

## IMPACT OF ALUMINUM CONTAMINATION IN MC-SI SOLAR CELLS

P.C.P. Bronsveld<sup>1</sup>, L.J. Geerligs<sup>1</sup>, G. Coletti<sup>1</sup>, E.J. Øvrelid<sup>2</sup>, R. Kvande<sup>3</sup>,  
G. Stokkan<sup>4</sup>, E. Olsen<sup>5</sup>

<sup>1</sup>ECN Solar Energy, P.O. Box 1, NL-1755 ZG Petten, the Netherlands  
Phone: +31 224 564331; Fax: +31 224 568214; email: bronsveld@ecn.nl

<sup>2</sup>SINTEF, Alfred Getz Vei 2, 7465, Trondheim, Norway

<sup>3</sup>FESIL, Sunergy AS, Leksviksgata 2, Lilleby, Norway

<sup>4</sup>NTNU, Alfred Getz Vei 2, 7465, Trondheim, Norway

<sup>5</sup>Norwegian University of Life Sciences, 1432 Ås, Norway

**ABSTRACT:** Ingots containing varying amounts of aluminum were compared by solar cell processing. The impact on cell performance was found to be related to the amount of Al. However, also counter intuitive results were obtained, in which a larger impact of the Al contamination on cell performance was observed for less Al and vice versa. Formation of harmful Al-O complexes, known to be responsible for Al-related minority carrier recombination, can qualitatively explain the differences between the cells, based on variations in the total oxygen content in the ingots. Possibly, competition between Al and B in the formation of oxygen complexes can also explain the improved cell performances in the presence of B.

**Keywords:** multi-crystalline silicon, impurities, defects

### 1 INTRODUCTION

Fabrication of crystalline silicon for application in solar cells, starts with feedstock that is clean enough to avoid adverse effects of impurities in the wafer on cell performance. Unfortunately, there are many different contaminants that can act as recombination centers and cause shunts, crystal defects and/or dislocations. In this paper, the effect of aluminum on cell performance is described. Aluminum is a common impurity in silicon for which detrimental effects on the performance of solar cells are expected based on earlier reports [1,2].

In this study, we have found that this detrimental effect is highly reduced in ingots with low oxygen concentration. Moreover, in an ingot with added B the impact is reduced compared to an Al-doped ingot. This will allow lower grade feedstock to make it to the market more easily. By understanding the mechanisms behind these effects, solutions to counter effects of impurities can be improved.

### 2 EXPERIMENTAL

P-type multicrystalline silicon ingots were cast by directional solidification in a 12 kg Crystalox furnace. As feedstock, clean polysilicon was used, to which known amounts of Al and/or B were added (Table 1). Wafers, selected from different positions in the ingot were processed into solar cells, together with wafers from a reference ingot. The wafer positions given in the figures refer to the full height of the ingot (including edges, which are normally cut off).

A state-of-the-art cell process was used, with a tube furnace  $\text{POCl}_3$  diffused phosphorous emitter and  $\text{SiN}_x$  anti-reflection coating (ARC) on the textured front side of the wafer. The metallization consisted of screen printed and co-fired Ag and Al on the front and back, respectively.

IV, spectral response and reflectance were measured. Fourier Transform Infrared (FTIR) measurements were performed on wafers neighboring to the cells to determine interstitial oxygen and substitutional carbon. The bulk resistivity was determined by inductively coupled coil measurements on bare as-cut wafers using the Sinton WCT120 tool.

**Table I:** Concentrations of dopants added to the feedstock of the test ingots.

	[B] (ppmw)	[Al] (ppmw)
AIB 5	0.07*	5
AIB 8	0.55	8
Al 8	0	8
Al 55	0	55

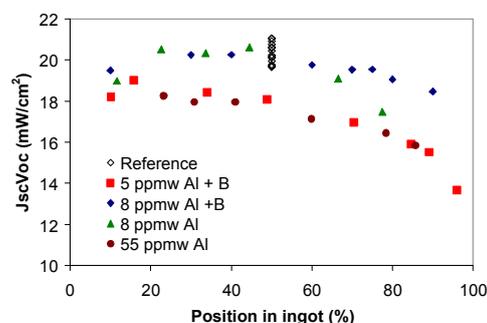
\* Estimated from resistivity

### 3 RESULTS

#### 3.1 Solar cell results

In Fig. 1 the trends of the  $J_{sc} \times V_{oc}$  product are given as a function of ingot height. The green triangles represent cells made from a reference with relatively high bulk resistivity in the range of 1.5-2.0 Ohm cm. To avoid effects of the "exact" processing of the different cells, the product of  $J_{sc}$  and  $V_{oc}$  will be used as a basis for the comparison of the different ingots instead of the conversion efficiency of the cell, which is a more common used parameter, but more subject to small differences in process conditions.

For all ingots,  $J_{sc} \times V_{oc}$  displays a downward trend towards the top of the ingot. Such a trend is expected, based on the increased Al concentration towards the top of the ingot due to segregation during directional solidification of the ingots. This strong segregation effect is also clear from the resistivity profiles (Fig. 5).

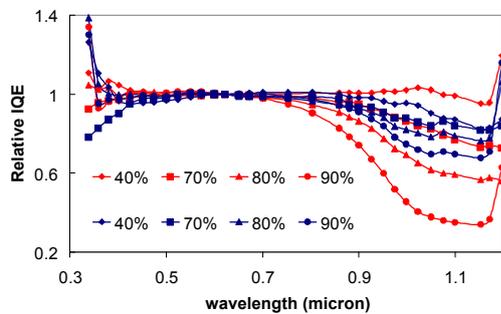


**Figure 1:** trends of the  $J_{sc} \times V_{oc}$  product as a function of ingot height.

Two unexpected results are shown in Fig. 1. The first

is the fact that cells from the ingot contaminated with 5 ppmw Al (and B) performs significantly less than the cells from the ingot with 8 ppmw of Al (and B). The latter are in the range of ~20-80% ingot height, comparable to the reference, while the first perform about 10% less in the bottom, which effect increases towards the top to about 30% efficiency loss.

The second unexpected outcome of these tests follows from a comparison of the results from the two ingots contaminated with 8 ppmw of Al, with and without addition of B as co-dopant. The ingot where no B was added, shows a much larger impact of the Al contamination above ~60% ingot height than the ingot with B. The best cell from the ingot with only Al had a slightly better  $J_{SC} \times V_{OC}$  value than that of the one with Al and B, 20.6 mW/cm<sup>2</sup> and 20.3 mW/cm<sup>2</sup>, respectively. However, on average the one with B was much better, on average 19.5 mW/cm<sup>2</sup> vs. 17.5 mW/cm<sup>2</sup>, due to a large decrease towards the top.



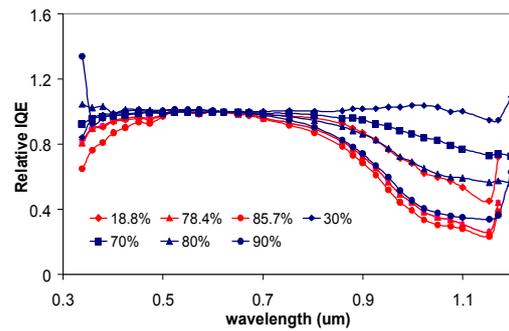
**Figure 2:** Comparison of relative IQE of the two ingots with 8 ppmw of Al with B (blue) and without B (red). The different curves are for different heights in the ingot.

In Fig. 2 the IQE values of the Al 8 and AlB 8 ingots are compared, relative to the reference ingot. For both ingots the reduction in  $J_{SC} \times V_{OC}$  is due to suppression of the red-response of the cells. This effect increases towards the top for both ingots, but less for the ingot with B. The Al concentration in the top is much larger than in the bottom due to segregation and both the resistivity and the Al concentration of the two ingots is comparable here. Therefore, either the impact of high concentrations of Al, or the segregation, must be influenced by the presence of B.

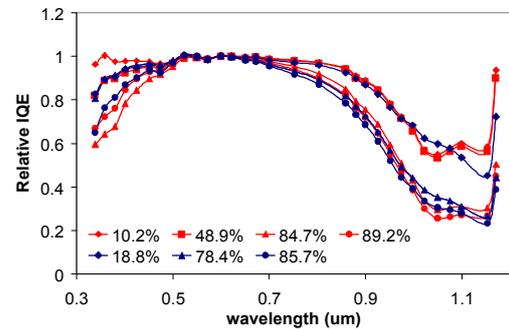
Below 60% ingot height, the red response of the cells without B is better than that of the cells with B. This effect is most likely a result of the higher bulk resistivity of this ingot in the bottom (Fig. 5).

For the ingot with 55 ppmw Al (Fig. 3), the reduction in red response is larger than for the ingot with 8 ppmw Al, but the decrease of relative IQE saturates between, 80% and 90% of the ingot height where the relative IQE values are nearly equal. For the 8 ppmw ingot, the red response decreases much faster as a function of ingot height and reaches a minimum close to the saturation level of the Al 55 ingot.

In Fig. 4, for the 5 ppmw Al ingot, the observed decrease of IQE at a wavelength of 1000 nm is similar to that of the Al 55 ingot. Apparently, there is an effect on red response due to Al. However, there must be an additional parameter which governs the degree to which the Al level impacts the cell performance.

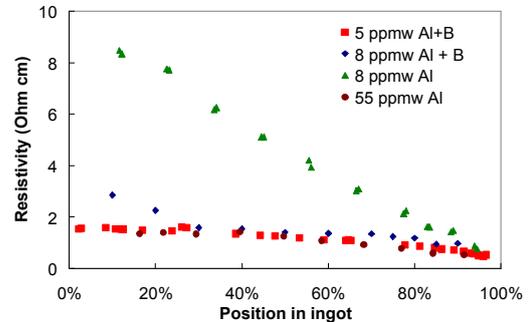


**Figure 3:** Comparison of relative IQE of the ingot with 8 ppmw of Al (blue) and the ingot with 55 ppmw of Al (red).

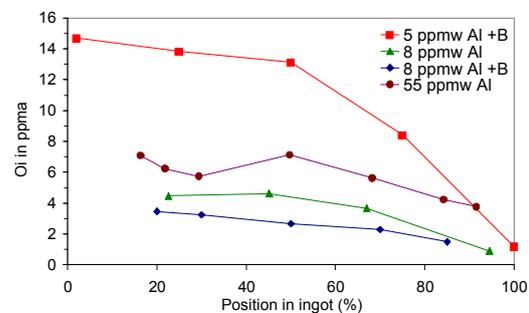


**Figure 4:** Comparison of relative IQE of the ingots with 5 (red) and 55 ppmw of Al (blue).

### 3.2 Wafer characterization



**Figure 5:** Resistivity trends, measured on wafer level by coupled coil measurements, for all four test ingots.



**Figure 6:** Interstitial oxygen content as measured by FTIR for all test ingots.

From Figs. 5 it is clear that the resistivity trends are comparable for all ingots, except for the 8 ppmw Al doped ingot. Therefore, differences in the relative IQE between these ingots cannot be explained based on the bulk resistivity. Fig. 6 indicates that there is a large

difference in oxygen content between the ingots doped with 5 ppmw and those doped with 8 ppmw of Al.

#### 4 DISCUSSION

Marchand and Sah [4] studied the formation of deep level centers in Al-doped Czochralski grown silicon by transient capacitance measurements. They found three hole traps and one electron trap. It was argued that the traps should be associated with complexes involving Al, O and/or C. The free energy of formation of aluminum oxide is extremely large, which favors pairing or complexing of Al with O atoms. Rodot et al. [3] found that one of these traps, at a distance of 0.315 eV from the valence band, can act as a recombination center and is most likely responsible for Al-related minority carrier recombination in Al-doped silicon.

There is not much known on the exact nature of these Al-O related complexes, e.g. both the composition and the probability of formation as a function of O and Al concentrations are unknown. Therefore, we have made a qualitative approximation of the expected impact of these pairs throughout the ingot, by comparing the variation of the Al concentration through the ingot with that of the interstitial oxygen, as measured by FTIR.

To make such a comparison, we need an estimation of the Al distribution in the ingots. The Al concentration profile, in an ingot doped with only Al, can be derived from the resistivity trend, assuming that the resistivity follows the following general relationship,

$$\frac{1}{\rho} = \alpha \mu e C_{0Al} k_{Al} (1-x)^{k_{Al}-1},$$

where  $\rho$  is the majority carrier density,  $x$  the position in the ingot,  $\mu$  the mobility,  $e$  the electron charge,  $\alpha$  the doping efficiency of Al,  $C_{0Al}$  the Al concentration in the feedstock and  $k_{Al}$  the segregation coefficient of Al in silicon.  $k_{Al}$ , and therefore the Al distribution throughout the ingot, can then be estimated from the exponent of a power law fit to  $1/\rho(x)$ , as is demonstrated in Fig. 7 for the 8 ppmw Al ingot. The data is in agreement with  $k_{Al} = 2 \times 10^{-3}$ , which is close to the literature value of  $3 \times 10^{-3}$

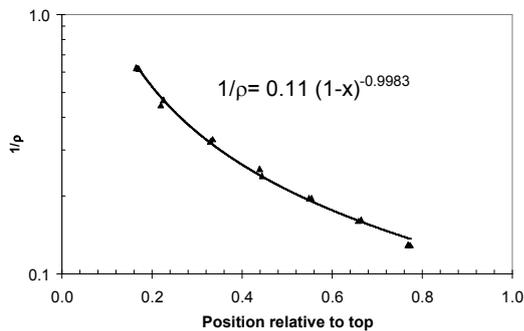


Figure 7: Power law fit to  $1/\rho$  trend of the Al 8 ingot.

found by Yoshikawa and Morita [5], which we will use to calculate the Al distribution according to segregation.

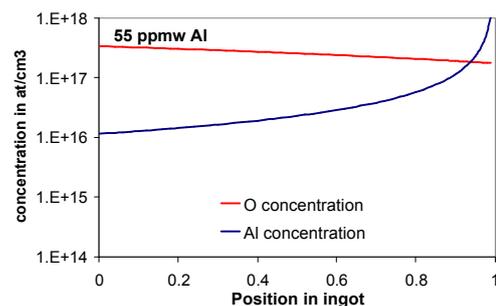
In Fig. 8, the interstitial oxygen concentrations are compared to the Al concentrations for the 4 different ingots. Since we do not know the dependency of the recombination centers on the Al and O concentrations, it is difficult to draw conclusions from these graphs. However, some of the observed phenomena can be explained qualitatively.

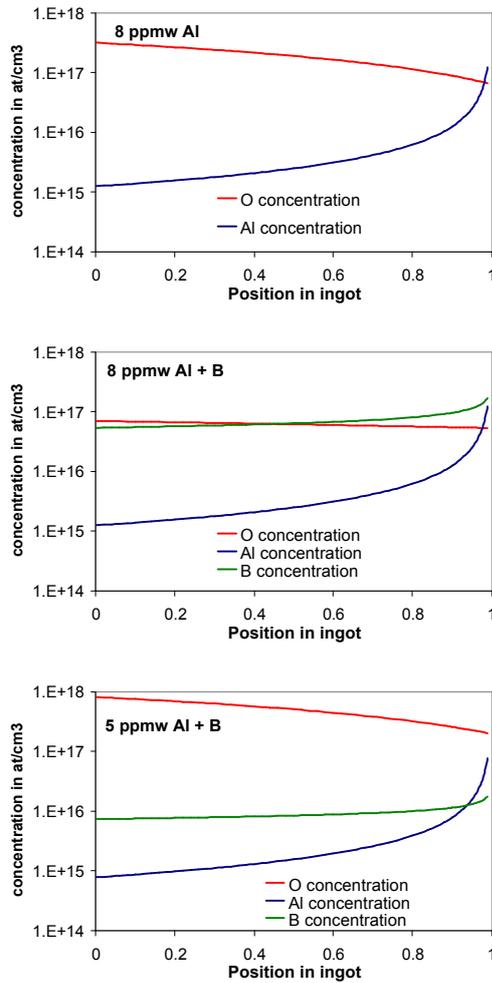
Below ~50% ingot height, the 55 ppmw ingot contains ~10 times as much Al as the 8 ppmw ingot, for comparable oxygen levels. Also, up to about 50% ingot height, the aluminum level of the 5 ppmw ingot is comparable to that of the 8 ppmw ingot, but for this ingot the oxygen concentration is about 10 times higher here. Since we assume that the current loss is due to Al-O pair related recombination, it is, therefore, within expectations that both the 5 ppmw and the 55 ppmw ingots display a similar current loss relative to the ingot with 8 ppmw of Al. For all four ingots, there is much more oxygen present than Al in the bottom, which makes the Al-concentration the limiting factor in the formation of Al-O pairs. However, the probability of Al-O formation might still increase for larger oxygen content at comparable Al concentration.

Towards the top of all ingots, the Al level increases and becomes more comparable to the oxygen level. Above a certain ingot height, Al-O formation will become limited by the relatively flat O profile. For a higher Al concentration, and comparable O profile, this saturation level will lie at a lower ingot height than for a lower concentration. Therefore, saturation of the IQE decrease of the Al 55 ingot will start at an ingot height where the relative IQE of the Al 8 ingot is not yet saturated, as was observed in Fig. 3. An even 10 times higher oxygen content than in the Al 8 ingot, as is the case for the AIB 5 ingot, can shift this saturation point to even larger heights.

Finally, there is also the difference in current loss with and without addition of B. With B the Al-O related decrease in IQE and  $J_{SC} \times V_{OC}$  is seriously diminished compared to the situation without B (Fig. 2). A possible explanation for this is that the B which is present in an Al + B ingot also forms B-O complexes, which effectively reduces the total amount of Al-O that can be formed. For the AIB 5 ingot this effect would be less prominent since here the B concentration is much lower than the oxygen concentration throughout the ingot.

Further analysis is required to confirm the above described analysis quantitatively. However, it seems that the effect of Al in the feedstock can be reduced by controlling the oxygen content of cast ingots, which could be of great advantage to ingot manufacturers that consider to use UMG silicon feedstock.





**Figure 8:** Comparison of trends of oxygen and aluminum density.

point of the Al and O concentrations, saturation is expected at lower ingot height for the 55 ppmw ingot than for the 8 ppmw ingot.

Possibly, competition between Al and B in the formation of oxygen complexes can explain the improved results in the presence of B, by decreasing the available oxygen content.

#### ACKNOWLEDGEMENTS

The authors would like to thank the European projects "Solsilc Demonstrator" (TREN/07/FP6EN/S07.70065/038373) and "CrystalClear Integrated Project" (SES6-CT\_2003-502583) for financial support and supply of material.

#### REFERENCES

- [1] L.J. Geerligs, P. Manshanden, G.P. Wyers, E.J. Øvrelid, O.S. Raaness, A.N. Waernes and B. Wiersma, Proceedings 20th European Photovoltaic Solar Energy Conference, Vol (2005). 619
- [2] R.M. Hopkins, J.R. Davis, A. Rohatgi, R.B. Campbell, P.D. Blais, P. Rai-Choudhury, R. E Stapleton, H. C Mollenkopf, J. R McCormick, Quarterly report Westinghouse Research and Development Center, "Effect of impurities and processing on silicon solar cells", 1980
- [3] M. Rodot, J.E. Bourée, A. Mesli, G. Revel, R. Kishore, S. Pizzini, J. Appl. Phys. 62 (1987) 2556
- [4] R.L. Marchand and C.-T. Sah, J. Appl. Phys. 48 (1977) 336
- [5] T. Yoshikawa and K. Morita, J. Electrochem. Soc. 150 (2003) 465

#### 5 CONCLUSIONS

Wafers from ingots containing varying amounts of aluminum were compared by cell processing. Cells from 2 ingots containing 8 ppmw of Al, with and without B co-doping, displayed better  $J_{SC} \times V_{OC}$  values than cells from an ingot containing 5 ppmw Al. Reduced formation of harmful Al-O complexes in the 8 ppmw Al ingot might explain this difference, since the oxygen concentration was ~10 times higher in the 5 ppmw ingot. In the top of the 8 ppmw Al ingot, the IQE is comparable to that in the top of the 55 ppmw Al ingot, where a saturation of the IQE decrease was observed. Since the position of the saturation point shifts with the cross-over