New feedstock materials

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1. Introduction

The PV industry has a growth rate that many other industries only can dream about. Today, the majority of solar cells are based on silicon, and most experts assume that crystalline Si PV technology will dominate the PV market for the next decade. Currently, the only commercial source for solar grade silicon (SoG-Si) is rejected and non-prime silicon from the semiconductor industry. This makes the PV industry highly exposed to the cyclic changes in the semiconductor market.

Photovoltaics covers today a very small part of the power demand in the world. However, electrical energy from the sun could be a giant on the energy market in a generation or two. Some futurologist says that PV could be comparable to the oil and gas as of today.

2. Market for silicon feedstock

The demand for solar grade silicon (SoG-Si) is growing rapidly, as the growth rate of the PV industry is estimated to be more than 25% per annum in the coming 10 years, see Figure 1/1,2,3/.

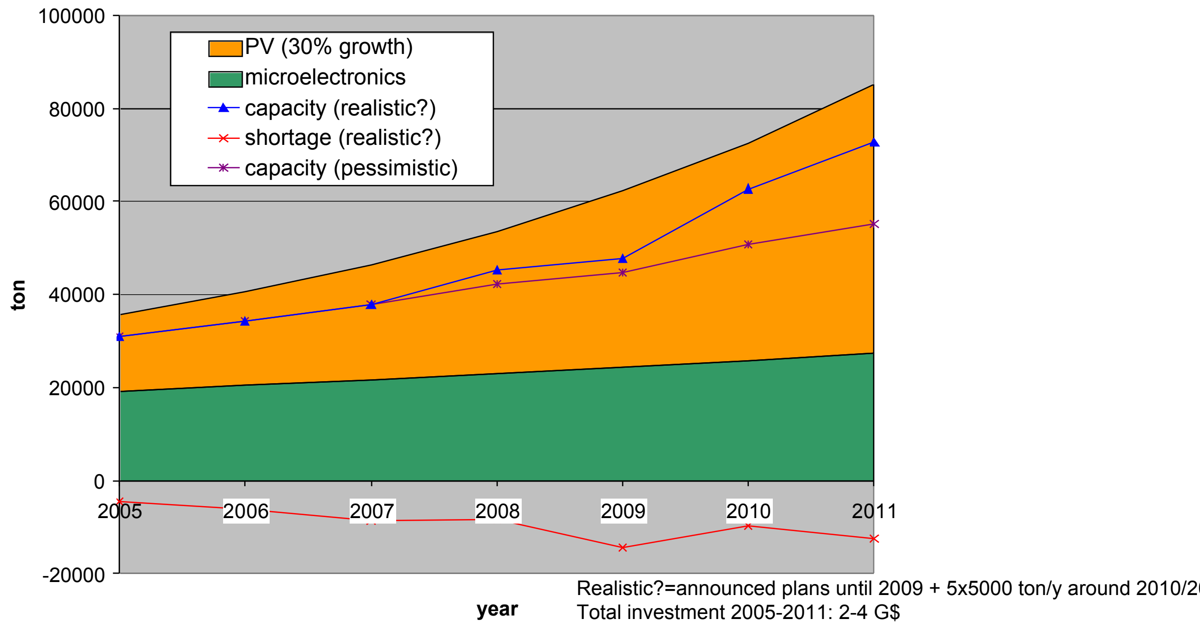

Figure 1 The demand and supply of SoG-Si with a growth rate in the PV industry of 30%.

At present, the world production of high-purity silicon is limited to 31.000 tons in 2005. Approximately 19.200 tons is supplied (including inventory) to the semiconductor industry, and 16.300 to the PV industry. Figure 1 shows the predicted growth in demand of silicon from

PV industry with 16.000 tons in 2005 and 47.000 tons in 2010. The graph is based on a growth rate of 30% in the PV industry.

This growth can not be reached only by the present supply route. The main goal for the next coming years is to secure the availability of solar grade silicon at low costs, through mass volume production. Therefore, it is essential to develop an independent, dedicated energy efficient silicon feedstock supply chain, which secures supply of low cost silicon to the PV industry. The shortage of SoG-Si is leading to high prices and a secure supply of SoG-Si for wafers and cells at reasonable costs is crucial for being in business.

At the 2nd Solar Silicon Conference in Munich in April 2005, all producers of silicon to the PV industry were expressing their concern for the future supply. The PV industry has predicted a deficit in silicon feedstock already in 2005 resulting in prices as high as 40 – 50 €/kg silicon. Producers of wafers are postponing the realisation of expansion plans. The consequences could be a lower annual growth in the PV industry, predicted already this year.

In principle, there is not a shortage of silicon in the world today. In the metallurgical industry, metallurgical grade silicon (MG Si) is produced by carbothermic reduction of quartz at a capacity of 900,000 ton/y with a purity of about 99 %. The main pollutants are iron, aluminium, phosphorus and boron. Half of the silicon produced is used as an alloying element for aluminium, and 45% is used in the silicone industry. The remaining 5% are raw material in the chemical processes of semiconductor industry. The silicon has to go through a very energy consuming process in order to achieve the purity that is required by the semiconductor industry. Research shows that the quality requirements for solar grade silicon are lower than for EG-Si, at least for specific cases such as carbon and dopants. .

Silicon from the semiconductor industry is not a very good alternative as the price is too high (30-40 times higher than MG silicon and twice as much as the reject or non-prime material in today's solar cells). This is the reason way the industry and the researchers are hunting for new process routes for feedstock to solar cells.

3. Different routes for silicon feedstock to solar cells

The silicon value chain to feedstock for solar cells is shown in figure 2. In principle, there are several different ways to SoG-Si.

1. The traditional route to semiconductor silicon is shown on the left hand side of Figure 2. Scrap, rejected, and non-prime material from this production is the main supply route of today.
2. Several companies (Wacker, ASIMI, etc) are making a big effort to economise the chemical route by shifting from rod decomposition of TCS to fluidised bed in the last step of the polysilicon production
3. The purification of metallurgical silicon has, so far, not resulted in a commercially viable process for a feedstock to solar cells. Several companies (Elkem, FerroAtlantica etc) are working on this route to SoG-Si.
4. The last potential source of solar grade silicon might be from the direct carbothermic reduction of quartz and carbon as indicated on the right hand side of figure 2. The Solsilc route is an example of this.

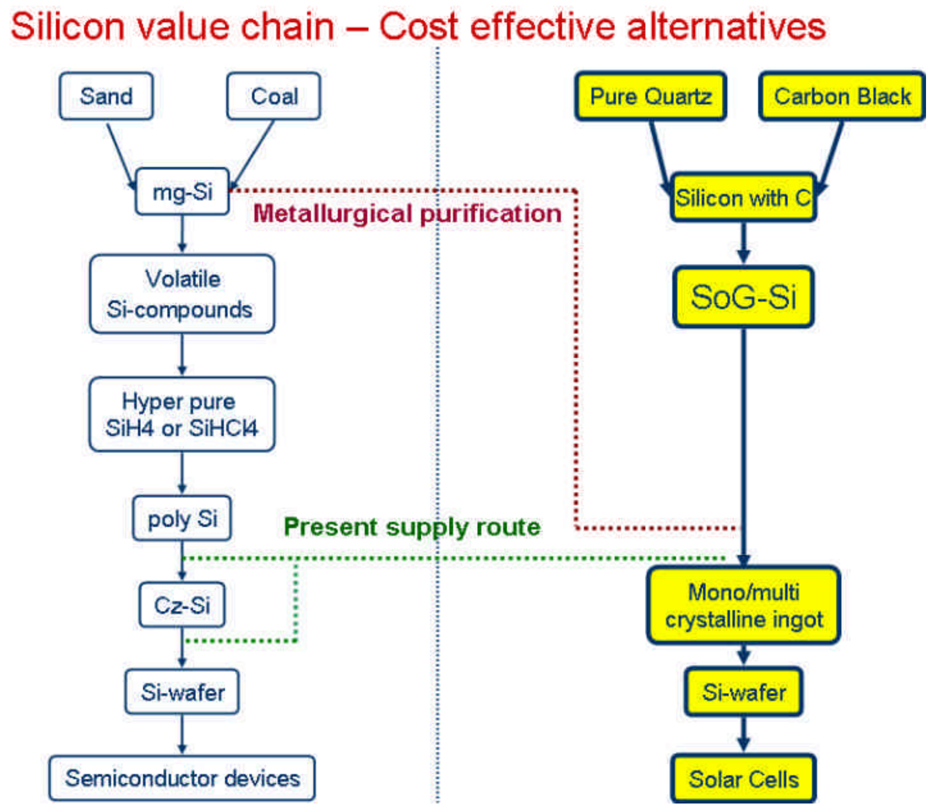

Figure 2. Alternative routes to Solar Grade Silicon

Chemical routes based on electronic grade silicon

In the chemical route, metallurgical grade silicon is reacted with HCl and transformed into the gaseous phase. The gas phase is distilled and by-product removed before the gas (often TCS) is decomposed on filaments in a bell jar CVD reactor. Conventional plants for the production of electronic grade silicon, produce silicon via distilled (chloro-)silane-gasses.

The plants require large investments for relatively modest production capacities. They also consume huge amounts of electrical energy. Several companies (Hemlock Wacker, Solar Grade Silicon LLC (2300 MT/year), Tokuyama, Joint Solar Silicon) have all plans for expansion in the near future. The processes are still based on (chloro-) silanes but in several cases they are using new deposition technology, often fluidized beds. However, in many cases the companies don't seem to be decided about the ratio bell jars/new reactors in the expansion. This is related to the fact that the new reactors are at most in early pilot testing.

Direct Metallurgical Route

SOLSILC

The Direct Metallurgical route produces silicon from ultra-high purity raw materials. Silicon production according to the SOLSILC technology/4/ has resulted in silicon of very high purity and has already been running at a pilot scale of 50-100 ton/y. Research is presently in a progressive stage through the EC funded SiSi project. This carbothermic production route can, in principle, reduce the cost of feedstock to below € 15/kg.

The idea behind the SOLSILC Technology was to develop a new two-step high temperature plasma-process for solar grade silicon (SoG-Si) production, based on carbothermic reduction.

The SOLSILC Technology relied on expertise of the metallurgical production methods for Silicon and SiC, and PV cell processing, see figure 3.

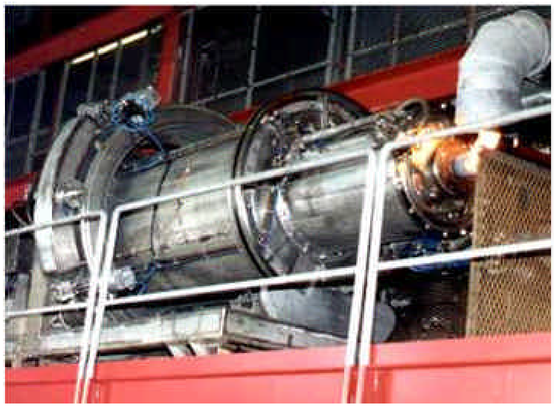

Figure 3. Solsilc pilot silicon metal production. SiC is formed in the plasma rotary furnace based on quartz and Carbon Black. Liquid silicon is produced from SiC and SiO_2 in an electric arc furnace.

The work started with the development of a low-purity Si-process facility in order to control the production process before a clean environment was established. In order to control the purity of the silicon, the selection and supply of raw materials were crucial. Special selected Carbon Black and quartz were used. The work was successful, and the production was transferred into a high-purity Si-production process with a capacity of 20 kg/hr for both steps of the process. The high purity Si production process has been tested and optimised, and is now running smoothly.

The bottleneck that all producers of SoG-Si based on carbothermic reduction of quartz face, is to remove carbon and metals impurities like iron, aluminium etc from the silicon. The source of the impurities is mainly the quartz. In order to comply with the objective of low cost, this has to be done on large-scale in a cost effective and reliable manner. A large number of experiments were carried out first in small scale. By combining experiments with simulations, relevant parameters were studied and optimised to enable selection of the most economical large-scale purification technique. The purification has been studied on a scale of up to 50 kg batches, see Figure 4.

As the quality of SoG-Si is not a standard yet, a lot of effort has been made to assess the SOLSILC material with respect to cell performance. Artificial solar grade silicon was used to evaluate whether the material properties were compatible with a solar cell production process. The processing and efficiency of cells based on Solsilc material has shown promising results.

The perspective of the SOLSILC technology is a low cost SoG-Si of constant quality in sufficient quantities and at a low price. In order to achieve this goal, the process has to have a low-energy consumption, high yield and low impurity level.

The Solsilc partners are working on a basis of design for up-scaling of the Solsilc route to a demonstration plant with capacity of 1500 ton per annum.

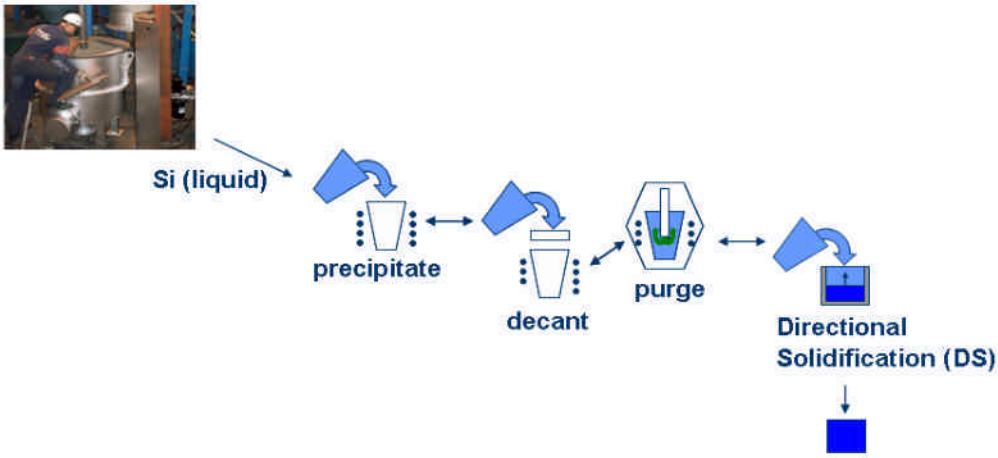

Figure 4. Possible steps in the Carbon removal process.

Kazakhstan carbothermic route/5/

A research group at the Kazakh National Technical University in Kazakhstan, is also working on a carbothermic reduction process for solar grade silicon. They are using very clean quartz from deposits in Kazakhstan. The production is carried out in a 300 kVA pilot arc furnace with a capacity of 250 kg/day. The silicon has a purity of 99.95% Si. The results look promising, but more information about the process is needed.

Metallurgical purification

Elkem-route for cleaning of metallurgical silicon

Elkem has been working on the development of a new process for the production of SoG Si for a very long time/6,7,8/. They started already in the 80ties and 90ties together with the oil company Exxon and Texas Instruments. Today, Elkem has funded a company, Elkem Solar that is responsible for the SoG-Si development.

Elkem has a considerable competence in the production and refining of silicon. They are the world's leading company in the production of metallurgical silicon. In Elkem, the chosen route to produce SoG-Si is to further enhance its "standard" metallurgical products through slag refining. They have developed a two step refining process. The first step is slag refining of the silicon to remove certain elements. The next step is a leaching process that will remove other elements. The energy consumption of the silicon process is 20 – 25% of the traditional Polysilicon route.

Elkem Solar has shown that their SoG-Si may be used to produce cells of an efficiency of 15 to 16% /6/ Elkem will build a pilot-scale plant in 2005. A full scale industrial plant is planned in 2007. Elkem emphasize low costs, big volumes and low energy consumption as the main asset

Silicon by electrolysis

Electrolysis has been the way to aluminium for more than 100 years. Silicon can also be produced by electrolysis. A process was patented by Stubergh/8,9/ in 1994. The process is based on the dissolution of quartz in a fluoride-containing bath at 1000°C, and decomposition of the quartz into silicon and oxygen. Silicon precipitates at the electrode. Afterwards, the silicon is crushed and cleaned with acid. In order to obtain a clean product, the silicon is melted and thereafter crystallized into ingots for subsequent sawing into wafers. The slag that comes with the silicon from the electrolyte has a high solubility for impurities and can be separated from the silicon.

Today, Stubergh has scaled up his tests to a larger laboratory scale. The work is partly done in cooperation with SINTEF and IFE. He has established a company "Norwegian Silicon Refinery" and has made plans for a full scale test facility.

SINTEF is also doing research on production of silicon by electrolysis. The process was patented in 2003 and is based on a chloride melt/8/.

Supplementary feedstock through recycled material

Approximately 30% of the silicon used to grow a multicrystalline ingot ends up as solar cells. Thanks to the present rapid growth of the photovoltaic industry, the amount of by-products is increasing as well. In this context, reclaim of solar grade silicon by-products from ingot growing, shaping, failed runs, broken wafers and solar cells, etc., becomes more and more interesting from a commercial and scientific point of view. Typically it might be sufficient to remove a surface layer of the silicon with accumulated impurities. There is no knowledge about the new feedstock material and the accumulation of impurities and their tolerable levels in recycling material.

4. Conclusion

There are several initiatives for making new feedstock materials for the PV industry. The prospect for the future for the PV industry is very promising as long as the supply of silicon is adequate. The consequence is that it will probably be room for more than one new process.

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