# DOPING ENGINEERING
# AS A METHOD TO INCREASE THE PERFORMANCE OF PURIFIED MG SILICON DURING INGOT CRYSTALLISATION

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## ABSTRACT

This paper presents an overview of significant crystallisation results obtained with purified metallurgical grade silicon in the framework of the French Photosil project.

Especially we show that in case of a high Boron concentration in the feedstock ($>2.10^{17}$ $cm^{-3}$), the higher the compensation level is, the higher the solar cells efficiency will be. Several ingots were crystallised with different concentrations of boron and phosphorus and the best solar cell efficiency (15.2%) was obtained with the highest compensated ingot.

Moreover we show that this performance improvement is due to an increase of carrier lifetime which largely counterbalances the decrease of carrier mobilities, likely caused by scattering effect of ionized dopants.

However, due to the different segregation coefficients of the major dopant atoms, Boron and Phosphorus, compensated multi-c Silicon ingots often show n-type regions, decreasing the overall material yield.

Based on these findings, we suggest a novel concept of doping engineering, allowing a control of the compensation level through the entire ingot height, by introducing a well defined mix of dopant atoms (B, P and Ga) to the silicon before crystallisation. This can lead at the same time to a higher electrical performance and a higher material yield of the crystallised Silicon. As a further perspective the use of lower grade and less expensive Silicon with a high electrical performance and material yield can be expected,

## INTRODUCTION

The continuing rapid growth of the PV industry and the resulting silicon shortage have stimulated new approaches in purification and crystallisation of metallurgical silicon to a quality level compatible with the requirements of the PV industry [1]. However, new solar grade silicon obtained from metallurgical purification techniques is generally not as pure as EG Si and an important point related to the use of this material is the presence of both, n-type and p-type dopant atoms (Phosphorus and Boron). The impact of using such compensated silicon for solar cells is not well understood.

On one hand compensation may offer several advantages, as an inexpensive means of avoiding low resistivity ingots made from lower quality feedstock or a way to mitigate the impact of certain recombination centers by reducing the equilibrium majority carrier concentration. On the other hand, effects of compensation on more fundamental electrical properties are not clear. In addition to a probable reduction of carrier mobilities, due to scattering effects of the high level of ionized dopants, the impact on carrier lifetime is subject to ongoing discussions [2-4].

Recent results obtained in the framework of the Photosil project with lower quality silicon have shown a beneficial effect of dopant compensation on the minority carrier diffusion length i.e. on solar cells performances, when the carrier lifetime is limited by dopants [5,6]. These results indicate the possibility to accept a higher Boron concentration in the feedstock when the required amount of Phosphorus is added to arrive at the desired compensation level, thus reducing the constraints on the up front Silicon purification process and associated costs.

However, due to the more efficient segregation of phosphorus during crystallization the higher the required level of compensation is, the sooner the inversion of polarity type from p-type to n-type will occur in the ingot, in particular for a Silicon feedstock with a high initial Boron concentration ($>2.10^{17} cm^{-3}$).

In this paper we firstly give an overview of results obtained in the Photosil project with compensated ingots. Electrical characterizations, especially of the carrier mobility and the carrier lifetime are also presented to try to explain possible mechanisms behind the beneficial effect of compensation. Finally we describe a simple method for controlling the net dopant concentration $N_a$-$N_d$ through the entire ingot height by the addition of a well defined mix of Boron, Phosphorus and Gallium.

## BACKGROUND OF THE PHOTOSIL PROJECT

One of the most remarkable results was obtained with a multic-Si ingot grown from an n-type feedstock resulting in a resistivity of 0.2 Ω.cm. Chemical analyses conducted by GDMS revealed a relatively high concentration of Boron and Phosphorus after purification, $2.5x10^{17}$ and $3.5x10^{17}$ $cm^{-3}$ respectively. Despite this high phosphorus concentration, the crystallized ingot was p-type on 70% of its height due to the more pronounced

Phosphorus segregation and solar cells obtained from this ingot part exhibit an average efficiency of 14%. However, beyond this noticeable result, the most surprising thing was the fact that the best solar cells were located just before the change of polarity type i.e. in the strongest compensated region (low $N_a$-$N_d$ region, high ρ). In this area we observed an increase of the short circuit current $J_{cc}$ of 3% compared to solar cells from the bottom ingot as shown on Table 1.

**Table 1:** Comparison of electrical parameters of solar cells from a lowly (Cell A) and highly (cell B) compensated region.

| | ρ (Ω.cm) | η (%) | Voc (mV) | Icc (A) | FF (%) |
|---|---|---|---|---|---|
| Cell A<br>High Na-Nd | 0.64 | 13.9 | 611 | <u>4.65</u> | 76.4 |
| Cell B<br>Low Na-Nd | 1.3 | 14.3 | 610 | <u>4.80</u> | 76.3 |

A wafer from this region was characterized in terms of resistivity and minority carrier diffusion length ($L_n$) and a perfect correlation was found (Fig.1). The highest $L_n$ value (150µm) is located in the wafer center i.e. in the highest resistive region (2.5Ω.cm) while the lowest $L_n$ value (75µm) is situated in the wafer edges, a region exhibiting a lower resistivity (0.5Ω.cm). This observation clearly suggests that $L_n$ increases with the compensation level i.e a decrease of the net doping density.

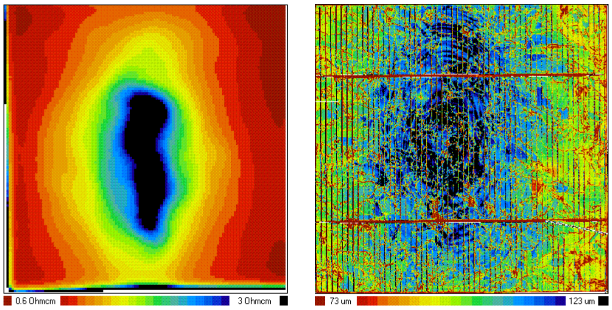

**Figure 1:** Resistivity and $L_n$ maps of a mc-Si solar cell from an ingot grown from a strongly compensated silicon feedstock purified via the Photosil process.

More spectacular is the result obtained with an ingot grown from a p-type feedstock containing Boron and Phosphorus concentrations equal to $4.5\times10^{17}$ and $2.5\times10^{17}$ $cm^{-3}$ respectively. The crystallized Si ingot was p-type over 95% of the ingot height and lightly compensated.

As shown in Figure 2 a large part of the ingot (70%) exhibits a very low resistivity (0.1Ω.cm) due to the high net doping density, estimated to $2.7\times10^{17}$ $cm^{-3}$ and the solar cells efficiencies in this part do not exceed 9%. This low efficiency is clearly due to a low carrier lifetime affected by carrier recombination of dopant atoms.

However, as soon as the resistivity starts to increase in the upper part due to a decrease of the net doping density provoked by Phosphorus segregation, the solar cells efficiencies drastically increase, to reach a maximum of 12.3% at 93% of the ingot height, a region exhibiting a resistivity close to 1Ω.cm.

Moreover, it should be noted that the maximum efficiency could have been higher, taking the fact that at this ingot height metallic impurities concentrations are relatively high due to segregation and their effects on efficiency is thus expected to be strong.

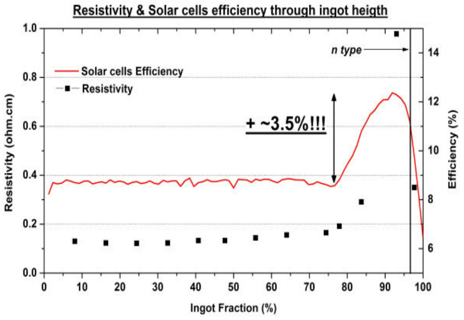

**Figure 2:** Evolution of the resistivity and distribution of solar cell efficiencies of an ingot made from p-type purified MG Silicon feedstock.

Once again, analysing the cell parameters (Table 2) we observed that this performance improvement is mainly due to a significant increase in the $J_{cc}$ values (+35 %!). And since $J_{cc}$ is most strongly related to excess carrier lifetime, the lifetime in the highly compensated wafers seems to be considerably higher than the lifetime in wafers with a larger net doping density.

**Table 2:** Comparison of electrical parameters for solar cells in a lowly (Cell C) and highly (cell D) compensated region.

| | ρ (Ω.cm) | η (%) | Voc (mV) | Icc (mA/cm²) | FF (%) |
|---|---|---|---|---|---|
| Cell C<br>High Na-Nd | 0.1 | 8.7 | 580 | 19.5 | 76.3 |
| Cell D<br>Low Na-Nd | 0.4 | 12.4 | 608 | 26.4 | 76.3 |

## RECENT RESULTS OF THE PHOTOSIL PROJECT

In order to clearly illustrate trends in increasing the compensation level, two additional multi-crystalline (mc-Si) ingots, having the same Boron concentration but different Phosphorus concentrations were produced (Table 3).

**Table 3:** Boron and Phosphorus concentrations, maximum and average efficiency and material yield for ingot 1 and 2, yield corresponding to the percentage of the p-type region.

| | B ($cm^{-3}$) | P ($cm^{-3}$) | η Max | η ave. | Yield |
|---|---|---|---|---|---|
| Ingot 1 | $2.3\times10^{17}$ | $4\times10^{17}$ | 15.2% | 15% | 45 % |
| Ingot 2 | $2.3\times10^{17}$ | $2\times10^{17}$ | 14.7% | 13.8% | 90 % |

Again, both ingots show an increase of the electrical performances with increasing compensation level. Maximum efficiencies of 15.2% and 14.7% for ingot 1 and 2, respectively, are reached just before the change of polarity type at 45% and 90% of the ingot height. Furthermore, comparing the best cells of each ingot obtained in the highest compensated region, it is remarkable that despite the same net doping density of $1.10^{16}$ $cm^{-3}$, a difference of 0.5% in efficiency is observed. This is likely due to their respective position in the ingot. In ingot 2 we estimated an iron concentration almost 10 times higher. At last, due to the higher level of compensation in ingot 1, solar cells have reached a higher average efficiency than ingot 2, 15% and 13.8 % respectively but on the other hand the material yield is only 45% for ingot 1 instead of 90% for ingot 2. These examples clearly show the duality of compensation.

Hall measurements were also conducted to put in evidence reduced mobilities in the compensated wafers. Figure 3 shows the evolution of hole mobilites as a function of ingot height in case of ingot 2.

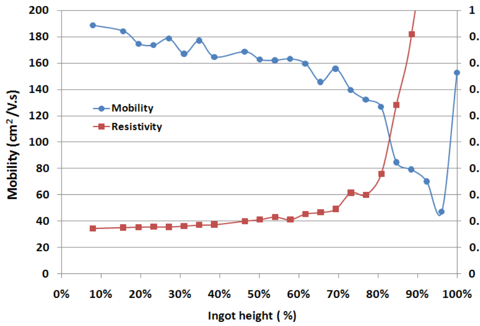

**Figure 3:** Resistivity and majority carrier mobility as a function of ingot height for ingot 2.

As predicted by Reggiani's model [7], a reduction in mobilities in compensated material compared to non compensated silicon for the same net doping density is likely caused by additional scattering centres, and a clear degradation with the compensation level is found. Similarly to what we observed for majority carriers, the same reduction can be expected for minority carriers.

Nevertheless, this mobility decrease is largely counterbalanced by an improvement of carrier lifetime.

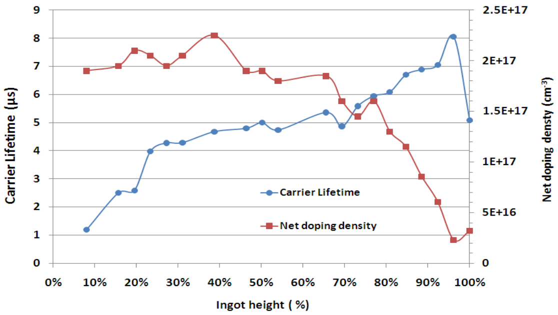

**Figure 4:** Carrier lifetime and net doping density as a function of ingot height for ingot 2.

Figure 4 shows carrier lifetime, measured by QSSPC and the net doping density of ingot 2 as a function of ingot height. It appears to be a significant increase in the lifetime as the net doping density decreases i.e as the compensation level increases. In fact, the minority carrier lifetime $\tau$ is multiplied by 8 when $N_a$-$N_d$ varies from $2.10^{17}$ to $3.10^{16}$ $cm^{-3}$.

Based on these results, S. Dubois suggested that in case the carrier lifetime is limited by dopant atoms, compensation allows to increase the electrical performance. He explained this effect theoretically by using simplified Schockley-Read-Hall statistics [3]. An increased minority carrier lifetime with increasing compensation level is due to a decrease of recombination strength of the dopant atoms. This results from the fact that in strongly compensated Silicon a reduction of the free carrier concentration translates to a shift of the Fermi level towards mid bandgap, by which the attraction of neutral acceptors for electrons is reduced and therefore the minority carrier (electron) lifetime increases. And this increase largely counterbalances the reduction of carrier mobilities.

## DOPING ENGINEERING FOR CONTROLING COMPENSATION LEVEL

Considering previous results, it becomes obvious that dopant compensation may allow the use of higher Boron doped silicon for solar cells. Indeed, the carrier lifetime seems to depend only on the net doping density, not on total doping concentration. This means that a p-type silicon wafer with a doping level of $5.10^{16}$ $cm^{-3}$ will have the same carrier lifetime as a wafer containing $1.10^{17}$ $cm^{-3}$ of boron and $5.10^{16}$ $cm^{-3}$ of phosphorus. However as aforementioned, due to the more efficient segregation of phosphorus during crystallization the level of compensation is not uniform throughout the height of the ingot, which leads to an increasing resistivity and an inversion of the polarity type in the upper part of the ingot which also limits the material yield (Figure 5).

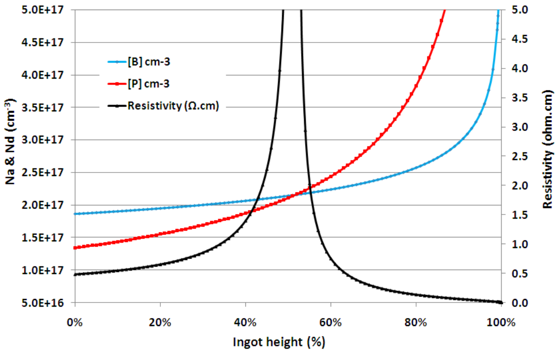

**Figure 5:** Dopant concentrations ($N_a$ and $N_d$) and the resulting resistivity as a function of the ingot height for ingot 1.

A more useful scenario, in terms of improved material yield and improved electrical performance, can be achieved thanks to "dopant engineering". Doping engineering involves a third p-type dopant, or acceptor, like Gallium (Ga). Thanks to its very low segregation coefficient (k=0.008), Ga accumulates in the upper part of the ingot and may counterbalance the phosphorus segregation and thus avoid the change in polarity type without significantly affecting the net doping density in the bottom part. But on top of that, it would be possible to control the net doping density through the entire ingot height.

Indeed, by solving the following equation based on Scheil's law, one can calculate a well defined mix of dopant atoms to be added to the silicon before crystallisation, allowing to control the maximum net doping density in the ingot and avoiding an n-type inversion.

$$K_B C_{0B}(1-f_s)^{K_B-1}+K_{Ga}C_{0Ga}(1-f_s)^{K_{Ga}-1}–K_P C_{0P}(1-f_s)^{K_P-1}<N_a-N_d \quad (1)$$

In case of ingot 1 for example, an addition of Ga to the feedstock in order to reach a concentration of $5.10^{18}$ $cm^{-3}$ would be required. After crystallisation and segregation of the dopant atoms, the net doping density does not exceed $10^{17}$ $cm^{-3}$ and is more uniformly distributed throughout the ingot, as illustrated by the resistivity distribution. Moreover the polarity type inversion is completely suppressed.

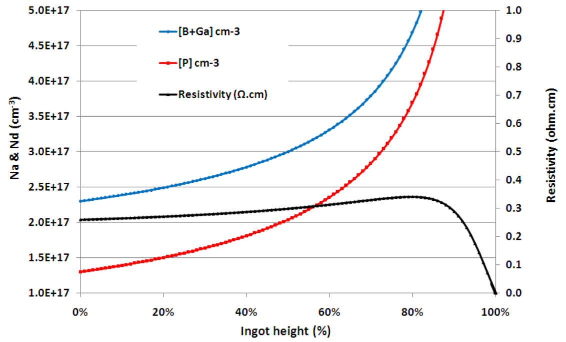

**Figure 6:** Calculated distribution of [B+Ga] and [P] and the resistivity evolution associated.

To experimentally confirm this method, a first crystallisation experiment has been carried out using a similar feedstock used for ingot 1 and dopant engineering by Gallium addition. The resulting 10kg ingot was entirely p-type instead of 45%, and the resulting resistivity distribution is shown in Fig. 7.

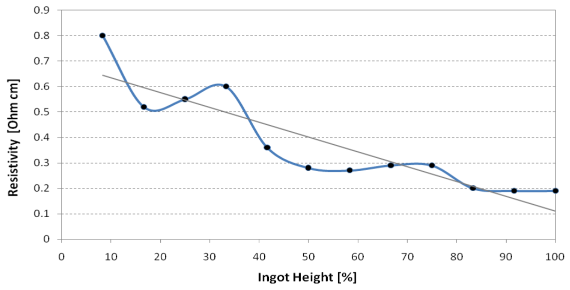

**Figure 7:** Resistivity as a function of ingot height in case of an ingot grown from a feedstock similar to ingot 1, making use of dopant engineering.

As can be seen, the resistivity decreases towards the top of the ingot, which is not ideal yet, probably due to a lack of melt stirring, but the obtained range of resistivity is already acceptable for solar cell processing. Carrier lifetime measurements were also conducted on the ingot and we obtained 3µs which is very encouraging for solar cells fabrication, which is under way.

## CONCLUSION

This overview of crystallization results of purified MG-Si clearly put in evidence the beneficial effect of compensation when the boron concentration is relatively high in the feedstock (>$2.10^{17}$$cm^{-3}$). Electrical characterization of compensated ingots has shown that this performance improvement is due to an important increase of carrier lifetime, which largely counterbalances the reduction of carrier mobilities, and thus explains high minority carrier diffusion length in highly compensated regions. This observation suggests that the resulting carrier lifetime does not depend on the total concentration of dopant impurities but on the net doping density. However, due to a relatively important segregation of phosphorus, the compensation level is not uniform throughout the height of the ingot. Based on these findings, a simple method to control the net doping density through the entire ingot height is given. Preliminary results are promising which can open new opportunities for the use of silicon feedstock with higher Boron concentrations. Moreover PV costs can be drastically reduced taking the fact that a primary driver in the cost to produce SoG-Si is the removal rate of boron.

## ACKNOWLEDGEMENTS

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