

solar-grade silicon by a direct route based on carbothermic reduction of silica: requirements and production technology.

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Abstract

In the European projects SOLSILC and SPURT, a process is developed for the production of solar grade silicon (SOG-Si) by carbothermic reduction of silica, based on very pure raw materials. The purity of the raw materials greatly reduces the requirements on purification of the silicon, from dopants and other impurities. This paper reports the technology used for the Si production, which is suitable for the available high purity silica and carbon materials. It also reports results from the carbon removal process, which brings the carbon content of the silicon from several hundred ppmw to below 5 ppmw. Finally, it discusses experiments on the allowable impurity concentrations in SOG-Si feedstock for directional solidification. Segregation observed during directional solidification is better than previously published, and allowable concentrations of Fe and Ti are similar to what was previously published for monocrystalline material by Westinghouse Corp.

1. Introduction

The amount of feedstock required for silicon solar cells is increasing by several thousand metric tons per year. The two present sources of silicon for PV are limited: reject and waste silicon from the electronics industry is about constant and limited to 3000 mt/a, and the excess production capacity in the same industry is presently 10000 mt/a but expected to disappear in a few years. Therefore, around 2004 one or more sources of dedicated “solar grade silicon” (SOG-Si) must be available. Nevertheless, firm plans for large scale SOG-Si production plants have not yet been announced.

There are two main approaches towards the production of SOG-Si: i) try to make the production and purification of (halo)silane precursor gasses and their pyrolytic decomposition into high-purity Si as low-cost as possible, or ii) try to produce Si by inherently low-cost metallurgical procedures – for example, carbothermic reduction of quartz.

In the SOLSILC and SPURT projects, we are developing the production of SOG-Si by carbothermic reduction of silica, based on very pure raw materials. The purity of the raw materials greatly reduces the requirements on purification of the silicon, from dopants and other impurities. We have developed, at pilot scale, a Si production technology suitable for the available high purity silica and carbon materials. We have developed, at lab scale, a carbon removal process, which brings the carbon content of the silicon from several hundred ppmw to below 5 ppmw. We are in the process of optimising and scaling up this technology. The price goal is below 20 €/kg.

2. The SOLSILC Si production process

The idea of using high-purity raw materials for production of solar grade silicon by carbothermic reduction has been followed before by several groups¹. There are several ways in which the Si production in SOLSILC differs from these previous efforts. First, the SOLSILC route is the first to use both high purity quartz from natural sources as well as high purity carbon black, combined together in one process. In all previous work, either for at least one of the raw materials the purity was in fact not sufficient, or elaborate and probably costly purification methods were used (Table 1).

	SiO ₂	carbon
SOLSILC	cleaned powder from natural quartz	high-purity gas black
Dow Corning	lumpy quartz	oil black
Siemens	molten+fibre leached quartz	leached oil black
Kawasaki	leached water glass	gas black
Heliosil	sand/lumpy quartz	carbon black

Table 1. Raw material characteristics of “direct reduction” projects.¹

The result of the SOLSILC approach is that for acceptable costs, the impurity content of the raw materials is compatible with application as feedstock for ingot production. For the first time, raw materials are combined which have dopant (B, P) impurity levels below 1 ppm, and other contaminants in the 1-10 ppm range.

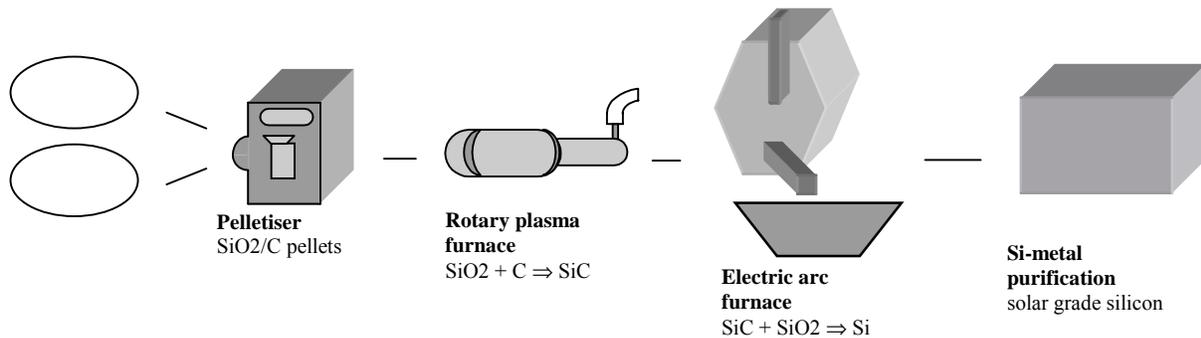


Fig. 1. Schematic process sequence of production of solar grade silicon in SOLSILC.

The second main difference of the SOLSILC Si production with previous attempts is the use of a two-step process (Fig. 1). Conventional Si production takes place in a submerged arc furnace, where the use of lumpy materials allows for the high gas flow rates (of CO and SiO) which occur during the process. High-purity raw materials in powdered form, however, have to be pelletized and are then less suitable for this conventional process. Consequently, the Si production has been separated in two process steps, the first producing SiC in a rotary plasma furnace (at Sintef, ref.²), and the second producing Si from this SiC in a submerged arc furnace (at ScanArc). Both these processes have been operated successfully, with the high-purity raw materials, at pilot scale. Within the available accuracy of chemical analysis (1-10 ppm) the first step does not add significant quantities of contamination. The submerged arc furnace and its environment are presently being upgraded for clean operation, to verify the same important issue for the second step of the process.

3. The Si purification

The liquid silicon which is produced by carbothermic reduction at high temperature (up to 2000 °C) contains a high concentration of dissolved carbon, usually several hundreds of ppm. Virtually all of this carbon has to be removed to make the Si suitable for ingot production. In the past this problem was tackled with a variety of techniques, varying from, e.g., plasma treatment to directional solidification.

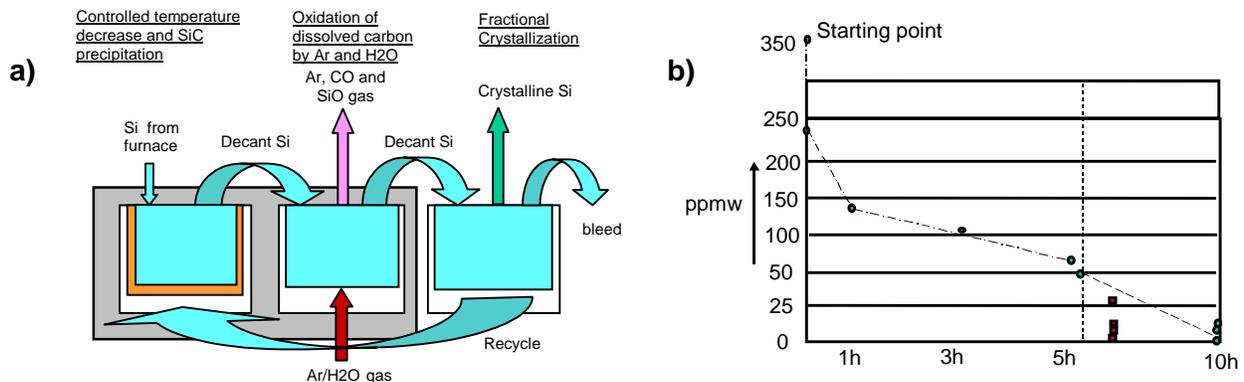


Fig. 2 a) process for carbon removal. b) results.

Fig. 2a shows the approach to carbon removal in the SOLSILC process. First, during a controlled cool-down the excess carbon is precipitated as SiC and separated. This results in Si saturated with carbon at the melting point (~70 ppmw). Next, by a combination of oxidative melt treatment and solidification, the carbon is reduced to less than 5 ppmw. Fig. 2b shows results. Typical carbon concentrations which have been obtained in the final Si are ≤3 ppmw with a yield of 70%.

4. Evaluation of purity and requirements

The Si produced via the SOLSILC route is meant to be suitable as feedstock for directional solidification or Cz growth (after remelting, the material would also be suitable for ribbon growth). Contamination from the quartz and carbon black can be up to the 1-10 ppm level, whereas the limits allowed in Si wafers are around the 1 ppb level or lower. Hence, the segregation of contaminants to the liquid phase which occurs during directional solidification (DS) is essential in order to produce solar grade ingots. Equilibrium segregation coefficients have been listed, for example, by Hopkins or Schei et al.³. The actual segregation approaches these values closely during Cz growth, but may be different for DS of mc ingots.

To investigate this problem systematically, we have produced a number of purposefully contaminated ingots (similar to older work⁴). The feedstock for these ingots was electronic grade silicon doped with varying combinations and concentrations of contaminants either to simulate the quartz and carbon raw materials, or to provide model ingots for segregation and sensitivity studies of particular impurities. The ingots of ~10 kg were grown in a Bridgman-type directional solidification furnace at Sintef, according to industry-like procedures. The ingots were wafered by HCT AG and processed to solar cells in the industry-type process line at ECN⁵.

Fig. 3a shows short circuit current density for two ingots: one made from electronic grade silicon, and one with 10 ppmw Ti added to the Si feedstock for a Ti-sensitivity study. Fig. 3b shows the FeB profile⁶ in the uncontaminated ingot. With these ingots, the effective segregation during DS, and the effect of Ti and Fe on solar cell properties was estimated.

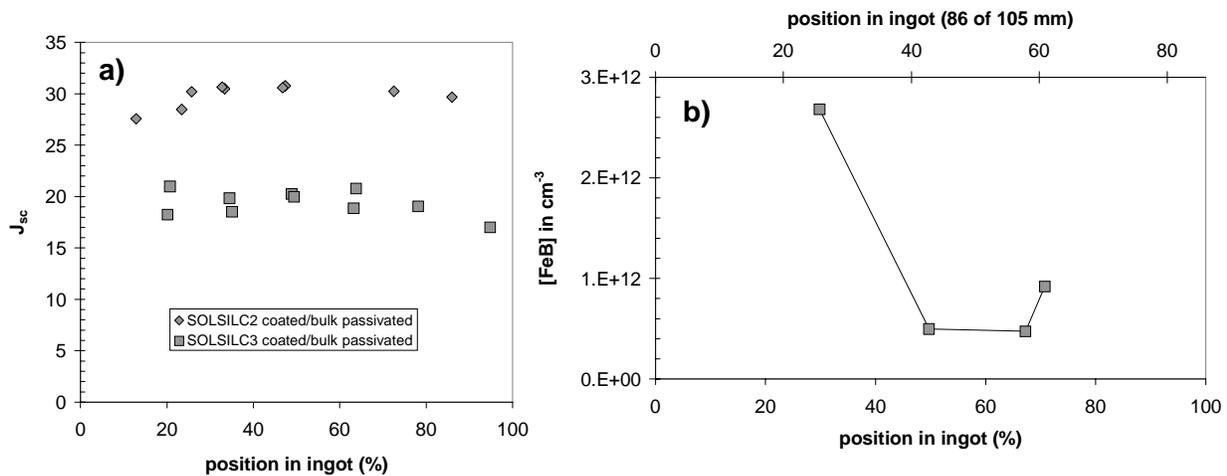


Fig. 3 a) J_{sc} in mA/cm² for uncontaminated feedstock (SOLSILC2, diamonds) and feedstock contaminated with 10 ppmw Ti (SOLSILC3, squares). b) FeB concentration in the uncontaminated ingot SOLSILC2 from lifetime measurements.

DLTS⁷ measurements of the Ti-contaminated ingot showed a number of traps, with concentrations of approx. $1\text{-}3 \cdot 10^{13}$ cm⁻³. Unfortunately the oxygen content in this ingot was high due to air leak-in during growth, but because oxygen traps are usually not visible in DLTS in p-type material, we attribute the traps to 0.34-1 ppbw of Ti. The effective segregation coefficient then follows to be approx. 10^{-4} , decreasing to $2 \cdot 10^{-5}$ cm as growth proceeds and gets slower. For comparison, the equilibrium segregation coefficient of Ti is $2 \cdot 10^{-6}$. In agreement with DLTS, chemical analysis could not detect Ti within the detection limit of 20 ppbw.

The $I_{sc}V_{oc}$ product of the cells from the Ti-contaminated ingot was 60% relative to uncontaminated reference cells. The work by Hopkins et al.⁸ reported a decrease to 60% relative efficiency for 1.7 ppbw Ti. Hence, these results do, at least, not disagree with each other. Another ingot from feedstock with 10 ppmw Ti as the main impurity and without the accidental oxygen contamination resulted in an $I_{sc}V_{oc}$ product between 70% and 80% relative to uncontaminated cells.

The Fe in the uncontaminated ingot is due to solid state diffusion from crucible and segregated material in the top of the ingot. There are just four data points in Fig. 4b but the magnitude as well as the shape of the profile are also found

systematically in commercial material.⁹ A wafer at 90% of ingot length had such low lifetime (0.3 μ s) that the concentration of FeB could not be determined reliably. Judging from the lifetime it was several times 10^{13} cm⁻³. These Fe-contaminated wafers were used to assess the effect of Fe on cell efficiency. The wafers in Fig. 4b with FeB up to $3 \cdot 10^{12}$ cm⁻³ showed no significant reduction of cell performance. For the wafer at 90% position the efficiency reduction is at most $\sim 5\%$ relative. Again this is in rough agreement with Hopkins.

5. Discussion and conclusions

Finally, we conclude on some implications for solar grade silicon feedstock. From DLTS it appears that the segregation of Ti in directional solidification is very good, much better than the sparse reports in literature¹⁰ suggest. We also conclude that the model curves from Hopkins so far give a reasonable prediction also for present-day mc material and processing.

If we assume that the ratio of effective to equilibrium segregation coefficient for Fe will be the same as for Ti, this leads to the following requirement for feedstock for DS¹¹:

max allowable loss in cell efficiency (% relative)	impurity upper limits, in ppmw in feedstock	
	Ti	Fe
2 %	0.07	2.5
5%	0.2	8
10 %	0.4	25

Table 2. Tentative requirements for Fe and Ti in SOG-Si feedstock for mc ingot growth

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- ⁷ deep level transient spectroscopy
- ⁸ R.H. Hopkins, in ref. 3.
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- ¹⁰ e.g., C.P. Khattak and F. Schmid, in *Silicon processing for photovoltaics II*, p. 285 (1987); N. Yuge et al., 11th Int. PVSEC, technical digest p. 115 (1999); M. Rustioni in ref 1.
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