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Solar-grade silicon – is 'Siemens' the only answer?

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ABSTRACT

Solar-grade silicon (SoG-Si) based on metallurgical refining processes, often called upgraded metallurgical-grade silicon (UMG-Si), is expected to play an important role in achieving the solar industry's necessary cost targets per Wp in order to compete with other energy sources. The broad term 'UMG-Si' currently embraces types of silicon feedstock that differ quite substantially in product quality and performance. This paper presents a summary of the work carried out by Elkem on low-cost production of silicon feedstock via a flexible, recycling metallurgical processing route with the lowest carbon footprint on the market. Results are given that qualify Elkem Solar Silicon® (ESS™) as a SoG-Si, with comparable efficiencies to polysilicon (poly-Si) from the traditional Siemens process. The latest results on the performance of modules based on ESS are reported. An indication of the stability of older modules based on SoG-Si feedstock from Elkem is also considered. On the basis of the results, there is no reason to expect modules based on ESS to differ from other commercial modules based on poly-Si. ESS is therefore shown to be a viable alternative to conventional poly-Si, but with the additional benefit of lowering specific energy use and cost per Wp.

Introduction

Elkem has been working with metallurgical routes for solar-grade silicon (SoG-Si) since the late 1970s, and several approaches have been tested and evaluated. The results indicate that the outcome of a metallurgical route will depend on the different process steps included. In the early stages, Elkem focused on employing high-purity raw materials, and then, during the 1990s, introduced several additional purification steps, before arriving at the concept that was industrialized in 2009. This concept includes silicon-reduction furnace operation, slag treatment, leaching, one-directional solidification and post-treatment (see Fig. 1). The first step is simply a form of production of metallurgical silicon, but designed to fulfil the criteria for the subsequent refining of the silicon to a solar-grade quality. This is followed by three purification steps in the process chain, which are:

1. Slag refining – removal of dopant
2. Leaching – removal of dopant and metallic elements
3. Solidification – further reduction in dopants and metallic elements.

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Subsequent to the three purification steps is the post-treatment, which includes cleaning and packing of the finished product. As indicated in Fig. 1, the Elkem metallurgical route is flexible regarding the use of recycled material. In addition to the internal recycling, the Elkem process can also potentially recycle ingot cuts – often known as carbide cuts – from the solar industry, which normally do not end up as solar cell material. This practice also contributes to the Elkem metallurgical process route being the most environmentally friendly SoG-Si process route in the world, for which the energy payback time of a finished solar module is less than one year because of the low energy intensity of the Elkem process compared to any of the different versions of the Siemens process. The emissions of CO_2 equivalents (CO_2-eq) per kg SoG-Si from Elkem are between 10 and 30% of those from polysilicon production by a traditional Siemens process route (11g vs. 40–150g CO_2-eq/kg SoG-Si), depending on the specific

Figure 1. The five steps in the metallurgical route industrialized by Elkem: reduction furnace, slag treatment, leaching, one-directional solidification and post-treatment. The robustness and flexibility of the process in terms of handling recycled ingot cuts is highlighted.

Elements		Specification SEMI PV17-0611	Elkem Solar Silicon typical values
Boron	Target tolerance	≤ 0.38 ppmw ± 0.06 ppmw	0.22 ppmw ± 0.05 ppmw
Phosphorus	Target tolerance	≤ 0.79 ppmw ± 0.17 ppmw	≤ 0.62 ppmw ± 0.15 ppmw
Carbon		≤ 43 ppmw	25 ppmw
Aluminium		-	< 0.01 ppmw
Transition and post-transition metals Ti, Cr, Fe, Ni, Cu, Zn, Mo		≤ 200 ppba	< 50 ppba
Alkali and earth alkali metals Na, K, Ca		≤ 4000 ppba	< 200 ppba

Table 1. The specifications of the SEMI PV17-0611 standard compared to typical values obtained from chemical analyses of the ESS SoG-Si feedstock.

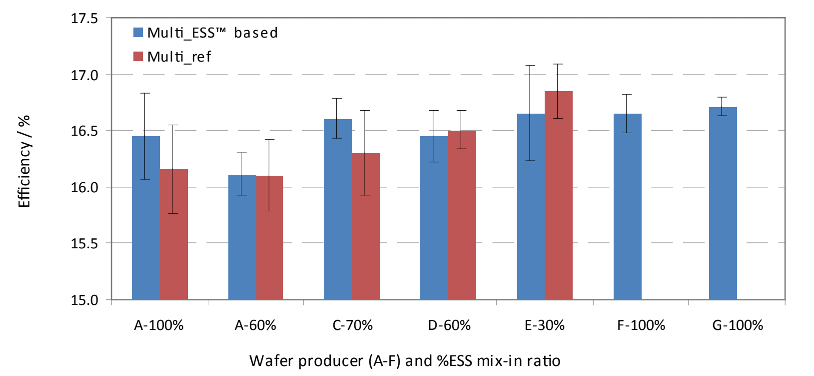

Figure 2. Cell efficiencies obtained by different producers (A–G) using ESS in different blending ratios. Polysilicon reference data are provided where available, and the standard deviations for all batches are indicated. The results are based on cells processed by ISC Konstanz or industrial cell manufacturers using their standard cell production lines in a similar way to that for polysilicon material.

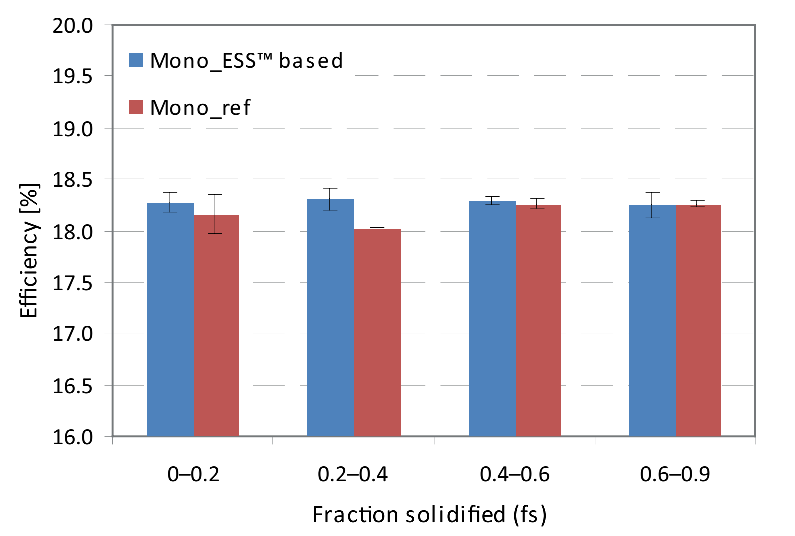

Figure 3. Cell efficiencies as a function of fraction solidified for crystals from a mix of 50% ESS and 50% virgin polysilicon (Mono_ESS), and for crystals from 100% virgin polysilicon (Mono_ref). The results for Mono_ESS are the average obtained from wafers from four crystals grown by four different crystal growers; the results for Mono_ref are from two different monocrystals grown by two different crystal growers. The standard deviations are indicated. All wafers were processed by the standard industrial cell production line at ISC Konstanz.

process details and location of the polysilicon plant [1].

An industrial prototype plant was constructed in Kristiansand, Norway, with an initial production capacity of 5000MT/year, which later increased to 6000MT/year in 2011. A further increase in capacity to ~7500MT/year during 2012 will strengthen Elkem's position even more in terms of cost per kg SoG-Si. In parallel to this increase in production capacity, the content of boron (B) and phosphorus (P) in Elkem Solar Silicon® (ESS™) has decreased: typical values are now 0.22 ppmw B and 0.62 ppmw P.

In the last 30–40 years several companies have explored metallurgical routes for the production of solar-grade silicon (SoG-Si). The above-mentioned efforts have made the Elkem process the leading route within this category in terms of both quality and cost. Silicon produced from these different metallurgical refining routes is often called upgraded metallurgical-grade silicon (UMG-Si). This term, however, can be very misleading. The silicon quality – or the quality of the UMG-Si – is obviously dependent on the route chosen, so it is therefore possible to find significant variations in the chemical purity, homogeneity and physical appearance of the so-called UMG-Si on the market. In order to clarify the quality requirements of SoG-Si, SEMI has published a standard, namely SEMI PV17-0611. Elkem has developed an SoG-Si that currently falls in group IV of this standard – this feedstock is branded under the name ESS. A typical analysis of the feedstock is given in Table 1.

Cell results for wafers based on ESS

During the last decade Elkem Solar has regularly presented the test results obtained for cells with ESS-based mono- and multicrystalline wafers [2–4]. A large test consisting of 150,000 multicrystalline cells was presented by Q-Cells in 2008 [5]. Since then, several producers of multicrystalline ingots have used ESS mixed with polysilicon in various blending ratios. Elkem Solar has supervised the quality of its wafers by continuous testing at ISC Konstanz in Germany. Fig. 2 shows the results from ISC Konstanz for cells made from wafers produced by different industrial competitors in their normal wafer production lines. The results obtained for ESS-based cells correspond to reference cells, and the efficiencies mostly fall in the range 16.5–17%. An important point has been to demonstrate that ESS is not limited to a standard cell process, but has the potential for future use in high-efficiency cells [6].

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Elkem Solar has been testing the use of ESS in monocrystalline wafer production for the past few years. In the initial trials the wafers were limited by the boron content, but during the last two years the boron level in ESS has been significantly reduced. Monocrystalline cells based on a mix of 50% ESS and 50% virgin polysilicon show comparable efficiencies to reference cells based on 100% virgin polysilicon, with very small variations along the crystal (see Fig. 3). Light-induced degradation (LID) has been measured on cells from the different crystals and is comparable to that of the reference cells, with a typical degradation loss of 1–3% relative. Several recent papers have pointed out that LID in compensated silicon seems to be dependent on the net dopant quantity ($N_A - N_D$) rather than on N_A itself, where N_A is the concentration of acceptor atoms and N_D is the concentration of donor atoms. However, consensus has not yet been reached on this issue [3,7]. Nevertheless, ESS has demonstrated its suitability for monocrystalline ingot production, and it has been shown that it is possible to reach very uniform resistivities over the crystal length [8]. Elkem Solar is currently in the process of also testing a higher percentage mix of ESS for monocrystalline wafer production, with up to 100% ESS in the crystals.

Stability of cells based on ESS

The ESS production process today consists of five separate steps, including a silicon furnace, slag treatment, leaching, one-directional solidification and post-treatment, where the three middle steps are designed to remove different types of impurity. There has been a particularly large focus on the boron (B) and phosphorus (P) content, since these elements are directly related to the resistivity of the ingot in the final customer solar cell. Over the years, Elkem has lowered the content of B and P for ESS from less than 4 ppmw in the early 1980s, to today's typical values of 0.22 ppmw B and 0.62 ppmw P.

It has been challenging for customers to distinguish between the different UMG-Si qualities on the market; the large variation between different UMG-Si qualities also raises the question of how reliable solar cells based on UMG-Si will be. This problem was not pinpointed in the early stages of UMG-Si development, and for old modules there are no published data that relate to

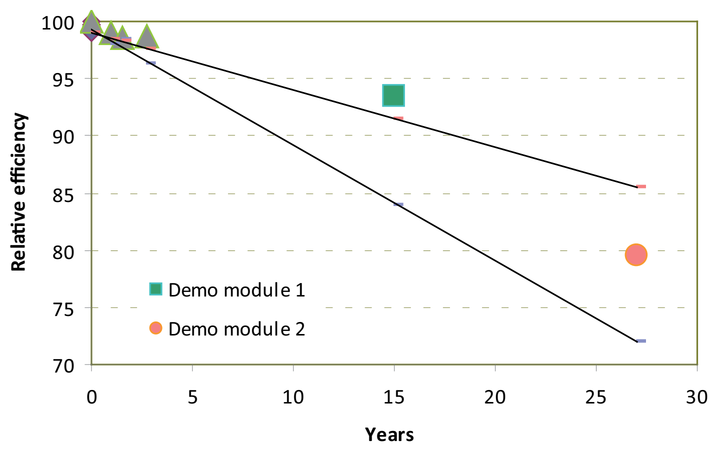

Figure 4. Change in relative efficiency over time, measured for different 100% ESS-based solar modules. The more recently produced modules (green symbols in the top left corner) are highlighted and explained later in Fig. 5. The degradation for a test module based on Elkem SOG-Si from 15 years ago is represented by demo module 1, whereas the average for smaller demo modules made from Elkem solar-grade silicon from 27 years ago is indicated by demo module 2. The upper and lower solid lines correspond to linear long-term degradations of 0.5% and 1% per year, respectively.

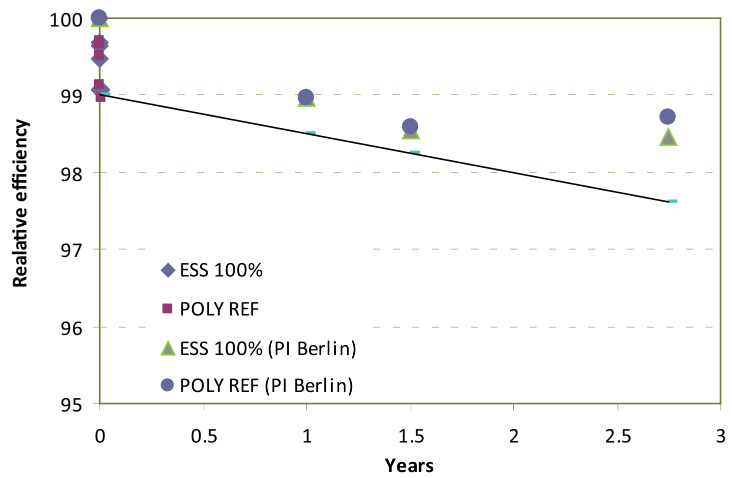

Figure 5. The initial change in the relative efficiency for different ESS-based and corresponding polysilicon reference solar modules. The modules labelled 'PI Berlin' were tested at the certified solar module test facility Photovoltaic Institute Berlin. The solid line corresponds to a linear long-term degradation of 0.5% per year.

long-term degradation. Elkem, however, has recently measured one module from the early stages of the development, as well as even smaller demo modules, in order to get an indication of the degradation. The results (< 7% degradation after 15 years and ~20% after 27 years) indicate that the module based on UMG-Si (< 2 ppmw B and P) should not be worse than commercial modules from the late 1980s or early 1990s. Modules from that time period have been reported as showing a linear degradation of approximately 0.7% per year [9,10], which is comparable to the oldest demo module containing ESS (see Fig. 4). The results have encouraged Elkem to start a programme to systematically measure degradation of solar modules that are based 100% on industrial-produced ESS. Results for degradation of both older demo modules and more recent modules based on industrially produced ESS are shown in Fig. 4.

"All the results so far regarding the degradation of solar modules based on 100% ESS show comparable results to polysilicon after the first few years of operation."

The results obtained from more recently produced ESS and polysilicon reference modules are highlighted in Fig. 5 for their first years of operation. The points that are scattered on the *y* axis indicate LID, which is commonly seen within the very first hours of operation of any silicon-based solar module. The results indicate equal amounts of LID – below 1% on the module level – for both the ESS and polysilicon modules. Note that the last two data points in the figure show lower degradation than the previous measurements. The differences, however, are small and within the analysis accuracy for the measurements at the certified institute PI Berlin.

All the results so far regarding the degradation of solar modules based on 100% ESS show comparable results to polysilicon after the first few years of operation. According to Osterwald et al. [11], the anticipated degradation for today's solar modules is of the order of 0.5% per year, and, as can be seen from Fig. 5, all the modules show lower degradation than this trend. In any case, the primary causes of performance loss in solar modules are claimed to be related to mechanisms that are external to the solar cell material itself [12]. Some of the solar module research projects initiated by Elkem now focus on the performance of ESS modules relative to polysilicon references during high-temperature and low-light conditions, for example < $300W/m^2$. This is because there are indications that ESS performs better than polysilicon under such conditions – results will be published when this research is complete.

Summary

ESS will always be a cost-competitive alternative to polysilicon from a Siemens process route. Technical cooperation with the customer, including guidance on dopant addition strategies based on in-house resistivity-profile modelling, helps in achieving the optimal use of ESS. The flexibility of the Elkem metallurgical process route to SoG-Si is also used in cooperation with the customer, by potentially recycling customer carbide cuts back to SoG-Si. The results presented above show that efficiencies obtained for ESS-based multicrystalline cells, using standard industrial cell processing conditions, are comparable to those for polysilicon reference material. This is valid throughout the whole range of blending ratios, and the efficiencies range from 16.5 to 17%. Even for monocrystalline cells, comparable results to those for polysilicon have been obtained, specifically efficiencies of between 18 and 18.5%.

The results so far show no indications of a higher degradation rate for solar modules containing 100% ESS than for polysilicon reference modules. Measurements performed on older demo modules containing SoG-Si from Elkem show a degradation which is to be expected for a module produced at that time. The ESS is the 'greenest' SoG-Si on the market mainly because of the low energy intensity of the process, which leads to an energy payback time of less than one year for ESS-based solar modules. This also leads to a carbon footprint of 11g CO_2-eq/kg SoG-Si as compared to polysilicon, which varies between 40 and 150g CO_2-eq/kg SoG-Si, depending on the process route and plant location.

> "As a relatively new silicon feedstock in the market, ESS has now shown that it is a compatible alternative to conventional Siemens polysilicon."

As a relatively new silicon feedstock in the market, ESS has now shown that it is a compatible alternative to conventional Siemens polysilicon. Further verification and documentation of the performance and compatibility of ESS will entail identifying potential advantages such as high-temperature and low-light performance. To this end, Elkem Solar is working actively with different research institutes to carry out various cell and module long-term tests, with the aim of exploiting its product's potential even further than has been indicated in this paper. In conclusion, as a solar-grade feedstock, ESS will bring down the cost of a finished solar module and will offer a clear environmental benefit.

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About the Authors

Anne-Karin Søiland graduated in 2005 from the Norwegian University of Science and Technology (NTNU) with a Ph.D. degree in materials technology. Her thesis topic was the formation of SiC- and Si_3N_4-inclusions during crystallization of multicrystalline silicon ingots. Anne-Karin joined Elkem Solar in 2004; her main activities have included working on customer processes, mono- and multicrystalline ingot production, and the use of Elkem Solar Silicon in these processes.

Jan Ove Odden graduated from the University of Oslo in 2004 and received his Dr. Scient degree in inorganic chemistry. For his thesis he researched the decomposition of monosilane under high-pressure conditions in free-space reactors. In 2007 Jan began working as an R&D engineer at Elkem Solar, where he focuses on technical customer support and leads research projects evaluating the performance of ESS in solar modules in the field.

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