HIGH PERFORMANCE SOLAR CELLS MADE FROM 100% UMG SILICON OBTAINED VIA THE PHOTOSIL PROCESS

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ABSTRACT

The presented work is part of the French PHOTOSIL project which deals with the purification of metallurgical grade (MG) silicon to obtain Solar Grade (SoG) silicon by a combination of innovative refinement/up grading techniques such as segregation and plasma purification. The main objectives of this project are production costs <15€/kg, a photovoltaic performance of >15% solar cell efficiencies, and material yields >85% after crystallization.

In this paper we present the latest results obtained with a highly purified metallurgical silicon via a modified PHOTOSIL process. Chemical analysis by Glow Discharge Mass Spectroscopy (GDMS) on this feedstock revealed a boron concentration below 0.5ppmw after the plasma treatment and a phosphorus concentration close to 1ppmw after the metallurgical purification by segregation. The total amount of metallic impurity concentrations have been reduced below 2ppmw (Fe, Al, etc…) thanks to the successive segregation steps.

A multicrystalline silicon ingot made from 100% of this purified metallurgical silicon was crystallized using an innovative crystallization method. The obtained ingot was p-type on 80% of its height and exhibited a resistivity range between 1-10 ohm.cm, due to phosphorus segregation. For reference purposes, a second ingot was crystallized in identical conditions from EG silicon, that was intentionally boron-doped to 1ohm.cm.

Solar cells have been processed on 12.5x12.5 cm² wafers from both ingots using industrial type standard screen printed processes at the CEA-INES. Solar cells from the PHOTOSIL ingot were fabricated with an industrial process optimized for SoG silicon directly purified from MG Silicon. In case of the EG ingot the average efficiency was 16.3% with a maximum of 17%. In case of the ingot from PHOTOSIL silicon, solar cells from the p-type region have reached an average efficiency of 15.7 % including a best cell with 16.2 %.

In addition, a 6” Cz ingot was crystallized from the same purified silicon feedstock. This ingot turned out to be entirely monocrystalline which confirms the very low impurity content of the feedstock. Solar cells were fabricated on 12.5x12.5 cm² pseudo-square wafers and a high average efficiency of 17,4% was reached with a maximum efficiency of 17,6%, which is one of the highest efficiency reported so far if not the highest on purified metallurgical silicon.

These results clearly demonstrate the potential of the metallurgical silicon route for application in PV and the possibility to reach high efficiencies.

INTRODUCTION

Over the past several years, the continuing rapid growth of the PV industry and the resulting silicon shortage have stimulated new approaches in purification of metallurgical grade silicon to a quality level compatible with the requirements of the PV industry [1].

However, these new solar grade silicon production techniques are generally less efficient in removing dopant impurities leaving relatively high residual concentrations of boron and phosphorus in the order of $>10^{17}$ cm^{-3}.

Despite such doping levels, relatively high solar cells efficiencies have been achieved on this type of silicon [2,3]. In case of the PHOTOSIL project, we recently demonstrate a 15,9% solar cell efficiency with a starting material containing a boron and phosphorus concentrations of $3x10^{17}$ cm^{-3} and $2,2x10^{17}$ cm^{-3} respectively [4].

At the very beginning, the good solar cells results obtained from this strongly compensated silicon were not well understood but now different studies explained this phenomenon particularly thanks to the beneficial effect of compensation [5,6].

However in the same time, other studies have demonstrated that such silicon is very sensitive to light induced degradation (LID) [7] and exhibits a low breakdown voltage [8] when the net doping density is too high.

It is understandable, that in a context of silicon shortage, this silicon can be used, especially because dedicated solar cell processes could strongly mitigate the LID effects. However considering the recent economical crisis and the resulting market reversal which drove SoG Si prices downwards combined with the drastic up scaling of production capacities for SoG Si via the Siemens route during the last few years, purified metallurgical Si obtained by state-of-the-art techniques is no longer competitive, and new entrants in the field of SoG Si production via the metallurgical route have to improve their purification techniques in order to close the gap to standard SoG silicon.

In this paper, we describe the status of the PHOTOSIL project and focus on the latest results obtained through a highly purified metallurgical silicon which clearly demonstrates the potential of the PHOTOSIL metallurgical route.

STANDARD PHOTOSIL PROCESS

The main important feature of the PHOTOSIL approach is its complete vertical process integration, starting with the selection of the raw materials (quartz and carbon reductant) for the production of MG Si, the base material for solar grade silicon feedstock.

This vertical integration allows for a number of process simplifications by having the possibility to transfer silicon at different stages of purification in its liquid state and thus to preserve the melting energy. It allows also for recycling of silicon rejects during the different purification steps, thus to optimize material yields. In consequence, process times and costs can be strongly reduced.

A first important part, which takes place before the PHOTOSIL process itself, concerns the production of metallurgical Si. This operation takes place under the responsibility of FerroPEM, making use of existing electrical arc furnaces for the carbothermic reduction of silica. The careful selection of the starting material (SiO_2 and C) allows avoiding high concentrations of certain impurities, which are difficult to remove, for example P and B. The liquid MG silicon is directly subjected to a segregation treatment which allows to remove metal impurities, but also P. The obtained, so called “Upgraded Metallurgical” (UMG-1) silicon, is the starting material for the PHOTOSIL process.

As a first step of the PHOTOSIL process, the UMG-1 silicon is remelted in an induction furnace and submitted to a second segregation process. In this purification step, a large part of the liquid silicon solidifies inside a specially designed segregation vessel. At the end of the process the final part of the liquid silicon, into which elements with a small segregation coefficient have been rejected during the solidification, is separated by pouring it into a waste container (See Fig. 1).

Figure 1: Pictures showing the transfer of the melted silicon in the segregation vessel (left) and the elimination of the impurities enriched silicon (right).

The obtained solid UMG-2 silicon is then transferred to the plasma purification unit. An argon plasma gas that contains reactive species is created by induction and blown onto the surface of liquid silicon which is constantly renewed by electromagnetic stirring (See Fig. 2).

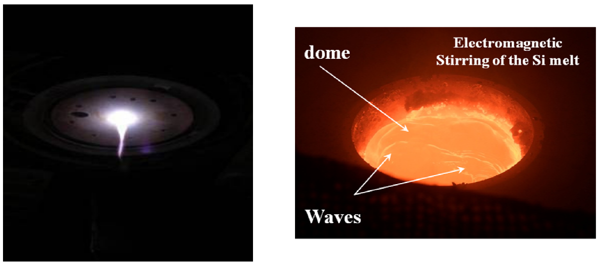

Figure 2: Pictures of the argon plasma gas (left) above the silicon bath which is agitated by an electromagnetic field (right).

During this step which is critical for the process, reactive species based on oxygen and hydrogen are able to volatilize boron. One key point of the process is the control and the monitoring of the B removal by resistivity and conductivity type measurements of Si samples taken at different stages of the treatment.

At the end of the plasma treatment, the purified silicon is either rapidly cooled resulting in randomly solidified silicon, or preferentially solidified in a directionally way (See Fig. 3) in order to lower again the total amount of impurities.

Indeed, due to the oxygen introduced during the plasma treatment and the graphite crucible used for the melting, the silicon bath gets contaminated by oxygen carbon, and a more controlled solidification helps to partially remove these elements.

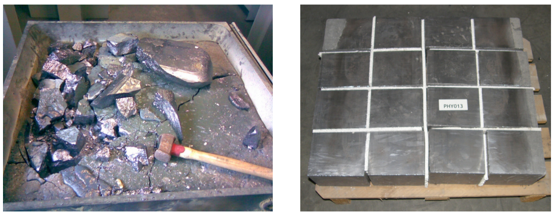

Figure 3: Pictures of plasma purified silicon rapidly solidified (left) or in a directionally way (right).

Finally, at the end of this process, the typical impurity concentrations of the purified metallurgical silicon is as indicated in Table 1.

Table 1: GDMS chemical analysis of the silicon obtained through the Standard PHOTOSIL process

Element	Al	B	Fe	Cu	P	Ti
	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw
STD PHOTOSIL Silicon	< 2	~ 1,5	< 5	< 2	~ 4	< 2

Using such a material, 10 multi-crystalline Si ingots were grown in 2009 and an average solar cell conversion efficiency close to 15% was obtained. However, it appears that this silicon is very sensitive to LID, with a loss exceeding 1% absolute in certain cases[4]. Notice that cell processes are under development at the CEA-INES to strongly mitigate these deleterious effects.

OPTIMIZED PHOTOSIL PROCESS

In order to clearly demonstrate the competitiveness and the potential of the PHOTOSIL metallurgical route to reach high efficiencies, we optimized all the different steps of the purification process described above to elaborate a highly purified metallurgical silicon.

At the end of the process, the total amount of impurities presents in this produced silicon was very low as shown in table 2.

Table 2: GDMS chemical analysis of the highly purified metallurgical silicon obtained via the optimized PHOTOSIL process

Element	Al	B	Fe	Cu	P	Ti
	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw
Optimized PHOTOSIL Silicon	< 2	~ 0,3	< 2	< 2	~ 1	< 2

MULTICRYSTALLINE SILICON INGOTS

Crystallization runs were then carried out in a Cyberstar furnace using an innovative crystallization process [9] in order to obtain high crystal quality ingots.

Two ingots with different types of silicon were grown: (i) Electronic grade (EG) silicon, boron doped with a resistivity of 1 Ωcm, for reference purposes; (ii) Highly purified metallurgical silicon from PHOTOSIL (See Fig. 4).

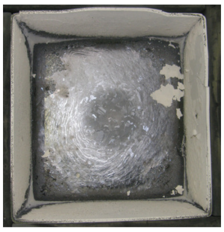

Figure 4: Picture of the highly purified multi-c Si ingot**.**

After crystallization, the two resulting 40 kg ingots were cut by the Fraunhofer ISE into 125 x 125 mm² wafers with a thickness of 200 µm and solar cells have been processed using industrial type standard screen printed process at the CEA-INES Restaure pilot line.

In case of the EG ingot, the efficiency distribution is very homogeneous at a high level of 16.4% from the bottom to the top of the ingot with a maximum efficiency of 17% (See Table 3).

Table 3: Average and maximum solar cells data for the EG ingot.

	η (%)	**Voc (mV)**	**Icc (mA/cm²)**	**FF (%)**
Average	16,4	621	34	77.8
Best	17	623.8	34.3	79.5

In case of the ingot from PHOTOSIL silicon, as expected, due to the residual concentration of phosphorus and its more efficient segregation than boron, the ingot turns to n-type at around 80% of its height, but the resistivity is relatively high in the range of 1-10 ohm.cm (Fig. 5).

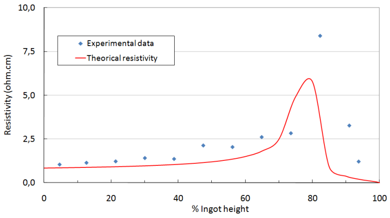

Figure 5: Resistivity as a function of the ingot height for the highly purified silicon ingot.

12.5x12.5 cm^2 multicrystalline wafers from the p-type region were then processed using industrial screen printed solar cells processes. Actually, 3 different solar cells processes were applied, a standard one and 2 others were specially developed by the CEA for UMG-Si.

As shown in Fig. 6, the best solar cell reached an efficiency of 16.2% and a fill factor of 79.7% (cell process B), which is one of the highest efficiency obtained on purified MG Si. In addition the often observed light induced degradation on solar cells fabricated from purified MG Si, turned out to be lower than 1% relative in case of the cells from this ingot.

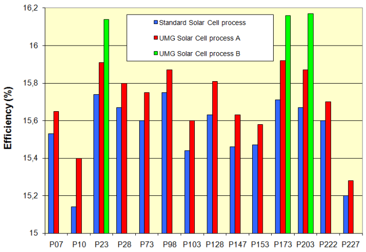

Figure 6: Efficiency distribution as a function of the highly purified silicon ingot height for 3 different solar cell processes developed by the CEA-INES.

MONOCRYSTALLINE SILICON INGOTS

In order to reach a higher solar cell efficiency, we tried to crystallized a 6" Cz ingot using the same highly purified feedstock. Surprisingly, we obtained an ingot entirely monocrystalline which clearly demonstrates the very low total amount of impurities since they could act as nucleation centres during Cz growth (See Fig. 7).

Figure 7: Picture of the 6'' Cz monocrystalline ingot made from 100% of the highly purified PHOTOSIL silicon.

The Cz ingot was then squared to 125 mm x125 mm pseudo-square geometry and cut into 200 µm thick wafers by the Fraunhofer ISE.

To assess the electronic quality of this material, µ-PCD carrier lifetime measurements have been carried out on SiN passivated wafers resulting in values in the range of 20-80 µs (See Fig. 8).

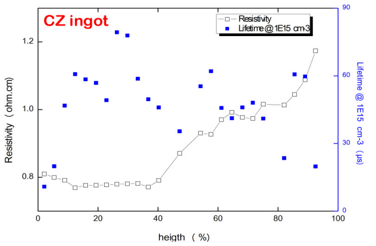

Figure 8: Resistivity and carrier lifetime measurement conducted on 12.5x12.5 cm² pseudo-square wafers as a function of the Cz ingot height.

Again, screen-printed solar cells were manufactured by CEA-INES at the Restaure pilote line with a proprietary process. And as expected, given the high carrier lifetimes measured, high efficiencies solar cells were obtained (See Fig. 9).

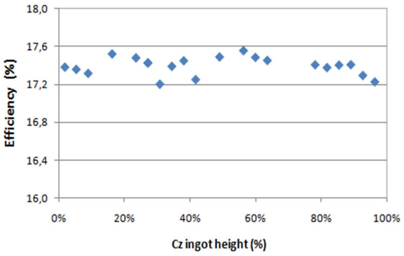

Figure 9: Efficiency distribution as a function of the highly purified Cz silicon ingot height.

An average solar cell efficiency of 17,4% was reached with a best screen-printed UMG-Si solar cell exhibiting an efficiency of 17.6% with a fill factor of 79.9%, which is one of the highest efficiency reported so far, if not the highest on UMG Silicon (See Table 4).

Table 4: Average and maximum solar cells data for the Cz ingot.

	η (%)	**Voc (mV)**	**Icc (mA/cm²)**	**FF (%)**
Average cells	17.4	617.5	35.5	79.5
Best cell	17.6	619.3	35.5	79.9

Nevertheless these efficiencies have to be taken with care. Indeed, solar cells made from boron-doped Cz silicon are known to suffer from light induced degradation in performance when exposed to light until a stable efficiency is reached. And considering the oxygen concentration measured in the Cz ingot (See Table 5) and the initial boron concentration, LID is expected to be present. An evaluation of this loss in performance by the CEA-INES is under way.

Table 5: Oxygen concentration in the Cz ingot.

[O]	**Bottom**	**Top**
ppmw	4,1	6
at.cm^{-3}	3.6×10^{17}	5.3×10^{17}

CONCLUSION

In this paper we demonstrate the potential of the PHOTOSIL metallurgical route. Highly purified metallurgical silicon was elaborated by optimizing the PHOTOSIL process. Results on multicrystalline silicon ingot, i.e. 16.2% as a maximum solar cell efficiency was obtained. Moreover, the high quality of the feedstock allowed the growth of a Cz ingot entirely monocrystalline. By reaching 17.6% maximum efficiency for solar cells from this ingot, this result is probably the highest reported for this material so far.

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