread use because it is more difficult to work with and ignites spontaneously in air. However, it is being used by one company for a commercial Siemens process and in at least two fluidized-bed processes.

The polysilicon rods created in the

■ Figure 1. Renewable Energy Corp.'s new plant in Moses Lake, WA, will use a fluidized-bed process to produce polysilicon, using trichlorosilane as the carrier gas. Photo courtesy of Fluor Corp.

Siemens reactor are broken up and remelted in a crucible. In the next step, the Czochralski (Cz) process, a seed crystal is introduced into the melt and slowly withdrawn to produce a single crystal or ingot that measures several inches in diameter and several feet long. Subsequently, the crystals are sliced to obtain wafers for semiconductors or photovoltaic cells.

Silicon produced by the Cz method has a purity of up to 11 nines (99.999999999%), versus about 99% for metallurgical-grade silicon, says Richard Winegarner, president of the consulting firm Sage Concepts, Inc. (Healdsburg, CA; www.sageconceptsonline.com). However, a purity of six nines is adequate for photovoltaics, he says, so about 60% of the production for solar cells is done by the less-expensive Bridgman ingot-growth process. This is a casting technique in which molten silicon is fed into the top of a disposable vessel and slowly cools and crystallizes as it flows downward.

SOLAR ENERGY: A FAST-GROWING MARKET FOR POLYSILICON

Until the year 2000, the solar energy industry accounted for less than 10% of the polysilicon market, and the waste from semiconductor silicon production met most of its needs. No more!

The solar market has been growing at about 40%/yr for the last four years, vs. 4–6%/yr for semiconductors, and now accounts for half the total demand, says consultant Richard Winegarner, of Sage Concepts. “In another five years, photovoltaics will be using about four times as much silicon as semiconductors,” he adds.

To catch up with the demand, which has far outstripped capacity in recent years, polysilicon manufacturers are building new plants at an unprecedented rate. If all goes as planned, world polysilicon capacity will quadruple to 200,000 m.t./yr by 2012, from about 50,000 m.t. in 2007, says Winegarner.

Hemlock Semiconductor Corp. (Hemlock, MI; www.hscpoly.com), the world’s leading producer of polysilicon, has started production at a new 9,000-m.t./yr facility that brings its total capacity to 19,000 m.t./yr. The company is planning further expansions that will increase the total capacity to 36,000 m.t./yr by the end of 2011. Wacker, the second leading producer, will increase its capacity from around 10,000 m.t. to more than 22,000 m.t./yr by 2010.

The dynamic market has created a bonanza for engineering companies, particularly Fluor Corp., whose photovoltaics projects amount to 35% of its $6 billion chemicals business backlog. “We have the largest backlog of PV projects in the world,” says vice president Arnie Smith. The biggest of those projects is a 15,000-m.t./yr polysilicon plant for China’s LDK Solar. Located in Xinyu City, Jiangxi, it is scheduled to start up in mid-2009.

Germany is a world leader in the use of photovoltaics as a result of long-term incentives for energy generated from renewable resources. In 2007, Germany added 1,100 MW of PV power, or 49% of the total new capacity installed in the world last year, says Claus Habermeier, director of the New York office of Invest in Germany, the investment promotion agency of the German government. Spain was second, with 13%, followed by the U.S., with 12%. The added capacity in Germany brought the country’s total installed PV power to 3.8 GW, says Habermeier.

The rapid growth of the industry is also helping to bring down the cost of PV systems, says Raghu Das, CEO of IDTechEx, Inc. (Cambridge, MA; www.IDTechEx.com), a market research and analysis company. The installed cost of PV systems is now around $4/W, compared to about $1/W for a coal-fired electricity plant. However, Das points out that the cost of photovoltaics has dropped from around $6–7/W in the past three years. “The general trend,” he says, “is that for every doubling of manufacturing capacity we see the cost fall by 25–30%.”

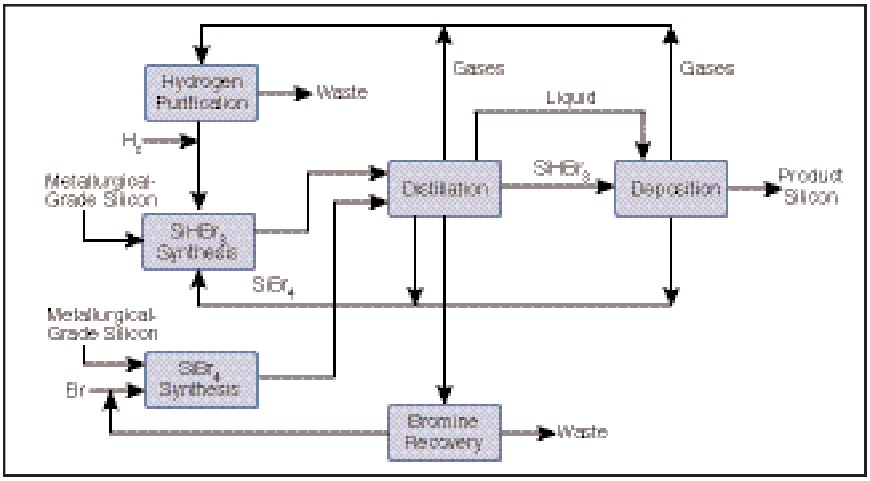
Fluidized beds

In a typical FB process, silicon deposition takes place at ambient pressure in a vertical column. Pure silicon seed granules of about 100-μm dia. are introduced into the top of the column and silicon-bearing gas is injected upward from the bottom. As the granules grow and gain weight, they gradually fall and are removed from the bottom of the column as particles of approximately 1-mm dia.

The main benefits claimed for FB processes over the Siemens batch operation are that they are smaller for the equivalent throughput and use much less energy, and the silicon beads can be harvested continuously without having to shut down the reactor. “A fluidized-bed reactor can run continuously for months,” says Arnie Smith, vice president of process technology for Fluor Corp.’s Energy and Chemicals Business Group (Aliso Viejo, CA; www.fluor.com), a leading builder of polysilicon plants. In addition, the uniform, granular product can be metered and processed more effectively for the next step than silicon rods, which are broken into chunks.

Fluidized beds use less energy than the Siemens method because heat transfer is much more efficient, since the gases are heated. In contrast, in a Siemens reactor only the rod is heated (electrically), while the reactor wall is cooled to avoid homogeneous nucleation of silicon.

The company that may have the most experience operating fluidized beds for polysilicon production is MEMC Electronic Materials (St. Peters, MO; www.memc.com), a major producer of silicon wafers. MEMC has been using FB technology to produce granular silicon since the 1990s. The process, which uses a mixture of silane and hydrogen (to prevent homogeneous nucleation of silicon), was acquired from Ethyl Corp. (Richmond, VA), which developed



■ Figure 2. Peak Sun's fluidized-bed technology is a bromine-based process. Source: Peak Sun Silicon Corp.

and commercialized it in the 1980s.

Besides the FB plant, located in Pasadena, TX, MEMC has a plant in Merano, Italy, that uses the Siemens process. The company is expanding both facilities to increase total capacity to 15,000 m.t./yr by the end of 2010, up from about 6,000 m.t./yr at the end of 2007.

Another FB process that uses silane (plus H_2) as the carrier gas is being commercialized by Renewable Energy Corp. (REC; Oslo, Norway; www.recgroup.com) in Moses Lake, WA. Scheduled for startup early next year, the 6,500-m.t./yr plant (Figure 1, p. 8) will more than double polysilicon capacity at the site, where REC has two plants that make polysilicon by the Siemens process, also using silane. A second, similarly sized plant is being built, and is scheduled for completion in 2010.

REC's proprietary silane and FB processes are based on technology inherited from Union Carbide Corp. (UCC; now a subsidiary of Dow Chemical Co.), which originally operated the Moses Lake plants. The company makes silane by catalytic disproportionation of trichlorosilane to silane. UCC started working on the FB process in the 1980s, but never commercialized it. REC says the energy consumption of its process is as little as 10% of that of a trichlorosilane-based Siemens process.

A fluidized-bed process that uses trichlorosilane to produce granular polysilicon has been developed by Wacker Chemie AG (Munich, Germany; www.wacker.com). The company has piloted the process and is now initiating commercial production at a 650-m.t./yr plant in Burghausen, Germany. Wacker, the world's second-largest silicon producer, currently uses the Siemens process for most of its polysilicon production. The company developed the FB process specifically to serve the solar industry.

Wacker has also made changes in the Siemens process to improve efficiency in order to produce polysilicon at a lower cost for the solar industry. The company has modified the silicon deposition step to increase output and has developed a rod-crushing process that avoids the need for subsequent purification of the surface by chemical etching.

Many of the future advances in photovoltaics are likely to involve cheaper ways of processing polysilicon than the present method of slicing individual wafers from crystals. For example, Wacker has formed a joint venture for wafer production with Schott Solar GmbH (Alzenau, Germany; www.schottsolar.com), a wafer manufacturer. Schott has developed an edge-defined film-fed growth process, called EFG, in which the silicon starting material is pulled from the silicon melt in the form of an octagonal hollow tube. A laser then cuts out the wafers. The process greatly reduces material loss and makes for more-efficient use of silicon.

AE Polysilicon Corp. (Chatham, NJ; www.aepolysilicon.com) has also developed a FB process that uses trichlorosilane. A 1,800-ton/yr plant is scheduled to start test production late this year and commercial production is set for 2009.

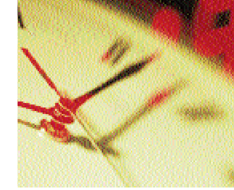
Peak Sun's FB process (Figure 2) differs from others in that it uses tribromosilane for silicon deposition. This is obtained by reacting metallurgical-grade silicon with hydrogen and silicon tetrabromide ($SiBr_4$) to form a mixture of $SiBr_4$ and tribromosilane ($SiHBr_3$), which is purified by distillation. The $SiHBr_3$ decomposes at about 800°C and ambient pressure to deposit silicon. Offgases from the distillation and deposition steps are recycled.

Schumacher says his process produces electronic-grade silicon of ten-nines purity. He acknowledges that bromine is more expensive than chlorine but, unlike trichlorosilane or silane, it does not have a homogeneous nucleation problem. "It's a closed-loop process with no waste," he says.

Peak Sun is building a 50–100-ton/yr pilot plant and plans to start up two 5,000-ton/yr commercial plants in 2011. Schumacher estimates that the capital and operating costs for a greenfield plant are roughly one-third less than those of an equivalent Siemens facility.

Metallurgical routes

Metallurgical-grade silicon, the starting material for making solar- and semiconductor-grade polysilicon, normally has a purity of around 99%. An



upgraded material that is said to be suitable for direct use in solar cell production, thereby avoiding the costs of gas-phase processing, will be available by year-end from Elkem Solar (Oslo, Norway; www.elkem.no).

Elkem declines to give details on its technology, except that it uses what are basically conventional metals-processing techniques to purify metallurgical silicon: slag treatment, leaching and solidification. The resulting ingots are sawed into bricks of around 10 kg.

Solar-quality silicon produced from an industrial demonstration plant has shown typical impurities of only 1.5 ppmw for phosphorus and 0.4 ppmw for boron (the critical pollutants), with total metallic impurities of <30 ppmw. Elkem is starting up a 5,000-m.t./yr commercial plant in Kristiansand, Norway, and says the production cost is less than $20/kg, vs. $25–35/kg for a traditional Siemens process. (Elkem says this is the fully absorbed cost, including finance, depreciation and amortization).

Dow Corning Corp. (Midland, MI; www.dowcorning.com) and Becancour Silicon, a subsidiary of Timminco Ltd. (Becancour, Quebec; www.timminco.com), are already produce solar-grade silicon by metallurgical routes. In both cases, for the most part, the product has to be blended with traditional polysilicon feedstock to achieve good solar cell performance characteristics. However, Timminco says it has improved the quality of its silicon by reducing the phosphorus content to 0.8 ppmv and boron to 3 ppmv, so that some customers are able to use it without blending.

In a radical switch from current technology, Mayaterials, Inc. (Ann Arbor, MI; www.mayaterials.com) is developing a process to produce silicon from agricultural wastes containing relatively pure forms of silica, using a proprietary chlorine-free process. The goal of the three-year, DOE-sponsored project is to produce solar-grade silicon for $25/kg, says Richard M. Laine, CEO. The process is still at an early stage of development, he says, but so far the company has removed mineral impurities in several low-temperature steps (polysilicon production will come later). He adds that initial data are promising, with purities of intermediates already near five nines. CEP