Innovative Crystallisation of Multi-Crystalline Silicon Ingots from different types of Silicon Feedstock

J. Kraiem[1*], R. Einhaus[1], F. Lissalde[2], S. Dubois[3], N. Enjalbert[3], B. Drevet[3], F. Servant[3], D. Camel[3]

[1]APOLLON SOLAR, 23 rue Claudius Collonge, 69002 Lyon, France
[2] CYBERSTAR, Parc Sud Galaxy, 1 rue des Tropiques, 38435 Echirolles, France
[3] CEA-INES, 50 avenue du Lac Léman, 73377 Le Bourget du Lac, France
[*]Corresponding Author: Tel: +33-681-392631, Fax: +33-478-604763, E-mail: kraiem@apollonsolar.com

ABSTRACT: Solar Grade Silicon obtained by purification of metallurgical grade Silicon becomes an important source of Silicon feedstock for the crystalline Silicon based PV industry. This paper presents a new process and furnace for the crystallization of multi-crystalline Silicon ingot, using purified metallurgical grade Silicon as feedstock. In particular, the influence of the remaining dopant concentrations, such as Boron and Phosphorus, in purified metallurgical Silicon on the electrical characteristics of the obtained ingots, wafers and solar cells are discussed. Indications have been found that compensation of n-type and p-type dopants can lead to an improved minority carrier diffusion length, improving the overall efficiencies of solar cells: Efficiencies of 14 % have been obtained on ingots that were grown from feedstock with relatively high concentrations of Boron ($2.5x10^{17}$ cm^{-3}) and Phosphorus ($3.5x10^{17}$ cm^{-3}) respectively. Although the feedstock is n-type due to the higher concentration of Phosphorus, the ingot showed a p-type polarity with a resistivity of 0.5 Ohm-cm over 75% of its height starting from the bottom, which is due to a more effective segregation of Phosphorus. This also leads to an accumulation of Phosphorus atoms in the top region of the ingot, which turns n-type again and a transition region of high compensation.

Keywords: Multi-Crystalline, Compensation, Solar grade Silicon

1 INTRODUCTION

The PV industry continues its rapid annual growth rates in order to satisfy the steadily increasing demand for PV energy conversion units worldwide. At the same time, crystalline Silicon remains by far the dominant material used for PV modules. This scenario has led to a shortage of suitable Silicon feedstock, the raw material that is used for the crystallization of mono- and multi- crystalline Silicon ingots, and a related drastic price increase. In order to overcome this bottleneck situation and to stabilize the costs of PV a number of industrial projects to develop new production techniques for solar grade Silicon feedstock have been initiated [1]. Among the different projects two major routes can be distinguished. The first, the so-called the chemical route, is related to the production of ultra-pure Electronic Grade (EG) Silicon by means of a simplified Siemens process, consisting of a gas phase purification and decomposition of trichlorosilane [2]. The alternative route, known as the metallurgical route, consists of purifying widely available Metallurgical Grade (MG) Silicon to arrive at a quality level that is sufficient and compatible with the requirements of the PV industry [3]. As has been shown in [4] the metallurgical route can be five times more energy efficient and requires thus much less production costs than the conventional Siemens process that uses more than 200 kWh/kg. However, the metallurgical purification techniques are generally less efficient in removing dopants and an important point related to the use of purified MG Silicon is the presence of both, n-type and p-type dopant atoms (Phosphorus and Boron).

In a first part this paper discusses a new technology that has specially been developed for the crystallization of multi-crystalline Silicon ingots using purified MG Silicon feedstock.

In a second part the electrical behavior of multi-crystalline Silicon with regard to the presence of remaining dopant concentrations in the purified MG grade Silicon feedstock in the order of lower 10^{17} cm^{-3} is highlighted. This work is part of the French PHOTOSIL project [3] that deals with the purification of metallurgical grade Silicon and includes the crystallization of multi-crystalline Silicon ingots as final production step.

2 CRYSTALLISATION TECHNOLOGY

In general, multi-crystalline Silicon ingots are crystallized by uni-directional solidification using Bridgeman-type furnaces or variations. This technology has been introduced several decades ago [5,6] and the principle can be summarized as follows: The Silicon feedstock is melted in a crucible and – by applying a vertical temperature gradient - crystallized from the bottom, slowly moving the solid liquid interface upwards. During the crystallization elements with a low segregation coefficient such as metals are segregated in the liquid phase and concentrated in the upmost layer of the ingot which is normally discarded.

2.1. Cyberstar/Apollonsolar Crystallisation Technology

The crystallisation technology developed by Cyberstar and Apollonsolar has already been presented in detail [7], its major features are briefely summarised. Two important key features can be distinguisded:

The first one is a new thermal furnace topology, consisting of two independently controlled, inductive heating elements below and above the crucible in combination with an efficient lateral thermal insulation. This new thermal configuration (Figure.1) is well adapted for establishing high temperature gradients (>10K/cm) and a planar solid/liquid interface, which are especially beneficial for the segregation of remaining impurities in lower quality silicon at high solidification velocities.

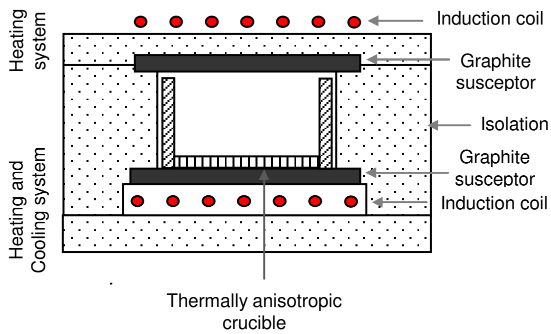

Figure 1: Schematic view of the principal elements of the new Cyberstar crystallisation furnace.

The second element is a thermally anisotropic quartz crucible, see Figure 2. Contrary to the fused silica crucibles presently employed by the industry in which the bottom presents an important thermal resistance (due to the low thermal conductivity of fused silica), the newly developed crucible is made from a transparent bottom and opaque side walls. By this way, during crystallization the heat flux is easily extracted through the transparent bottom of the crucible via IR radiation, whereas the opaque crucible walls support lateral thermal insulation, thus allowing the application of higher thermal gradients and a higher crystallization rate whithout risking to destabilise the solid liquid interface.

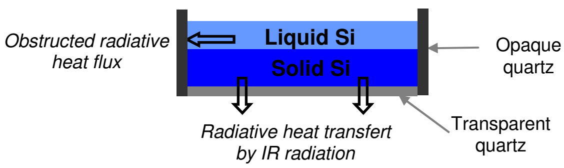

Figure 2: Schematic drawing of the newly developed thermally anisotropic crystallisation crucible.

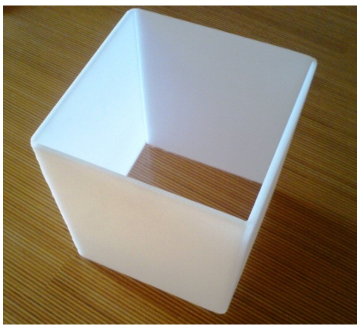

Figure 3: Anisotropic quartz crucible 200x200x220 mm^3 for 12 kg ingots.

In a second aspect, the use of quartz instead of fused silica as crucible material drastically reduces contamination of the ingot by solid state diffusion. Indeed, as shown in table 1 the total amount of impurities presents in quartz is much lower than in standard crucible material i.e. fused silica. This allows improving the material yield by reducing the regions of low minority carrier lifetime. As has been shown in [8] and [9], commercial fused silica crucibles present even a risk of dopant diffusion from the fused silica into the silicon during the crystallisation process.

Table 1: Impurity concentrations in standard grade silica crucible [9,10], and quartz crucible (ppmw).

Element	Fused Silica Crucible	Quartz Crucible
Mg	10	0.8
Al	950	17
Ti	60	2.5
Mn	2	0.1
Fe	120	0.8
Ni	1	0.1
P	2.6 – 3.6	<0.2
B	0.75 – 2.8	<0.2

2.2. Crystallisation of purified MG Silicon

In general, purified MG Silicon is characterized in that a certain number of impurities are still present at a low concentration level, which in case of metal impurities is often below the detection limit of chemical analysis techniques applied. Especially dopant atoms such as Phosphorus and Boron are difficult to remove and are thus still present as shown in the next section in the case of PHOTOSIL purified MG Silicon.

Moreover, due to their relatively high segregation coefficients (k_b=0.8, k_p=0.35) with an important difference in their absolute value, Boron and Phosphorus are not easily removable by segregation and show an important difference in their segregation behavior. As a result, during the crystallization of a multi-crystalline Silicon ingot purified MG Silicon feedstock, there are 2 major consequences: firstly, the simultaneous presence of p-type and n-type dopant atoms induces a decrease of the free carrier concentration and a decrease of the mobility (affected by scattering effects) and consequently the resistivity increases with ingot height. Secondly, the upper part of the ingot often turns n-type due to a more efficient Phosphorus segregation, which drastically reduces the material yield i.e. the productivity of the crystallization furnace and process.

One important question related to purified MG Silicon is the compensation effect. Up to now only few studies have been devoted to the effect of dopant compensation on electrical properties. If on one hand, some studies are suggesting that compensated dopants could have a significant impact on the carrier lifetime [11], others studies propose that electrical compensation of Boron with donors, like Phosphorus could be a solution [12]. Based on this divergence of results, one can imagine that there is a frontier between beneficial/detrimental effects which is still an unknown, and further investigations are required.

.

2 CRYSTALLISATION EXPERIMENTS

Crystallization experiments were carried out in a lab-scale Cyberstar furnace using the innovative crystallization process. Two ingots with different types of silicon were grown: (i) Electronic grade (EG) silicon, boron doped with a resistivity of 0.5Ωcm; (ii) Purified metallurgical Silicon (SoG) from PHOTOSIL with remaining impurities concentrations as shown in Table 2. The latter one reflecting the state-of-the-art of 2007, in the meantime, both Boron and Phosphorus concentrations have been further reduced.

Table 2: Impurity concentrations in Photosil purified MG silicon used for the crystallisation experiments in this article.

Element	Concentration [ppmw]
B	2-3
P	6-8
Al	< 5.0
Ca	8.8
Fe	26
Ni	< 2.0
Cu	< 2.0
Ti	< 1.0

After crystallization, the two resulting 6 kg ingots were cut into wafers including the bottom part of the ingot, which is usually removed, in order to assess the contamination resulting from the quartz crucible.

Figure 3 shows the obtained efficiencies of both ingots as a function of the ingot height.

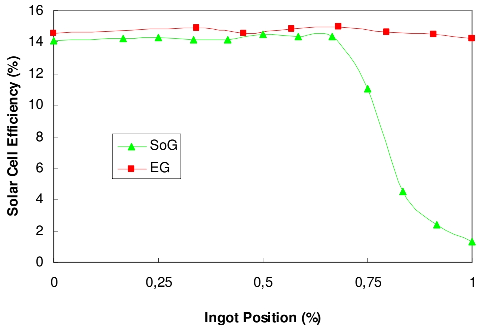

Figure 3: Solar cell efficiencies as a function of ingot position for ingots from EG Silicon and PHOTOSIL silicon**.**

In case of the EG ingot the efficiency distribution is very stable at a high level of 15% from the bottom to the top of the ingot. In case of the ingot from PHOTOSIL Silicon, numerous observations can be made: (i) As expected, due to the high residual concentration of Phosphorus and its better segregation than Boron, the ingot turns to n-type at around 70% of its height, from which solar cells efficiencies drastically drop. It also has to be noted that the feedstock shown in Table 2 is n-type due to the higher concentration of Phosphorus compared to Boron and again, due to the more efficient segregation of Phosphorus the major part of the ingot had p-type polarity. The segregation behavior of Phosphorus and Boron is illustrated on Figure 4, based on calculated concentration at different ingot height positions, using the Scheil equation.

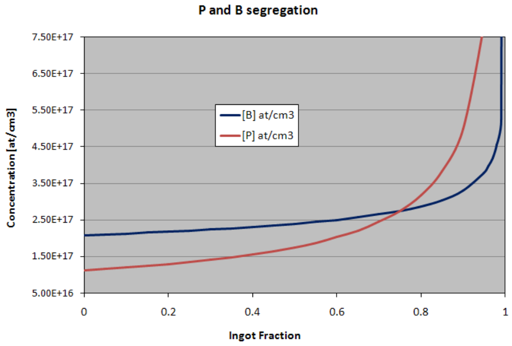

Figure 4: Calculated segregation behavior of Phosphorus and Boron, using the Scheil equation.

(ii) As withEG ingot no significant degradation of the efficiency for solar cells from the bottom ingot was observed, which confirms the interest to use pure quartz as crucible material. Moreover, the same result can be expected from the ingot sides, so a higher material yield can be reached for ingots grown using this technique, limiting the loss due to the solid state diffusion of impurities from the crucible;

(iii) A relatively high solar cells efficiency was obtained (14%) in the p-type region, regarding the residual impurities concentrations of the feedstock, especially in case of Boron and Phosphorus. More surprising, but not perceptible on the graph, is the fact that the best solar cells (14.3%) were obtained just before the change of polarity type i.e. in the strongest compensated region.

A similar observation has been made on another ingot, this time using purified MG Silicon feedstock, this time of p-type polarity. As can be seen on Figure 5, an efficiency peak towards the top of the ingot can clearly be identified. This region corresponds to the region with a high degree of compensation.

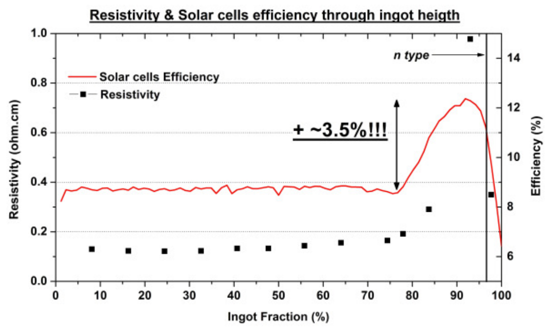

Figure 5: Distribution of solar cell efficiencies on an ingot made from p-type purified MG Silicon feedstock.

Characterizations of wafers and solar cells of the ingot shown in Figure 3 were then carried out. LBIC and resistivity mappings show a perfect match between the minority carrier diffusion length Ln and resistivity (Figures 6 and 7).

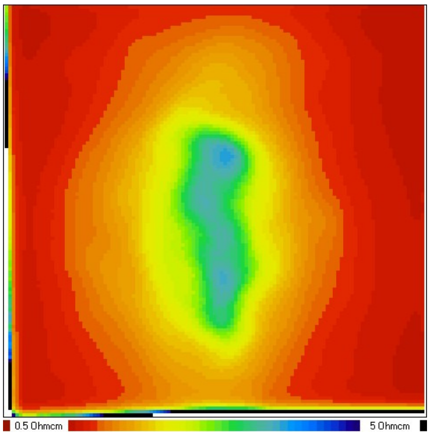

Figure 6: Resistivity map of a wafer from from the compensated region of the purified MG ingot.

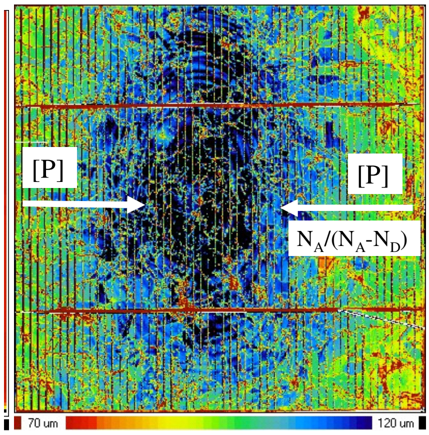

Figure 7: Minority carrier diffusin length map of a solar cell from the compensated region of the purified MG ingot.

Indeed, the highest Ln value (150µm) is located in the wafer center i.e. in the highest resistive region (2.5Ω.cm) whereas the lowest Ln value (75µm) is situated towards the wafer edges, a region exhibiting a lower resistivity (0.5Ω.cm). This observation clearly suggests that Ln increases with the degree of compensation. Chemical analyses (GDMS) on the entire surface confirm these results, indicating a higher phosphorus concentration in the center (4.6ppmw) compared to the edges (3.1ppmw), for the same boron concentration on the entire surface (2ppmw), thus explaining resistivity variation.

The variation of concentration is due to the transport conditions of dopants in the liquid ahead the crystallization front, which leads phosphorus to segregate towards the center of the wafers, leading to an increase in the compensation level from the edges to the centre of the wafers.

These results show clearly the beneficial effect of compensation and allow understanding why the best solar cells are located near the inversion of polarity type.

Combining these results and numerical simulation, S. Dubois proposed a theoretical model suggesting that when carrier lifetime is limited by doping species, dopant compensation could be a solution to increase solar cells performances [13].

CONCLUSIONS

A new crystallization technology for multi-crystalline Silicon ingots has been presented. This technology makes use of a newly designed thermal set up within the furnace and a thermally anisotropic and pure quartz crucible. Both contribute to a higher material yield and improved production time cycles, especially when using purified MG grade Silicon as feedstock.

It has further been found that compensation effects due to residual concentrations of Boron and Phosphorus in MG grade Silicon and their segregation behavior during crystallization lead to an improved minority carrier diffusion length and to increase solar cell efficiencies.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the co-financing of this work by ADEME, the French Agency for Environment and Energy Management under contract number 04 05 C0039, by the Rhône-Alpes Region and by the Savoie Department. The authors also acknowledge the support by the Photosil Consortium, the CEA-INES Restaure platform and Photowatt.

REFERENCES

[1] A.F.B. Braga, et al., Solar Energy Materials and Solar Cells 92 (2007), pp. 418-424.
[2] P. Woditsch et al., Solar Energy Materials and Solar Cells 72 (2002) pp. 11-26.
[3] R. Einhaus et al.:, Proceedings of the 21^{st} European PVSEC, Dresden 2006, pp.580-583.
[4] J. A. Waernes et al., 8^{th} Silicon for the chemical industry Conference, Trondheim, 2006
[5] C. Khattak et al., Proceedings of the 13^{th} IEEE PVSC, pp. 137- 141.
[6] J. Fally et al., Revue Phys. Appl. 22 (1987), pp. 529 – 534.
[7] F. Lissalde et al., Proceedings of the 22^{nd} European PVSEC, Milano 2007, pp. 948 – 951.
[8] M. Dhamrin et al., Proceedings of the 17^{th} International PVSEC, Fukuoka 2007, pp. 91- 92.
[9] T. Saitoh et al: Proceedings of the 17^{th} International PVSEC, Fukuoka 2007, pp. 418 – 421.
[10]R. Kvande et al., Proceedings of the 21^{st} European PVSEC, Dresden, 2006, pp.1052-1056.
[11]L. J. Geerligs et al., Proceedings of the 17^{th} NREL Workshop, Colorado, 2007, pp. 169-173.
[12]S. Dubois et al., Proceedings of the 23^{rd} European PVSEC, Valencia, 2008, to be published
[13]S. Dubois et al., Applied Physics Letters, 2008, to be published.