

PHOTOSIL – Simplified Production of Solar Silicon from Metallurgical Silicon

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ABSTRACT:

This article presents the status the PHOTOSIL project, which includes partners from industry, R&D institutes and equipment manufacturers. The objectives of this project are the production of solar grade (SoG) silicon at costs <15€/kg and of multi-crystalline ingots at costs <35€/kg, starting with metallurgical silicon and using a combination of innovative up-grading and purification techniques. On the basis of encouraging results on laboratory level, the PHOTOSIL consortium has obtained the funding for the construction of an industrial scale pilot line. This line will become fully operational in October 2006 and it will serve to demonstrate the industrial viability of the PHOTOSIL technology by up scaling the different laboratory scale processes to an industrial level. In a first stage, the pilot line operates with batch sizes of 60kg which will be doubled to 120 kg in a second stage, arriving at a nominal capacity of 200 tons per year. The PHOTOSIL process includes metallurgical and plasma purification techniques, giving rise to a complete vertical integration from the metallurgical Silicon production to the fabrication of exploitable multi-crystalline Silicon ingots for the PV industry, of either p- or n-type. At present, a resistivity level of 0.3 – 0.5 Ωcm has been reached after the combined metallurgical and plasma purification. Metal impurity concentrations have been reduced to 20 ppm for Fe, 15 ppm for Al and <2 ppm for Ti after the metallurgical purification by segregation.

Keywords: Silicon, Metallurgical Grade, Multicrystalline

1 INTRODUCTION

The crystalline Silicon PV industry continues to face a serious supply shortage of its raw material – solar grade silicon feedstock. This is mainly due to the non-availability of a dedicated solar silicon production and the growing demand for silicon feedstock. Detailed analyses on the shortage of silicon feedstock can be found in literature [1, 2]. Among the different projects to overcome this shortage by establishing a dedicated solar silicon production, two major routes can be distinguished: (i) simplified gas phase purification of silicon via (halogenated) silane gases, followed by their pyrolytic decomposition and condensation as high purity silicon [3,4,5], and (ii) direct purification of metallurgical grade silicon by metallurgical and/or other evaporation processes arriving at lower quality solar silicon [6,7,8].

The PHOTOSIL project is situated within the second approach. Its underlying fundamental development work project dates back to the mid 90s, when during the EU ARTIST project [9] first successful purification experiments of upgraded metallurgical Silicon with an inductive plasma treatment have been demonstrated by EPM [10], giving rise to multi-c solar cells with 12.2% efficiency [11]. In the following, the development work continued in the frame of direct collaboration contracts between some of the partners now involved in the PHOTOSIL project. An important point was the integration of the French Silicon producer FerroPem (formerly PEM/Invensil) as part of the Spanish Ferro Atlantica Group, the largest producer of metallurgical silicon worldwide. In 2001 Apollon Solar offered PEM/Invensil to set up a new collaboration contract with

the equipment manufacturer EFD-Induction to continue the development work towards the realisation of an industrial pilot line. The CNRS laboratories EPM and TECSEN were associated to this consortium. First intermediate results were published in 2004 [12]. Based on these encouraging results and thanks to the CEA-LITEN to join the consortium, the PHOTOSIL project was proposed and officially started in May 2005 with a running time of 3 years. The first year of the project was dedicated to the construction and installation of the pilot equipment. The financing is assured by the industrial partners involved and by public funds from the Rhône-Alpes Region, the French ADEME agency, CEA, and CNRS. The PHOTOSIL pilot line is integrated in the newly created "Institut National de l'Energie Solaire" (INES) close to Chambéry in the Rhône-Alpes Region and scheduled to be fully operational at the beginning of October 2006.

2 THE PHOTOSIL PROCESS

The important feature of the PHOTOSIL approach is its complete vertical process integration, starting with the metallurgical base process and leading to the crystallisation of multi-c Silicon ingots or the fabrication of 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 enthalpy. In consequence, process times and costs can be strongly reduced.

The following major objectives of the PHOTOSIL project have been set to be realised with the pilot line:

- Extension of volume from laboratory scale with batch sizes of 10kg to production scale with batch sizes of 60kg and 120kg arriving at a nominal capacity of 200 tons/year.
- Costs: 15€/kg for SoG Silicon feedstock and 35€/kg for multi-c Silicon ingots.
- Quality: Resistivity > 0.5 Ωcm, type: p or n, 15% solar cell efficiency on multi-c wafers.

Figure 1 shows the generic flow of the PHOTOSIL process. A first important part, which takes place before the PHOTOSIL process itself, concerns the production of metallurgical (MG) 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 in general 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 segregation process has been developed by FerroPem and is proprietary knowledge of the company. The obtained, so called, “Upgraded Metallurgical” (UMG-1) Silicon is the starting material for the PHOTOSIL process. Results in terms of impurity concentrations and electrical parameters that reflect the state of the art at the time of writing this article are given and discussed in Section 3.

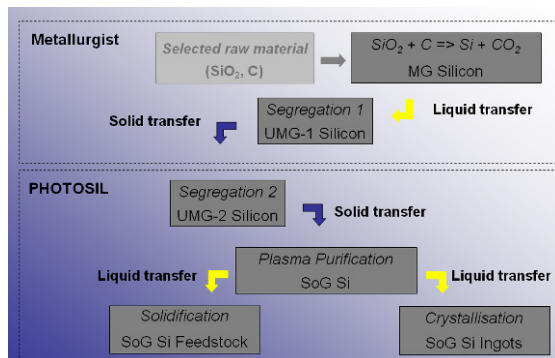


Figure 1: Generic flow of the PHOTOSIL process.

a) Purification by segregation

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. Figure 2 shows the transfer of the melted Silicon into the segregation vessel.



Figure 2: Transfer of melted Si into segregation vessel

The segregation equipment has been realised by EFD and can be seen on Figure 3.



Figure 3: Outside view of the segregation equipment for the production of UMG-2 Silicon.

During this purification process, 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.

b) Plasma purification

The obtained solid UMG-2 Silicon is transferred to the plasma purification and solidification unit that is shown in Figure 4.



Figure 4: Outside view of the plasma purification and solidification unit.

This central part of the pilot equipment was designed and realised by EFD-Induction, relying both, on long term internal experience with the construction of industrial plasma and induction heating equipment, and on the scientific experience with plasma and electromagnetic processes of EPM. Furthermore, the CEA-LITEN added their technical-scientific knowledge and experience to develop important parts of the equipment, for example a completely newly designed extraction unit for the flue gases and dust.

The inductive plasma purification process has already been described in detail in earlier publications [10, 12]. The PHOTOSIL plasma purification equipment is based

on the laboratory equipment used by EPM so far for the purification process development. In summary, an Argon plasma gas that contains other reactive species is created by induction and blown onto the surface of liquid silicon which is constantly renewed by electromagnetic stirring. The reactive species are able to volatilise impurities like B, C, Al, and Ca, with relatively large segregation coefficients, and are not removed during the preceding purification steps. B is mainly removed as boron hydride oxide by the addition of O₂ and H₂ to the plasma; C is removed as CO and O in the last step of the process by volatilization as SiO, which is gaseous at the silicon melting temperature. The key point of the process is the control and the monitoring of the B removal: the purification time depends directly on the oxygen concentration within the plasma. However, at high oxygen concentration, a thin layer of silicon oxide is formed at the surface of the liquid, which stops the exchanges between the liquid and the surface, and slows down dramatically the purification process. By modifying the plasma torch geometry and the reactive gas injection system, it has been possible to increase by a factor five the O₂ concentration in the plasma, avoiding the layer formation. This makes it possible to significantly reduce the purification time, arriving at time constants for the B removal in the order of 50 min.

The case of P is more complex. The most stable form for P at the silicon melting temperature is P₂. This molecule is volatile. But at very low concentrations, which are presently found, the formation kinetic is slow. The removal is improved by increasing the temperature of the liquid. At higher temperatures, the P₂ formation is easier, and the volatilisation as P is improved. However, the removal process remains slow, and the best solution is to reduce the P concentration before the plasma treatment which is the case with the UMG-2 Silicon.

The plasma purification process is in-line monitored by measuring the concentrations of characteristic elements, such as B and P in the exhaust gases. The gases are analysed by a commercially available ICP-OES system. In addition, the in-line analysis also allows to adjust the process parameters during the treatment, in order to produce either p-type or n-type Silicon, depending on the ratio of B, P, and Al removal.

c) Solidification and Crystallisation

After plasma purification, the liquid Silicon is transferred either into a special crystallisation crucible or into a solidification container. Both, crucible and solidification container are then automatically moved through a transfer unit under Ar atmosphere to an attached cooling unit – in case of the solidification container – or to an attached crystallisation furnace – in case of the crystallisation crucible. This gives the possibility to either produce multi-crystalline Silicon ingots by controlled directional solidification inside the crystallisation furnace or Silicon feedstock by rapid solidification inside the solidification unit. The crystallisation furnace has been developed by the Grenoble based company CYBERSTAR in close collaboration with APOLLONSOLAR.

One key element of the crystallisation process is a newly developed silica crucible with anisotropic thermal behaviour, which has been proposed by AS, EFD-Induction and CYBERSTAR. As shown in Figure 5, the crucible allows for a preferred heat extraction through its transparent bottom via radiation, whereas the opaque crucible walls support lateral thermal insulation. Combined with the newly designed crystallisation furnace, equipped with improved thermal elements, the heat extraction from the solidifying silicon inside the crucible can be better controlled to arrive at the required crystal quality.

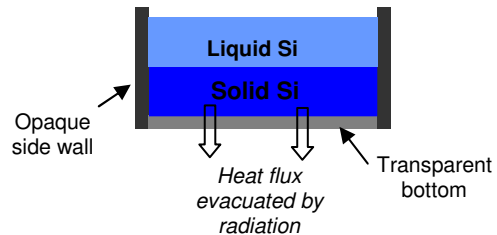


Figure 5: Silica crucible with anisotropic thermal properties used for the crystallisation of multi-c Silicon ingots.

The functioning of the crucible and the associated thermal elements in the furnace has been proven on lab scale, with 10kg ingots. The thermo-mechanic stability during the transfer of liquid silicon could also be validated.

At the time of writing this article, the plasma purification and solidification unit of the PHOTOSIL pilot equipment was in the final installation and test phase.

3 RESULTS AND DISCUSSION

3.1 UMG-1 and UMG-2 – impurity concentrations

The impurity concentrations of UMG Silicon shown in Table 1 are the latest obtained with the PHOTOSIL segregation furnace shown in Figures 2 and 3 with batch sizes of 75 kg. The fact that this furnace is already operational since the beginning of June 2006 allowed first process improvements. The UMG-2 Silicon used for the plasma purification runs shown in Table 2 was taken from earlier batches.

Table 1: Concentrations of selected impurities in UMG-1 and UMG-2 Silicon as analysed by ICP.

Impurity	UMG 1 (ppm _w)	UMG 2 (ppm _w)
Al	140	15
B	8	6
Ca	100	50
Cr	4	<2
Fe	400	20
P	17	8
Ti	20	<2
V	5	<2

The impurity concentrations shown in Table 1 were measured with an ICP system of the FerroPem laboratory whose detection limit is at 2 ppm for most of the analysed metals. The concentrations of Ni, Ti and V are therefore below the detection limit. The reduction of the P which has a high segregation coefficient of 0.35 is unusual. It can be explained by the fact that part of the P atoms might be present in form of stable complexes around the melting point of Silicon, which have a lower segregation coefficient. Further process optimization is under way.

3.2 UMG-2 Silicon after plasma treatment

The results shown in Table 2 were obtained with the laboratory plasma purification equipment at EPM. The batch size was 10kg. As can be seen, Al, B, C, Ca and O concentrations have been effectively reduced. Other metal impurities are not significantly affected by this treatment.

Table 2: Concentrations of selected impurities in UMG-2 Silicon before and after plasma purification.

Impurity	UMG 2 (ppm _w)	UMG 2P (ppm _w)
Al	12	5
B	9	3.5
Ca	70	9
C	100	15 – 20
O	90	20 - 25
P	4	2.5

Four point probe measurements on the obtained Silicon after plasma purification gave a resistivity of 0.3 to 0.5 Ωcm with a p-type polarity. Further process optimization work is under way for the up scaling on pilot line level, once the installation of the equipment is finished.

3.3 Electrical Characterisation of UMG-2 Silicon

The TECSEN laboratory of the University of Marseille has characterized UMG-2 Silicon coming from the first unit of the PHOTOSIL pilot line. The impurity concentrations of this Silicon are in the range of the material shown in Table 1 above. Samples were taken from a block of solidified UMG-2 Silicon whose surfaces were cut and polished. The characterizations came to the overall conclusion that this UMG-2 Silicon already shows semiconductor properties. More particularly, the material is p-type with a resistivity of 0.08 Ωcm, which demonstrates the potential of this intermediate product, before the final purification steps are applied.

4 CONCLUSIONS

The PHOTOSIL project, aiming at the production of solar grade Silicon feedstock and multi-c Silicon ingots from metallurgical Silicon has entered the industrial pilot phase. In the first year of this 3 years project the required infrastructure has been realised. The necessary equipment is in the final installation and test phase and in case of the segregation unit for the production of UMG-2 Silicon already operational. The obtained intermediate results on

Silicon purification are very encouraging for the continuation of the project, also on the background of the complementarity of the consortium that can rely on the scientific and technical experience from R&D laboratories, equipment manufacturers and the R&D experts from industry. During the following project phase the material evaluation will be extended up to solar cell processing and validated on manufacturing level.

5 ACKNOWLEDGEMENTS

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