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 STATUS OF THE PHOTOSIL PROJECT FOR THE PRODUCTION OF SOLAR GRADE SILICON FROM METALLURGICAL SILICON

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ABSTRACT: This article gives an up-date on the progress of the French PHOTOSIL project from a technical and an economical point of view. During the last 5 years, the French PHOTOSIL consortium formed by FerroPEM, CEA-INES, CNRS SIMaP and APOLLO SOLAR has been working on a combination of new, innovative up-grading and purification techniques for MG Silicon on an industrial pilot level, to arrive at UMG Silicon that is compatible with the purity and economical requirements of the PV industry. The objectives of this project are production costs <15€/kg, average photovoltaic performances of >15% solar cell efficiencies on multi-crystalline wafers from ingots made of 100% UMG Silicon and a material yield of >85% after crystallisation.

Keywords: Metallurgical Si, Solar Grade Silicon, High efficiency

1 INTRODUCTION

Most of the silicon feedstock for the PV industry is purified by the chemical route (TCS production followed by the SIEMENS process), that is characterized by relatively high investment costs and energy requirement but resulting in high purity intrinsic Silicon feedstock.

From 2004 to 2008, the solar industry experienced a shortage of silicon feedstock that led to a drastic increase of Silicon feedstock prices ($450/kg on the spot market). This situation combined with the continuing accelerated growth of the PV industry itself promoted investments into new production capacities for high purity Silicon. On the other hand the Silicon feedstock shortage also opened up an alternative low cost metallurgical route for the production of Silicon feedstock for the PV industry. This route is characterized by the direct purification of metallurgical grade (MG) Silicon to produce UMG (upgraded metallurgical grade) Silicon. During this period of solar silicon shortage, the PV industry made first attempts to use UMG Silicon as starting material, especially due to its potential large scale availability and low production costs. However, quality problems in terms of material yield and reproducibility with this type of Silicon could also be identified.

In 2009, the PV market activities strongly slowed down because of the general economic crisis. With the arrival of new silicon production capacities for high purity Silicon, the spot market prices for this Silicon dropped to $60/kg at the end of 2009. The consequence of this situation was a largely reduced use of the UMG silicon.

In 2010, with a renewed strong growth of the PV industry and less investments in new production capacities for high purity Silicon, the silicon prices are expected to slowly increase and some experts consider that a new shortage could appear in 2013 [1] which opens up a new opportunity for UMG Silicon, provided its quality is fully compatible with the requirements of the PV industry.

In this paper, we present recent progress of the PHOTOSIL project and focus on a highly purified metallurgical silicon which demonstrates the technical feasibility of the PHOTOSIL metallurgical route.

2 COMPENSATED SILICON FEEDSTOCK

The metallurgical purification techniques are generally less efficient in removing dopant impurities (B and P). Although with high doping levels, relatively high solar cells efficiencies have been achieved on UMG silicon [2,3] thanks to the beneficial effect of compensation, UMG silicon has still some limitations: it is sensitive to Light Induced Degradation (LID) [4] and exhibits a low breakdown voltage [5] when the net doping density is too high. As a consequence the target concentration for boron and phosphorus is today inferior to 1017/cm-3.

In order to be competitive with high purity Silicon obtained by the chemical purification route, the performance gap of UMG Silicon to high purity Silicon needs to be closed as much as possible.

3 STANDARD PHOTOSIL PROCESS

The PHOTOSIL project started in 2005 and is geographically located close to Chambéry in France. The first version of the PHOTOSIL pilot line was finished in 2007. The Silicon purification is entirely vertically integrated, from the selection of raw materials for the metallurgical silicon to the crystallization of multi-crystalline ingots from purified UMG solar silicon. This integration is essential to start with the best specifications of the metallurgical silicon and to allow the recycling of off-spec silicon after the different purification steps, thus to optimize the material yield. With a control of the entire value chain, process costs and times could be reduced.

The first part of the PHOTOSIL process takes place under the responsibility of FerroPEM at a production site of metallurgical grade (MG) Silicon and concerns the, drastic selection of the raw materials (quartz, wood, charcoal…) for the production of MG Silicon in an electric arc furnace. This allows to produce a metallurgical silicon with a relatively low boron and phosphorus contents. The following PHOTOSIL process can therefore rely on starting material of constant quality.
After the electrical arc furnace, the liquid metallurgical silicon is poured into a vessel for a first metallurgical segregation which remove mainly metallic impurities and a part of phosphorus. The obtained silicon UMG-1 is the starting material for the PHOTOSIL process.

As a first step of the PHOTOSIL process, the UMG1 silicon is melted 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. The final part of the liquid silicon, which contains a high quantity of impurities, is separated by pouring it into a waste container (See Fig. 1).

The so obtained solid UMG-2 silicon is then treated inside a plasma purification unit. After melting of the Silicon inside an induction furnace, an argon plasma gas with O$_2$ and H$_2$ as reactive gases is created by induction. Electromagnetic stirring of the liquid silicon (See Fig. 2) enhances the mass transfer of the impurities from the bulk to the surface of the silicon melt, where reactive species of the plasma react mainly with boron (See Fig. 2).

During this critical step, the radicals provided by the plasma volatilize the boron in form of HBO and BO$_6$. The key point of the process is the control and monitoring of the B removal by resistivity and conductivity type measurements on Si samples taken at different stage of the treatment.

After the plasma treatment, the purified silicon is rapidly solidified, or preferentially in a directionally way (See Fig. 3) in order to lower again the total amount of impurities. Due to the oxygen introduced into the plasma, and the use of a graphite crucible, the silicon is contaminated by oxygen and carbon.

Using this purified material, 10 ingots of 40 kg were crystallised in 2009 and an average solar cell conversion efficiency close to 15% was obtained. There was a good reproducibility, however this silicon is very sensitive to LID, with an efficiency loss exceeding 1% absolute in certain cases [7].

### OPTIMIZED PHOTOSIL PROCESS

To produce a UMG Silicon feedstock in accordance with the actual requirements of the photovoltaic market, a highly purified metallurgical silicon has been elaborated. All different purification steps have been optimized with the objective to demonstrate the competitiveness and the potential of the PHOTOSIL metallurgical route to process high efficiencies solar cells.

At the end of the process, the total amount of impurities present in this silicon was very low, as shown by chemical analysis of different impurities by GDMS in Table 2. This feedstock quality corresponds to the CRYSTALCLEAR specifications after the crystallization process [8].

### Table 1: Chemical analysis of the silicon obtained through the Standard PHOTOSIL process.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al (ppmw)</th>
<th>B (ppmw)</th>
<th>Fe (ppmw)</th>
<th>Cu (ppmw)</th>
<th>P (ppmw)</th>
<th>Ti (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD PHOTOSIL Silicon</td>
<td>&lt; 2</td>
<td>~ 1,5</td>
<td>&lt; 5</td>
<td>&lt; 2</td>
<td>~ 4</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Element</th>
<th>Al (ppmw)</th>
<th>B (ppmw)</th>
<th>Fe (ppmw)</th>
<th>Cu (ppmw)</th>
<th>P (ppmw)</th>
<th>Ti (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPTIMIZED PHOTOSIL Silicon</td>
<td>&lt; 2</td>
<td>~ 0,3</td>
<td>&lt; 2</td>
<td>&lt; 2</td>
<td>~ 1</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>

### MULTICRYSTALLINE SILICON INGOTS

Crystallization runs were made in a Cyberstar furnace using an innovative crystallization process [9] in order to obtain high crystal quality ingots. To evaluate the impact of the feedstock, two ingots were grown with exactly the same conditions:
(i) A reference ingot using high purity Electronic grade (EG) silicon, that was intentionally doped with boron to arrive at a resistivity target of around 1.0 Ω cm;
(ii) 100% of the highly purified metallurgical silicon from PHOTOSIL (See Fig. 4).

After crystallization, the two resulting 40 kg ingots were cut into 125 x 125 mm² wafers with a thickness of 200µm.

Figure 4: Picture of the highly purified multicrystalline silicon ingot.

Comparing both crystallization runs two major advantages related to the use of the PHOTOSIL Silicon could be indentified:
(i) The block shape of the PHOTOSIL Silicon allowed for a higher packing density in the crucible and therefore for a larger ingot mass ( x kg compared to z kg in case of the ingot from high purity electronic grade Silicon)
(ii) The melting time for the PHOTOSIL Silicon was lower than for the high purity electronic grade Silicon.

The solar cells of the electronic grade reference ingot exhibit a very stable efficiency distribution, from the bottom to the top of the ingot, the average efficiency being 16.3% with a maximum efficiency of 17.0%.

Table 3: Average and maximum solar cell efficiencies obtained on wafers from the EG Silicon ingot.

<table>
<thead>
<tr>
<th></th>
<th>η (%)</th>
<th>Voc (mV)</th>
<th>Isc (mA/cm²)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>16.3</td>
<td>580</td>
<td>19.5</td>
<td>76.3</td>
</tr>
<tr>
<td>Best</td>
<td>17.0</td>
<td>618</td>
<td>34.9</td>
<td>79</td>
</tr>
</tbody>
</table>

In case of the ingot from PHOTOSIL Silicon, as expected, the segregation of phosphorus (k₀=0.35) is more pronounced than for boron (k₀=0.8), the ingot turns to n-type at around 80% of its height, where also a strong increase of resistivity as seen on Figure 5 can be observed, due to the high degree of compensation in this region. However, the material yield is in the same order as for the electronic grade silicon ingot, for which a region of low quality on the top, due to the back diffusion of the impurities coming from the crucible and the silicon nitride coating could be observed.

Figure 5: Resistivity as a function of ingot height in case of the highly purified PHOTOSIL silicon ingot height.

Solar cells on 12.5x12.5 cm² multicrystalline p-type wafers from the PHOTOSIL ingot were processed using industrial-type screen printed solar cells processes. Actually, 3 different solar cells processes were applied, a standard one and two others that were specially developed by CEA-INES for UMG-Si. For details see Figure 6.

The best screen printed solar cells reached an efficiency of 16.2% and fill factors up to 79.7%, which is one of the highest efficiency on purified UMG Silicon. In addition, the light induced degradation on solar cells from the purified PHOTOSIL UMG Si, is lower than 1% relative which compares to the range of solar cells processed with electronic grade silicon.

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

MONOCRYSTALLINE SILICON INGOTS

In order to investigate the full potential of the purified PHOTOSIL UMG Silicon it was tried to crystallize a 6” Cz ingot in collaboration with Siltronix, using the same highly purified PHOTOSIL Silicon as for the previously described multi-crystalline ingots. Surprisingly, the ingot turned out entirely mono-crystalline which clearly demonstrates the very low total amount of impurities (See Fig. 7).

Figure 7: Photo of the 6” Cz mono-crystalline ingot made from 100% of the highly purified PHOTOSIL silicon.
The Cz ingot was then squared to 125 mm x 125 mm pseudo-square geometry and cut into 200 μm thick wafers by 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). The resistivity of this ingot varied between 0.8 and 1.2 Ωcm.

Figure 8: Resistivity and 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 processed by CEA-INES with their proprietary process. And as expected from the high carrier lifetimes, high efficiency solar cells were obtained (See Fig. 9). Also no strong decrease of the carrier lifetimes at the top of the ingot was observed, which confirms the low level of metallic impurities in the Silicon feedstock.

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

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 on unblended purified MG Silicon. These results clearly show the potential of the PHOTOSIL metallurgical route to produce high quality Silicon for PV application. This PHOTOSIL silicon could be used without blending to grow either mono- or multicrystalline ingots.

Table 4: Average and maximum efficiencies for the Cz ingot.

<table>
<thead>
<tr>
<th></th>
<th>η (%)</th>
<th>Voc (mV)</th>
<th>I sc (mA/cm²)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>17.4</td>
<td>617.5</td>
<td>35.5</td>
<td>79.5</td>
</tr>
<tr>
<td>Best</td>
<td>17.6</td>
<td>619.3</td>
<td>35.5</td>
<td>79.9</td>
</tr>
</tbody>
</table>

Nevertheless the Cz ingot presents a higher oxygen content (See Table 5) which affects the conversion efficiency in terms of light induced degradation (LID). However in the PHOTOSIL solar cells, the LID is around 3% relative which is close to standard electronic grade Cz p-type ingots. In the purified Photosil Cz ingot, the boron content is low enough in regards of LID.

Table 5: Oxygen concentration in the PHOTOSIL Cz ingot.

<table>
<thead>
<tr>
<th>[O]</th>
<th>bottom</th>
<th>Top</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppmw</td>
<td>4.1</td>
<td>6.0</td>
</tr>
<tr>
<td>at.cm⁻³</td>
<td>3.6x10¹⁷</td>
<td>5.3x10¹⁷</td>
</tr>
</tbody>
</table>

CONCLUSION

By improving the PHOTOSIL process, a highly purified UMG Si was obtained from MG Silicon. Solar cells processed from this UMG Si reached a solar cell efficiency >16% with a very low LID on multi-c wafers. Moreover, it was also possible to grow an entirely mono-c Cz ingot which gave rise to a maximum cell efficiency of 17.6% on 125×125 mm² pseudo-square wafers which is one of the highest efficiency reported so far on unblended purified MG Silicon. These results clearly show the potential of the PHOTOSIL metallurgical route to produce high quality Silicon for PV application. This PHOTOSIL silicon could be used without blending to grow either mono- or multicrystalline ingots.

ACKNOWLEDGEMENTS

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