STUDIES OF COMPENSATION BEHAVIOUR IN P-TYPE MC-SILICON

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ABSTRACT: We study the effect of different compensation levels on the electrical quality of mc-silicon ingots, on the solar cell performance along the ingot height and on the carrier lifetime after different process steps. Therefore three different mc-Si ingots with various compensation levels were grown (one slightly compensated, one stronger compensated, one uncompensated reference). Wafers from selected positions over the ingot height were characterised and processed to solar cells. The results showed no difference in the solar cell performance except for the top region of the stronger compensated ingot, where the doping changes at about 85% ingot height from p-type to n-type. We observed a beneficial effect of higher resistivities on the minority carrier lifetime in the stronger compensated top region. This effect is strongly pronounced after P-gettering, due to the decreased negative impact of segregated impurities in the top region. The beneficial effect is related to the reduced net doping, i.e. reduced majority carrier concentration in the top region.
Keywords: Multicrystalline Silicon, SoG-Silicon, Compensation

1 INTRODUCTION

Currently new low-cost SoG (solar-grade) and UMG (upgraded metallurgical) silicon feedstock from various purification techniques is entering the PV market offering an alternative to the very pure poly-Si material. The major task for such alternative purification techniques, compared to the purification of gaseous silicon compound (such as silanes, chlorosilanes…), is the removal of doping elements such as P and B, which require long high temperature steps increasing the thermal budget of the purification. An alternative to the removal of a specific dopant is the admixture of a complementary element in order to reach a suitable resistivity range for solar cells (0.5 - 5 Ωcm). This results in silicon ingots that have compensated doping. But resistivity control using compensation is difficult, due to the different solid to liquid segregation coefficients of boron and phosphorus, which produce a strongly varying resistivity along the mc-Si ingot. Often the material becomes over-compensated towards the top of the ingot, meaning a change from p-type to n-type, and is unusable for current industrial cell technology. Therefore an important question for such purification techniques is the accepted level of compensation in order to be able to grow an ingot with a rather homogeneous resistivity profile, but not to affect both solar cell performance and long term stability of the cell efficiency. The impact of using such compensated silicon for solar cells is still poorly understood. The two main properties of interest for solar cell performance are carrier lifetime and carrier mobility. In recent publications slightly decreased lifetimes [1,2] and lower mobilities [2-5] in compensated silicon have been reported.

In this work we investigated the effect of different compensation levels on the electrical quality of mc-Si ingots and on the solar cell performance along the ingots. The aim was to find a limit for the compensation level of mc-Si ingots that is still acceptable for the PV industry. The doping change from p-type to n-type should appear only in the topmost region of the ingot. Therefore two ingots with different compensation levels were grown at Deutsche Solar (DS). Wafers from selected positions over the ingot height were characterised by resistivity and lifetime measurements and processed to solar cells.

2 INVESTIGATED MATERIAL

Three 25 kg p-type mc silicon ingots with various compensation levels were grown in a small pilot scale furnace at DS using directional solidification: one uncompensated ingot with standard resistivity as reference, one slightly compensated ingot and one stronger compensated ingot, containing an overcompensated n-type region at the top.

Table I: Dopant-concentrations added to the melt before crystallization.

	Reference	Slightly compensated	Stronger compensated
Boron added to melt	1.95×10^{16} cm^{-3} (0.39 ppma)	1.95×10^{16} cm^{-3} (0.39 ppma)	1.95×10^{16} cm^{-3} (0.39 ppma)
Phosphorus added to melt	nil	0.92×10^{16} cm^{-3} (0.18 ppma)	2.04×10^{16} cm^{-3} (0.41 ppma)

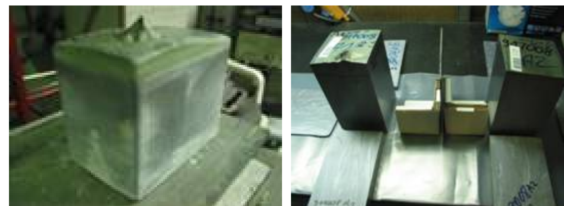


Figure 1: Pictures of one ingot after removal of crucible (left) and two bricks with side cuts (right).

For this experiment only pure poly-Si feedstock was used in order to ensure that impurity concentration and crystal structure are in the range of a typical industrial mc-Si ingot obtained by directional solidification. The dopant concentrations added to the melt of the ingots are given in Table I. Each ingot was cut into two bricks of

12.5 x 12.5 cm^2. The bricks were sawn into 210 µm thick wafers. One brick of each ingot was investigated. Pictures of one ingot and two bricks with side cuts are shown in Fig. 1.

3 CHARACTERISATION ON WAFER LEVEL

3.1 Resistivity measurements

The resistivity was measured on as cut wafers along the ingot height both by 4-point-probe technique and by eddy-current technique for control. The resistivity was measured at five points on each wafer and averaged. The resistivity curves of the three ingots are shown in Fig. 2.

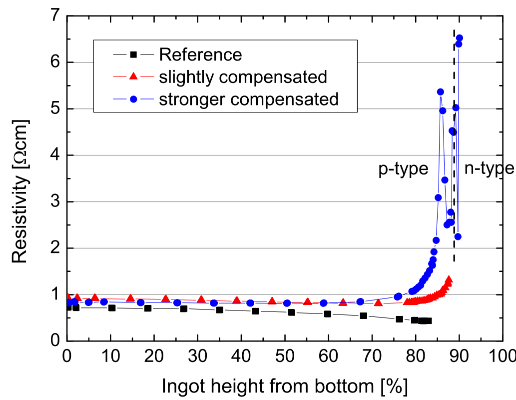


Figure 2: Resistivity along the ingot height for the reference ingot, the slightly compensated ingot and the stronger compensated ingot.

The uncompensated reference ingot shows a typical decreasing resistivity curve caused by the segregation of boron. The significantly different segregation coefficients of boron (0.8) and phosphorus (0.35) lead to increasing resistivity and higher compensation levels towards the top of the compensated ingots, for the stronger compensated more pronounced than for the slightly compensated ingot. In the case of the stronger compensated ingot it also leads to a conversion from p-type to n-type doping at about 85% ingot height. But the doping change appears not homogeneously over the wafer area. One reason for that might be an inhomogeneous temperature profile during crystallisation in the small pilot scale furnace. This could have caused a disturbed convex crystallisation front towards the top of the ingots leading to an inhomogeneous resistivity distribution on the horizontally cut wafers. Another reason could be convecto-diffusive solute transport of phosphorus in molten silicon, along with the curvature of the crystallisation front, inducing an increase in the phosphorus concentration from the edges to the center of the ingot. A similar effect was observed in compensated mc-material investigated by Dubois et al. [6] and in UMG material investigated by Kohler et al. [7]. The non-planar crystallisation front explains the large scattering of the resistivity measurements in the top region of the stronger compensated ingot in Fig. 2.

3.2 Lifetime measurements

Lifetime mappings of wafers from selected positions along the ingot height were done before and after tube furnace P-gettering. Minority charge carrier lifetimes of the samples were mapped spatially resolved using the method of microwave detected photoconductance decay (µ-PCD). At the beginning about 15 µm were removed on each side of the as cut wafers by an acidic etching step (CP6 solution). Before each µ-PCD measurement the wafers were chemically cleaned (piranha solution), dipped in HF and their surfaces were passivated with an iodine-ethanol solution.

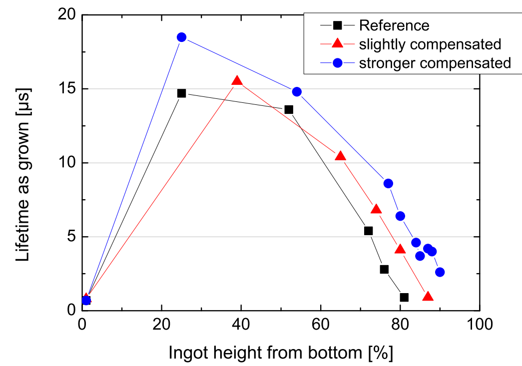


Figure 3: Lifetimes of as grown wafers along the ingot height. The lifetimes are averaged over the total wafer area.

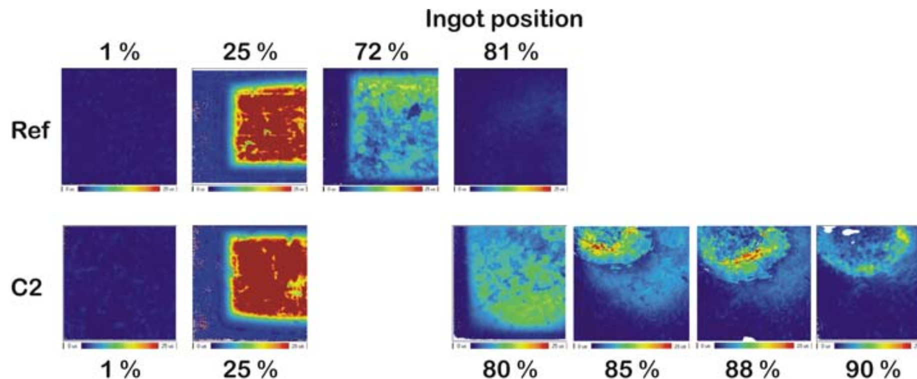


Figure 4: Lifetime mappings of as grown wafers (12.5 x 12.5 cm^2) along the ingot height for the reference ingot (Ref, top) and the stronger compensated ingot (C2, bottom). Colour code from 0 µs (dark blue) to 25 µs (red).

In Fig. 3 for all three ingots lifetimes, averaged over the total wafer area, are plotted as a function of the ingot position. In Fig. 4 the corresponding lifetime mappings of the as grown wafers for the reference ingot (Ref) and the stronger compensated ingot (C2) are shown. The scaling is the same for all mappings. The reference and the slightly compensated ingots show typical lifetime distributions along the ingot height: low lifetimes at the ingot bottom due to the detrimental influence of the crucible, higher lifetimes in the center region and again low lifetimes towards the top because of segregation of impurities. The detrimental impact of the crucible is also clearly visible at the edges of the ingots (see Fig. 4). In the top region the stronger compensated ingot shows a different behaviour compared to the other two ingots. After a drop the lifetime again increases slightly in the upper left corner of the ingot due to the strongly increasing resistivity or rather decreasing net doping in this region towards the top (see Fig. 4). This beneficial resistivity effect interferes with the negative effect of impurity segregation towards the top of the ingot. However, to get information about the real impact of compensation, meaning the impact of additional boron and phosphorus, on carrier lifetime of the bulk only wafers with similar net doping levels should be compared. This was done by Macdonald and al. on compensated Cz material [1,2]. They observed slightly reduced lifetimes in the compensated samples, compared to control samples of the same net doping.

After measuring the as grown lifetimes four 5 x 5 cm^2 wafers were cut out of each 12.5 x 12.5 cm^2 wafer receiving two different gettering steps (standard 50 Ω/sq and heavy 10 Ω/sq $POCl_3$-diffusion) according to Fig. 5. In order to evaluate also the impact of the corner region on the different gettering steps four instead of only two small wafers were investigated. After $POCl_3$ diffusion the emitter of the wafers was etched back in a CP6 solution (about 20 µm per side). Then again the wafers were measured by µ-PCD. For the four different wafer sets the averaged lifetimes over the ingot height are shown in Fig. 6a - 6d.

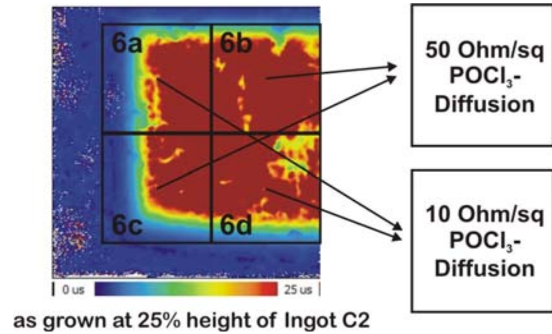
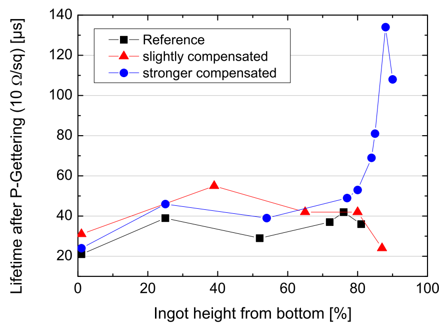
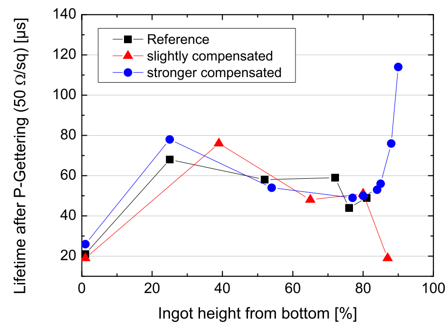


Figure 5: Scheme for cutting 12.5 x 12.5 cm^2 wafers in four 5 x 5 cm^2 wafers. Each one corner (left) and one center (right) wafer received a standard 50 Ω/sq and a 10 Ω/sq $POCl_3$-diffusion respectively.

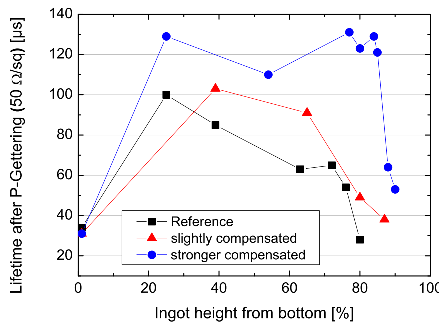
The second two wafer sets (see Fig. 6c and 6d) in contrast to wafers shown in Fig. 6a and 6b were measured in a Semilab WT2000 tool with bias light function and therefore these measurements were carried out with bias light. This resulted in generally higher effective lifetimes, especially in the center region of the



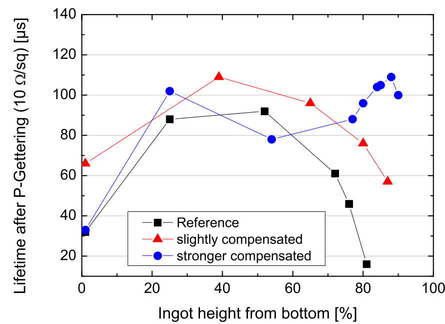
6a: τ_{eff} after 10 Ω/sq diffusion / corner



6b: τ_{eff} after 50 Ω/sq diffusion / center



6c: τ_{eff} after 50 Ω/sq diffusion / corner



6d: τ_{eff} after 10 Ω/sq diffusion / center

Figure 6: Averaged lifetimes after P-gettering along the ingot height for sets of 5 x 5 cm^2 wafers from the corner and the center region of the ingot. Two different gettering steps were applied.

ingots. But apart from this measurement related differences the results show that P-gettering works very well for both the compensated and the reference ingots. The material of all three ingots does not degrade after the heavy 10 Ω/sq $POCl_3$-diffusion (see Fig. 6a and 6d), which is in general not usual for multicrystalline material. It is hard to find a difference between the corner and the center region of the ingots. The lower lifetimes in Fig. 6a compared to Fig. 6d (both after 10 Ω/sq diffusion) might be due to the impact of the corner region or due to the measurement without bias light. On the other hand higher lifetimes occurred in the corner region after 50 Ω/sq gettering (comparing Fig. 6c with Fig. 6b), which might be also due to the impact of the corner region or due to the measurement with bias light. The beneficial resistivity effect in the top region of the stronger compensated ingot is strongly pronounced after P-gettering and lifetime measurement without bias light (Fig. 6a and 6b). It is not that strongly pronounced but also clearly visible after P-gettering and lifetime measurement with bias light (Fig. 6c and 6d).

4 CHARACTERISATION ON CELL LEVEL

About 30 wafers per ingot, continuously distributed over the ingot height, were processed to solar cells using a standard industrial type solar cell process with $POCl_3$-diffusion, full aluminium back surface field and SiN_x:H firing through, but without texture. The efficiencies, J_{sc} and V_{oc} values of the cells are given as a function of ingot height in Fig. 7, Fig. 8 and Fig. 9 respectively.

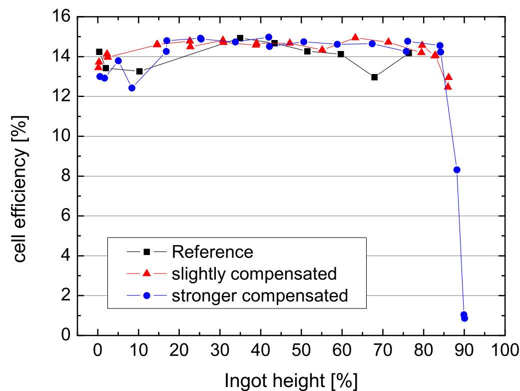


Figure 7: Efficiency of solar cells as a function of ingot height for the two compensated ingots and the reference ingot.

The solar cell performances of the two compensated ingots are comparable to the reference cells, which show standard efficiency values for an industrial type process without texture. Apart from the upmost top region of the stronger compensated ingot, where the doping change from p-type to n-type takes place, no obvious efficiency decrease is visible (see Fig. 7). Due to the doping change the efficiency strongly decreases in this region. The J_{sc} values of the three ingots also show no obvious difference apart from a slight increase for the stronger compensated ingot just before the doping change followed by a strong decrease exactly at the doping change (see Fig. 8).

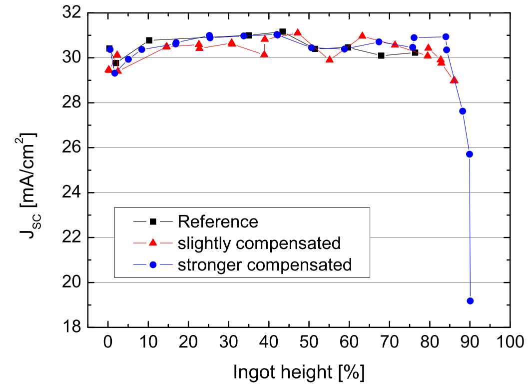


Figure 8: Short circuit current density of solar cells as a function of ingot height for the two compensated ingots and the reference ingot.

For the V_{oc} values in Fig. 9 the opposite behaviour can be observed. No difference is visible between the three ingots in the bottom and the center region. But from the center to the top region the stronger compensated ingot shows a slight decrease in V_{oc} compared to the other two ingots. This slight decrease in V_{oc} originates from the decrease of the net doping towards the top of ingot C2. At the pn change at about 85% height of ingot C2 as for J_{sc} and efficiency a strong decrease in V_{oc} is visible.

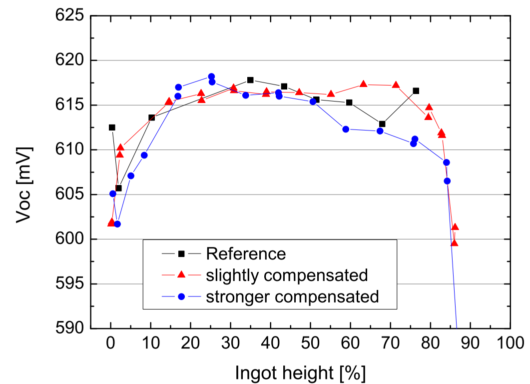


Figure 9: Open circuit voltage of solar cells as a function of ingot height for the two compensated ingots and the reference ingot.

For all three ingots spectral response measurements were done on sorted cells. In Fig. 10 the internal quantum efficiency (IQE) at 1000 nm dependant on the ingot height is shown, which is a measure for the bulk quality. Reference and slightly compensated ingot follow nearly the same, for standard ingots typical distribution: a maximum in the center and a decrease towards the bottom and the top of the ingots, while the slightly compensated ingot performs a little bit better towards the top. For the stronger compensated ingot the IQE primarily also decreases from the center towards the top, but at about 70% ingot height it again increases. This is a similar behaviour as was observed for the lifetime measurements in Fig. 3 and 6. Another point is that with decreasing net doping the performance of the Al-BSF

becomes better, as shown by Godlewski et al. [8]. This, of course, will also lead to an increased IQE. So, decreasing net doping in the top region is leading to higher effective lifetimes on wafer level as well as to an improved performance of the Al-BSF, both resulting in increased IQE values at 1000 nm on cell level. These higher IQE values finally result in slightly enhanced J_{sc} values shortly before the pn change, as can be seen in Fig. 8. The net result of the opposite trends in V_{oc} and J_{sc} in the top region before the pn change is a very similar efficiency compared to the other two ingots.

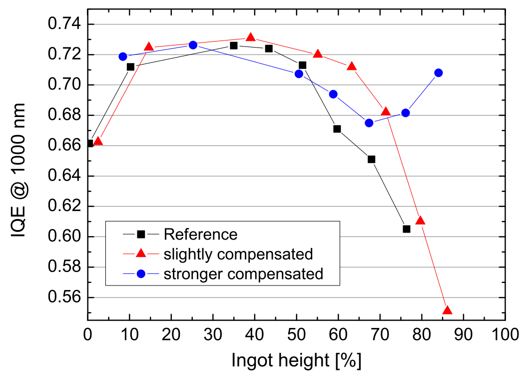


Figure 10: IQE at 1000 nm of solar cells as a function of ingot height for the two compensated ingots and the reference ingot.

5 CONCLUSIONS

Within this study two compensated ingots and one reference ingot were investigated. The results show that the chosen rather low compensation levels of the two compensated ingots had no detrimental impact on solar cell performance using an industrial type cell process. It can be assumed that the carrier mobilities and lifetimes are slightly reduced due to compensation (compared to material with the same net doping), but this seems not to be limiting for the applied industrial type cell process. The observed effects originate mainly from the variation of the resistivity or rather the net doping over the ingot height. For the top region of the stronger compensated ingot a beneficial effect of higher resistivities on the minority carrier lifetime was observed. The decreasing net doping towards the top of the stronger compensated ingot results on the one hand in decreasing V_{oc} values, but on the other hand in increasing effective lifetimes as well as in an enhanced red response and therefore slightly enhanced J_{sc} values. The opposite trends in V_{oc} and J_{sc} in the top region before the pn change result in very similar efficiencies compared to the other two ingots.

The results lead us to the conclusion, that the investigated rather low compensation levels should still be acceptable for ingot production in PV industry.

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7 REFERENCES

[1] D. Macdonald et al., 23rd EU PVSEC, Valencia 2008, p. 951
[2] D. Macdonald et al., J. Appl. Phys. 105, 093704 (2009)
[3] J. Libal et al., J. Appl. Phys. 104, 104507 (2008)
[4] K. Peter et al., 23rd EU PVSEC, Valencia 2008, p. 947
[5] S. Pizzini et al., J. Electrochem. Soc. 131 (1984), p. 2128
[6] S. Dubois et al., Appl. Phys. Lett. 93, 032114 (2008)
[7] D. Kohler et al., *Upgraded Metallurgical-Grade Silicon Solar Cells : A Detailed Material Analysis*, Proceedings of this conference
[8] M. P. Godlewski et al., 10th IEEE PVSEC, 1973, p. 40