EFFECT OF IMPURITIES ON SOLAR CELL PARAMETERS IN INTENTIONALLY CONTAMINATED MULTICRYSTALLINE SILICON

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ABSTRACT: Multicrystalline silicon blocks, intentionally contaminated with iron and copper, had been cast and characterized by the twelve German research institutes working together with twelve German companies in the network project SolarFocus. The results of the lifetime measurements, NAA, FTIR analysis, DLTS/MCTS investigations, determination and simulation of the Fe content, solar cell processing, shunt and microscopic investigations are presented in this paper. The combined analysis reveals the influence of the in-diffusion of metal impurities from the crucible as well as the back-diffusion from the top region of the block. Solar cell efficiency is influenced by multiple recombination active defects as well as shunts induced by a high metal contamination.

Keywords: Multicrystalline Si, impurities, characterization

1 INTRODUCTION

Transition metal impurities in silicon such as iron and copper are known to be detrimental for the electrical properties of solar cells made out of silicon wafers. The understanding of the underlying mechanisms and their importance in the face of multiple impurities present in solar cells is still rather limited. For the investigation of interactions of such metal impurities, well defined metal concentrations in silicon have been processed and subsequently characterised with different methods in order to clarify the mechanisms and thus the limits of tolerable amounts of impurities in solar silicon.

The described work has been done in the frame of the second topic of the network research project SolarFocus which is a joint venture of twelve German research institutes and twelve German PV companies working on silicon for solar cell processing [1]; the URL of the project is http://www.solarfocus.org.

2 PURPOSE AND APPROACH OF THE WORK

For the investigation of the effect of iron and copper being introduced in multicrystalline silicon (mc-Si) material either in the feedstock itself or during crystallization, experimental mc-Si blocks have been grown in a small casting furnace at Deutsche Solar AG. The dimensions of the blocks are approx. 270 × 177 mm² base area and 200 mm height equivalent to 23 kg silicon. Table 1 lists the six blocks investigated in this paper.

In a first ingot - representing the process reference - ultrapure Wacker poly-Si feedstock was used to produce a multicrystalline block with a resistivity of about 1.2Ωcm. In a second and third block pure metallic iron was added to the feedstock with concentrations of approx. 2 ppm and 20 ppm in the melt to study the influence of iron at high impurity levels. In the following blocks four to six, the first three blocks have been reproduced with additional pure metallic copper at a concentration level of 20 ppm in the melt. Thus the interaction between the two types of impurities and their precipitation behaviour with respect to structural defects such as grain boundaries and dislocations has been studied.

Two bricks were cut out of each block. One entire brick of each block was sawn into wafers of 250 µm thickness and 125 mm × 125 mm area size for blocks one to three and into wafers of 210 µm thickness and an area size of 156 mm × 156 mm for blocks four to six, respectively. From the second brick, analytical samples for Infra Red Microscopy (IRM), Fourier Transform Infrared Spectroscopy (FTIR) and Neutron Activation Analysis (NAA) were prepared. Every 10⁶ wafer has been processed into a solar cell by an industrial type process with screen printed back contact to evaluate the impurity effects on cell efficiency and other characteristic parameters. Selected solar cells and their neighbouring wafers were distributed among the research institutes for detailed analysis.

Table 1: Overview of the six blocks with intentional doping of iron and/or copper

<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
<th>Additional metallic impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Reference</td>
<td>0 ppm Fe + 0 ppm Cu</td>
</tr>
<tr>
<td>(2)</td>
<td>Lower Fe-content</td>
<td>2 ppm Fe + 0 ppm Cu</td>
</tr>
<tr>
<td>(3)</td>
<td>Higher Fe-content</td>
<td>20 ppm Fe + 0 ppm Cu</td>
</tr>
<tr>
<td>(4)</td>
<td>High Cu-content</td>
<td>0 ppm Fe + 20 ppm Cu</td>
</tr>
<tr>
<td>(5)</td>
<td>Lower Fe-content, high Cu-content</td>
<td>2 ppm Fe + 20 ppm Cu</td>
</tr>
<tr>
<td>(6)</td>
<td>Higher Fe-content, high Cu-content</td>
<td>20 ppm Fe + 20 ppm Cu</td>
</tr>
</tbody>
</table>
3 RESULTS AND DISCUSSION

3.1 Lifetime Measurements

The height dependent lateral lifetime distribution in the blocks, measured by the Microwave Photoconductance Decay method (MW-PCD) on the unpassivated inner side of a brick, shows a reduction of the lifetime level due to the additional iron. This can be observed in the second block (Fig. 1b) and even more in the third block (Fig. 1c) in comparison to the reference block (Fig. 1a). The inner parts of the second and third block exhibit an increasingly reduced lifetime with respect to the reference material. For all blocks, a region of strongly deteriorated lifetime can be observed close to the top. This region is getting bigger for higher iron levels. Boundary effects from the crucible walls still do have a great effect on lifetime. They are visible here as a yellow fringe in the image of the reference block near the block edges.

(1) reference (2) 2 ppma Fe (3) 20 ppma Fe

Histogram of reference block (colour coding applies for all maps)

Figure 1: MW-PCD images of unpassivated sides of the six blocks with added impurities, the height is ~200 mm – work done at Solar World Innovations GmbH.

Additional copper in block (4) doesn’t seem to have a strong negative impact on the lifetime in comparison to block (1). But adding copper and iron jointly in the fifth and sixth block causes an even stronger reduction in the top region of the block. The block volume however seems to be on a similar lifetime level as in the previous set of blocks. The result of simulation work supports the hypothesis that this effect is due to an increase of back-diffusion of impurities from the top of the block after crystallization with the addition of copper.

(4) 0 ppma Fe 20 ppma Cu (5) 2 ppma Fe 20 ppma Cu (6) 20 ppma Fe 20 ppma Cu

3.2 NAA Investigations

Height-dependent Neutron Activation Analyses (NAA) of all six ingots reveal very similar iron distribution curves for all ingots (Fig. 2, top). The general increase of iron concentration towards the block is due to the segregation effect and a small effective segregation coefficient of about $2 \times 10^{-5}$. The increased iron concentration at the bottom of all blocks of about $1 \times 10^{15}$ cm$^{-3}$ points to an inward diffusion from the crucible during crystallization. In the middle part, the Fe concentration mostly lies below the detection limit in ingots (1) and (4), whereas it is significantly higher in the intentional contaminated ingots (2) and (5) up to a level of about $1 \times 10^{14}$ cm$^{-3}$. Thus, both ingots without additional iron and the ingots with a lower additional iron doping exhibit comparable concentrations. This is most probably due to incorporation of iron from the crucible and crucible coating. Both ingots with the higher Fe addition ((3) and (6)) show an identical distribution of Fe independently of the extra copper (6) more or less. Interestingly, the iron profile in the top of block 4 seems to be higher than those of blocks (1), (2) and even (5). This may point to an interaction between iron and copper during the back-diffusion from the top into the block volume directly after complete solidification. But it cannot be ruled out that a cross contamination inside the crystallization furnace may have happened since block (4) was directly cast after block (6).

(1) Reference (2) + 2 ppma Fe (3) + 20 ppma Fe

Figure 2: Height dependent Fe- (top) and Cu- (bottom) distribution for all six blocks, measured by NAA method.
the back-diffusion from the metal enriched top which solidified latest. A significantly higher level of copper values was detected in all ingots to which copper and both iron and copper had been added ((4), (5) and (6)). Also here, an inward diffusion from the crucible is visible at the ingot’s bottom. But as copper diffuses comparably fast, the segregation profile is superimposed by the back-diffusion even below the middle of the block height. For block (3) a concentration profile lying between the two groups may again point to a possible cross contamination in the experiments.

3.3 FTIR Analysis

Height-dependent measurements of the substitutional carbon C\textsubscript{\textit{i}} and interstitial oxygen O\textsubscript{\textit{i}} content within the six ingots showed the typical increase for C\textsubscript{\textit{i}} and decrease for O\textsubscript{\textit{i}} from bottom to top. While the addition of Cu is leading to a slight increase in the O\textsubscript{\textit{i}}-content only (Figure 3), the addition of a higher amount of Fe (20 ppma) is resulting in a doubling of the O\textsubscript{\textit{i}}-content in the bottom region of the ingot. This indicates a strong interaction between oxygen and iron in the oxygen-rich part of the silicon ingot.

Most of the oxygen in the silicon matrix is bound as precipitates surrounded by its interstitial species O\textsubscript{\textit{i}}. Large quantities of iron seem to alter the precipitation behaviour of oxygen directly or indirectly via an interaction with crystal defects or iron precipitates. A slight increase of the O\textsubscript{\textit{i}}-content in the copper-enriched ingots can be found as well, but on a lower scale as for iron.

3.4 DLTS / MCTS Investigations

Deep Level Transient Spectroscopy (DLTS) and Minority Carrier Transient Spectroscopy (MCTS) measurements have been performed to reveal the type of electrically active defects and their distribution in the contaminated material. Figure 4 shows the results for samples from the bottom, middle and top region of ingots (1), (2) and (5).

The most dominant defect is the Fe\textsubscript{B}-complex with an active concentration of several $10^{13}$ cm\textsuperscript{-3}. This complex is more or less homogeneously distributed with a local maximum concentration of $6 \times 10^{13}$ cm\textsuperscript{-3} in the middle of ingot (2). This result matches very well with the NAA values (s. chapter 3.2). In the reference (1) and the Fe/Cu ingot (5) the concentrations are around $1 \times 10^{13}$ cm\textsuperscript{-3} in the top and bottom region and below the detection limit in the middle. Beside the Fe\textsubscript{B}-complex in ingot (5) Cu- and Ni-related defects with a concentration of $10^{13}$ cm\textsuperscript{-3} had been detected in the top region of this ingot.

Solar cells from the top region of the ingots (1), (2) and (5) had been investigated by means of MCTS (minority traps). In all three ingots a defect with a concentration of $10^{14}$ cm\textsuperscript{-3} had been detected but not clearly identified. Thermal donors (TD) may be the source of electrical activity for these results.

3.5 Determination and Simulation of Fe\textsubscript{i}

For the determination of the interstitial iron concentration 10 wafers along the height of ingots (2) and (5) had been selected and 50 x 50 mm\textsuperscript{2} pieces had been cut. In the measured lifetime images a part of the wafers show reduced lifetimes due to the influence of metals out-diffused from the crucible. Those wafers had been polish etched, HF-cleaned and then passivated by a PECVD-Si\textsubscript{3}N\textsubscript{4} layer. Subsequently injection-dependent lifetime measurements by means of Quasi-Steady-State Photocurrent (QSSPC) had been performed in the associated state and after light induced dissociation allowing the determination of the interstitial Fe-concentration Fe\textsubscript{i} (2) applying the defect parameters from Rein [3]. In the middle region of the ingots the experimental Fe\textsubscript{i} results reveal concentrations at about $2 \times 10^{13}$ cm\textsuperscript{-3} up to $1 \times 10^{14}$ cm\textsuperscript{-3} similar for both ingots. At top and bottom of the ingots, higher concentrations could be found.
Starting with the distribution of the total iron concentration in the ingot, measured by NAA (s. Fig. 2), the Fe content was simulated. In the model for the behaviour of iron in multicrystalline silicon, trapping of interstitial Fe at extended defects and precipitation at the extended defects are taken into account [4]. The simulated Fe concentrations for a medium ingot height are of the same range as the QSSPC results but rise with height due to segregation.

In comparison to the NAA measurements (s. Fig. 2) the interstitial iron concentration is reduced by roughly one order of magnitude for medium block heights. This is nicely supported by the simulation. The Fe in-diffusion from the crucible results in a higher concentration of Fe close to the bottom of the ingot, as shown by the simulation. The measured lifetime is reduced in the bottom region due to crystal defects, oxygen or metallic impurities and thus the determination of the Fe content is tainted with a large uncertainty. That applies also for the top region. Furthermore the measured Fe concentration depends on the crystal quality in the QSSPC region and is therefore affected by the inhomogeneous mc Si.

No influence of Cu on the measured Fe levels is observed for the given metal concentrations. Therefore it can be assumed that the precipitation behaviour of Fe is not changed by the addition of 20 ppma Cu.

3.6 Solar Cell Processing

Each tenth wafer of a column had been processed to a solar cell based on today’s high volume industrial standard cell process (texturing, phosphorous diffusion, phosphorus glass etching, SiNx AR coating, screen printing front and rear, contact firing, and edge isolation). The course of the open-circuit voltage in relation to the column height is illustrated in Figure 6 (top) for all cells. The values for the cells of ingot (2) and (5) are a bit slightly higher than the reference cells for a medium ingot height. This effect cannot be seen in the bottom region due to some systematic failures during cell processing.

It is clearly shown that the values of the open circuit voltage ($V_{oc}$) are slightly reduced in the bottom region in comparison to the reference ingot. In the top region the $V_{oc}$ stays high for the reference cells, while those from the contaminated ingots decrease towards the top of the ingot. The cells from ingot (4) with added 20 ppma Cu show a $V_{oc}$ slightly higher than the reference cells for 10 - 60% ingot height. This effect cannot be seen in the efficiency values (s. Fig. 7, bottom). Here the cells from the reference ingot show a constant high efficiency in the range of 16 % with slightly higher values in the top half of the ingot. A significant impact on the efficiency is visible in all other ingots, starting already at about 2/3 of ingot height.

Comparing the addition of either 20 ppma Fe or 20 ppma Cu, the effective negative impact on the efficiency of Fe is higher than for Cu. Combining both elements in ingot (6), the lower part of the ingot exhibits a higher open circuit voltage, short circuit current and efficiency than the ingot with the addition of 20 ppma Fe (3) only. In contrast, it shows lower values in comparison to the ingot with additional 20 ppma Cu (4) only. In the upper half of the investigated ingots, all parameters show the lowest values for ingot (6).

The high amount of added impurities significantly decreases the electrical output of the processed solar cells. The efficiency profiles as well as the open circuit voltage reflect the general trend of lower values in ingot parts with higher impurity concentrations. However, a clear inverse correlation of these profiles with the amount of interstitial iron or copper is not possible pointing to more complex defect interactions limiting the solar cell output.

The influence of gettering and passivation steps on the lifetime and the solar cell performance of material from ingot (1), (2) and (5) is investigated in detail at the University of Konstanz. A strong beneficial influence of high temperature hydrogenation for wafers with high Fe-content could be measured by means of IQE [5]. Furthermore, a remarkable lifetime improvement due to P-gettering could be achieved [6].

![Figure 6: Height dependent open circuit voltage (top) and efficiency (bottom) of solar cells from all blocks – work done at Sunways Productions GmbH and Fraunhofer ISE.](image-url)

3.7 Shunt Investigations

A solar cell from the top of ingot (5) was investigated by dark lock-in thermography (DLIT) to reveal the impact of contaminations on the shunt behaviour of solar cells. The DLIT image (s. Fig. 7) shows that the solar cell has a lot of strong non-linear shunts which are caused by inclusions and precipitates.

The DLIT image was taken at 500 mV displaying a current of $I = 1440$ mA, which is a current much too high at this voltage. The positions of the non-linear shunts correlate with the position of the inclusions and precipitates in the ingot which had been identified by microscopic investigations.
3.7 Microscopic Investigations

Transmission infrared microscopy (IRM) images of wafers of all blocks were taken. The analysis of ingot (5) with the addition of iron and copper revealed the presence of many precipitates and/or inclusions. Different morphologies of precipitates were found (s. Fig. 8), which could be categorised in three groups:

(i) star-shaped precipitates
(ii) big dot-shaped precipitates at grain boundaries
(iii) small dot-shaped structures in grains

Since the nature of the precipitates was unknown, they were further investigated by means of electron beam induced current (EBIC) and synchrotron analysis. It was found that the star-shaped precipitates consist of Cu and CuSi, and both small and big dot-shaped precipitates consist of Cu+Fe.

3 CONCLUSIONS

The combined analysis of the presented results reveals a complex picture of defects in intentionally iron and copper contaminated multicrystalline silicon materials. Only very high levels of contamination in the range of 20 ppma in the melt result in significant higher impurity levels in the block volume for the applied crystallization process. The in-diffusion of metal impurities from the crucible as well as the back-diffusion from the top of the block dominates the impurity profiles for standard blocks as well as lightly contaminated material. Strong interactions in the precipitation of different species can be seen for iron, copper and silicon as well as iron and oxygen. The net reduction in solar cell efficiency in the bottom and especially in the top of the ingots cannot be explained solely by interstitial iron, but indicates the influence of multiple recombination active defects as well as shunts induced by a high metal contamination.

A positive benefit cannot be found for adding copper to the melt. On the other hand Cu seems to be less deleterious than suspected. The presented work implies that the amount of introduced impurities such as iron and copper should be reduced in any case and adapted solar cell processes have to be applied in order to improve the silicon quality and thus cell efficiency.

4 ACKNOWLEDGEMENTS

Ingot casting from Claudia Knopf, Sunicon AG, Freiberg, MWPCD measurements from Bianca Gründig-Wendrock, Solar World Innovations GmbH, Freiberg, solar cell processing from Sunways Production GmbH, Arnstadt and Fraunhofer ISE, Freiburg is gratefully acknowledged. The network project is financially supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) within the research cluster SolarFocus (0327650) and all the industry partners.

6 REFERENCES