

## EFFECT OF THE CRUCIBLE AND ITS COATING ON THE RED ZONE IN MULTICRYSTALLINE SILICON – ANALYSIS ON SOLAR CELL LEVEL

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**ABSTRACT:** The purpose of this work is to investigate the influence of the crucible and its coating on the deteriorated edge zone (also called “red zone”) during directional solidification of multicrystalline silicon (mc-Si). Since the material quality is changed by the processing of solar cells due to, e.g., gettering and hydrogenation, this study was performed on material after having processed it into lab-type solar cells. The use of a standard industrial quartz/SiO<sub>2</sub> crucible coated with a standard Si<sub>3</sub>N<sub>4</sub> powder leads to a clear impact of the “red zone” on solar cells. This effect decreases over the block height. A thick very highly purified coating powder seems to considerably reduce the in-diffusion of the impurities from this standard crucible. Using a purified industrial crucible with a coating powder of very high purity results in a notable reduction of the “red zone” effect on solar cell level. Moreover, the use of a purified crucible shows no effect of the “red zone” on solar cell until to a distance of ~12 mm from the crucible wall. This is probably due to the reduction of metallic contamination from the crucible during crystallization as shown by Schubert et al. [5]. It is shown that the main source of impurities for contamination of the “red zone” is the crucible whereas the coating has solely an insignificant contribution. Efficiencies of up to 19.0% were achieved on 2 x 2 cm<sup>2</sup> solar cells using mc-Si material from a block crystallized with the highly purified crucible and coating. For the standard crucible, efficiencies of up to 18.9% were realised.

**Keywords:** multicrystalline silicon, crucible, coating, “red zone”

### 1 INTRODUCTION

In recent years, the industrial processing of multicrystalline (mc) silicon solar cells was greatly improved and efficiencies up to 19.5% were achieved [1]. An improvement of the material quality would most probably lead to further significant increase of the efficiency of mc-Si solar cells. The metallic impurities in directionally solidified mc silicon originate either from the feedstock, or the crucible and its coating. Since the quality of the feedstock can be adjusted to the needs for industry/PV applications, the crucible and its coating remain the largest source of metallic impurities. These impurities diffuse into the silicon melt and after crystallization into the ingot via solid-state diffusion at high temperatures. This leads to a zone in the vicinity of the crucible with very poor material quality, the so called “red zone”. Therefore, the main goal of this work is the investigation of the influence of the crucible and its coating on material quality of mc-Si and on the resulting solar cells. It is focused on the impact of the “red zone” on solar cells.

As material quality changes during solar cell processing (gettering, hydrogenation, activation of defects or dislocations), the influence of the crucible materials and the coating powders on efficiency potential has to be evaluated on solar cell level. For this purpose, 2 x 2 cm<sup>2</sup> lab-type solar cells are fabricated on mc-Si material crystallized using different crucible materials and different coating powders. The resulting solar cells are hence characterized via IV measurement and spatially resolved LBIC (Light Beam Induced Current) measurement.

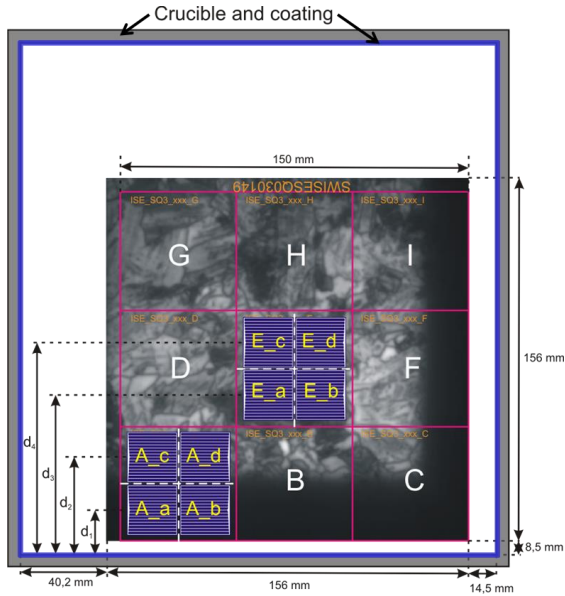
### 2 EXPERIMENT

#### 2.1 Investigated material

For the investigation, five mc-Si blocks were crystallized in a small G1 format using three different crucible materials (SQ, SP, and HP) and two Si<sub>3</sub>N<sub>4</sub>

coating powders (SC and HC). SQ is a standard industrial quartz/SiO<sub>2</sub> crucible. SP is another industrial crucible with a higher purity degree and HP is a high purity quartz crucible. SC is a standard industrial Si<sub>3</sub>N<sub>4</sub> coating powder and HC is a purified coating powder. These abbreviations are used in the following for identification of the blocks (e.g. “SQ + SC” for standard crucible with standard coating). The blocks are of G1 format (~22 x 22 x 12.8 cm<sup>3</sup>) and the same initial very pure silicon feedstock was used for all blocks, in order to separate the influence of metallic contamination in the feedstock from the impact of the crucible and coating. Moreover, crystallization parameters like time, gas flow, and temperature profile were kept constant, as far as possible, for all crystallizations.

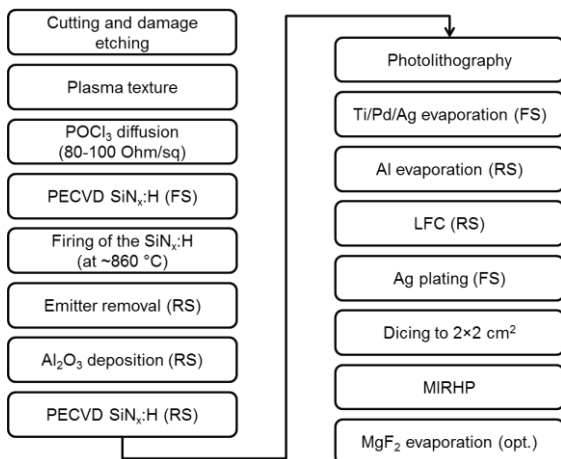
Fig. 1 shows the photoluminescence image of a six inch wafer from a block crystallized in a G1 crystallisation crucible. The ingot (15.6 x 15.6 cm<sup>2</sup> size) was cut asymmetrically from the block as depicted in Fig. 1. The crucible and the coating are colored grey and blue, respectively. Nine 5 x 5 cm<sup>2</sup> wafers were cut from each six inch wafer via laser. To investigate the influence of the crucible and also to evaluate the potential of the material, two columns of 5 x 5 cm<sup>2</sup> wafers were selected for the experiment. The column named A is at the edge of the ingot near the crucible wall, and column E is in the center region far from the crucible. From each 5 x 5 cm<sup>2</sup> wafer, four solar cells of 2 x 2 cm<sup>2</sup> (cell A\_a, A\_b, A\_c and A\_d from the wafer of column A and the cells E\_a, E\_b, E\_c and E\_d from the wafer of column E) were produced as shown in Fig. 1. The distances d<sub>i</sub> (i = 1, 2, 3, 4) are the distances from the center of each solar cell to the inner crucible wall (see Fig. 1). For the experiment, four sister wafers were chosen from three different block heights (bottom, middle and top) for each column (A and E).



**Figure 1:** Position of the selected wafers under investigation and the resulting solar cells (top view). Four  $2 \times 2 \text{ cm}^2$  solar cells are produced from each  $5 \times 5 \text{ cm}^2$  wafer.

## 2.2 Solar cell process

To evaluate the efficiency potential of the investigated materials, a photolithography-based laboratory cell process as depicted in Fig. 2 is used. A detailed description of this process is presented in [2]. This cell process is particularly well-suited for defect-rich mc-Si material, due to its low thermal budget, the applied plasma texture and the excellent hydrogenation of bulk defects [2]. The rear side passivation is realized by a  $\text{Al}_2\text{O}_3/\text{SiN}_x\text{:H}$  stack. Local contact formation between evaporated Al layer ( $\sim 2 \mu\text{m}$ ) on the rear and Si was carried out using the Laser Fired Contact (LFC) process [3].



**Figure 2:** Photolithography-based solar cell process flow as shown in [2]. The last processing step, the thermal evaporation of a second layer anti-reflection coating (ARC) of  $\text{MgF}_2$  on the front side, is optional and was not applied to all cells.

After thickening the front contacts using light induced Ag plating, four  $2 \times 2 \text{ cm}^2$  solar cells are cut out from each

$5 \times 5 \text{ cm}^2$  wafer with a dicing saw. This leads to solar cells having open pn-junctions on the edge like for most industrial processes. The following MIRHP (Microwave Induced Remote Hydrogen Plasma) step provides enhancement of hydrogen passivation, improvement of rear surface passivation and sintering of the contacts [2].

## 3 RESULTS

### 3.1 Influence of coating quality

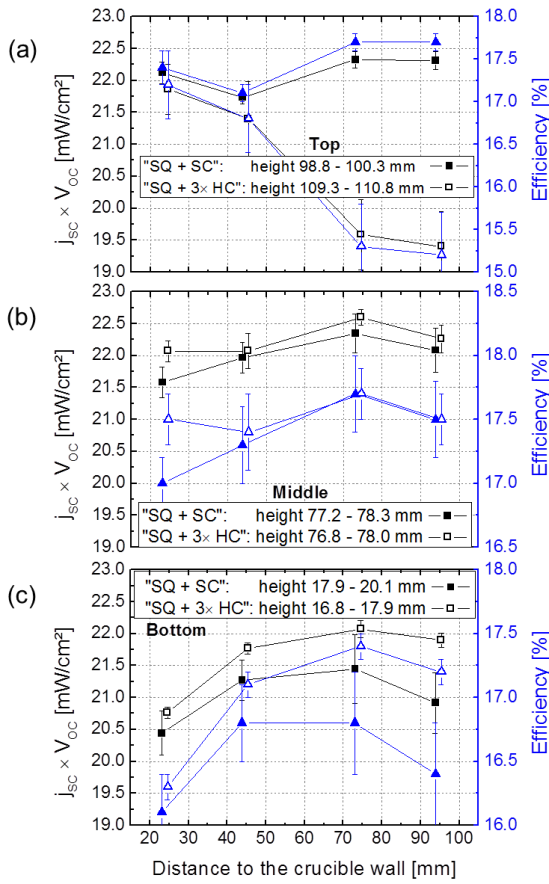
#### IV parameters

In Fig. 3, the pseudo power  $j_{\text{SC}} \times V_{\text{OC}}$  (black squares) and the efficiency  $\eta$  (blue triangles) are depicted as function of the distance to the crucible wall for the blocks “SQ + SC” and “SQ + 3× HC” for the three block heights (bottom, middle and top). For block “SQ + 3× HC”, the standard crucible “SQ” was coated three times with high purity  $\text{Si}_3\text{N}_4$  powder “HC”. All these IV data refer to solar cells with a single anti-reflection coating layer of  $\text{SiN}_x\text{:H}$ . As can be seen in Fig. 3,  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  show the same trend. In the bottom region (see Fig. 3 (c)),  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  increase from the edge towards the center of the ingot for both blocks indicating a possible effect of the crucible and its coating on solar cells. Furthermore, the values of  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  for the block “SQ + 3× HC” are higher than those for the block “SQ + SC”.

In the middle block height (see Fig. 3 (b)), the same trend for the block “SQ + SC” (closed symbols) is observed. However, the slope is less than in the bottom region. This indicates a decreasing influence of the crucible and its coating with increasing block height, as can also be seen in Fig. 4 (a) and in Fig. 4 (c). For the block “SQ + 3× HC” (see open symbols in Fig. 3 (b)),  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  do not show a large variation depending on the distance to the crucible wall. This indicates the absence of the “red zone” in the middle ingot height in contrast to the bottom height which emphasizes the decreasing impact of the crucible and its coating with increasing ingot height. In the edge region  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  are higher for “SQ + 3× HC” than for “SQ + SC”, but towards the center region, these two parameters are on the same level for both ingots.

In the top region (see Fig. 3 (a)),  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  drop firstly and then slightly increase from the edge to the center of the ingot for “SQ + SC”. This means that the influence of the “red zone” is very low or almost not present. For the block “SQ + 3× HC”,  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  strongly decrease from the edge to the center region. This is presumably due to the high concentration of segregated transition metals in the top region [4]. It is important to mention that the solar cells of block “SQ + 3× HC” are from wafers which are from an ingot height of about 10 mm higher than wafers of block “SQ + SC” (see legend in Fig. 3 (a)), and consequently have more segregated metallic impurities. Both blocks are therefore not directly comparable in the top region.

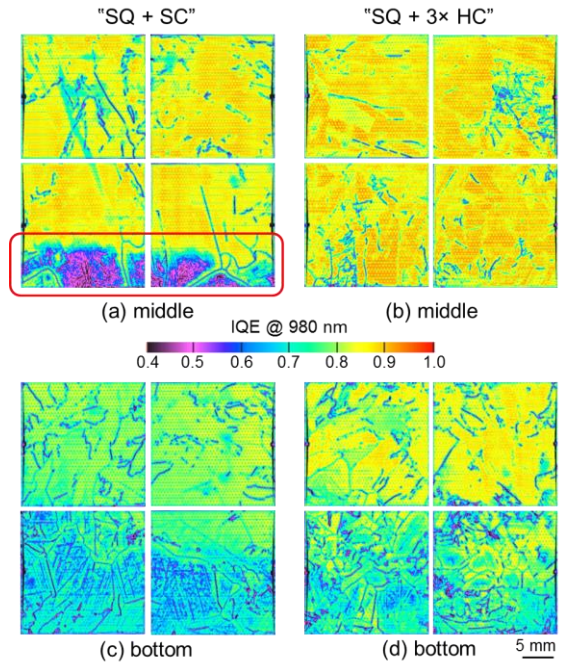
For block “SQ + SC”, values of  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  are on the same level in the middle and top region whereas their values are lower in bottom ingot height. Block “SQ + 3× HC” exhibits highest  $j_{\text{SC}} \times V_{\text{OC}}$  and  $\eta$  values in the middle ingot height, compared with the other two heights.



**Figure 3:** Pseudo power  $j_{sc} \times V_{oc}$  (black squares) and efficiency (blue triangles) depending on the distance to the crucible wall for the two blocks “SQ + SC” and “SQ + 3× HC”. In (a) the top, in (b) the middle and in (c) the bottom block height is shown. Values were averaged from 4-8 cells and standard deviations are given. All data with single ARC, lines are guides to the eye.

**LBIC measurements**

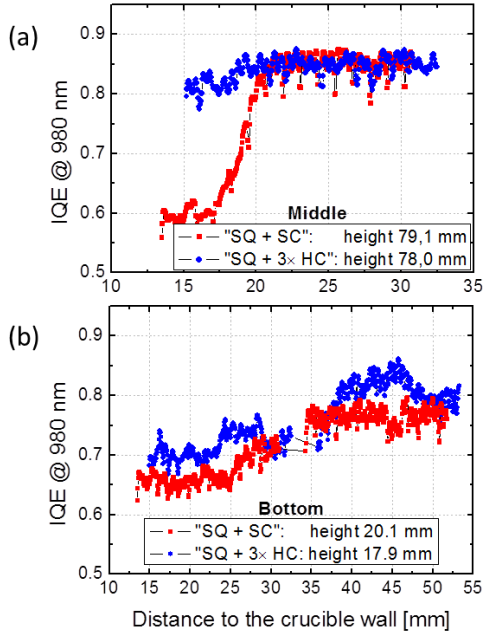
Fig. 4 shows IQE (Internal Quantum Efficiency) topograms of the four solar cells A<sub>a</sub>, A<sub>b</sub>, A<sub>c</sub> and A<sub>d</sub> (compare Fig. 1) close to the crucible wall from the bottom (Fig. 4 (c) and (d)) and the middle block height (Fig. 4 (a) and (b)). The two lower cells of each group are close to the crucible wall. A clear influence of the crucible and coating is observed for the cells of the block “SQ + SC” crystallized in a standard industrial crucible using the standard industrial coating powder. The solar cells of the block “SQ + 3× HC” show a possible presence of the “red zone” only in the bottom region (see Fig. 4 (d)). In the middle block height, there is no clear influence of the crucible and its coating (see Fig. 4 (b)). Furthermore, it can be seen, also from the IV parameters of both blocks, that the size of the “red zone” decreases with block height.



**Figure 4:** IQE topograms at 980 nm wavelength (with 50  $\mu\text{m}$  spatial resolution) of the four solar cells A<sub>a</sub>, A<sub>b</sub>, A<sub>c</sub> and A<sub>d</sub> near the crucible wall (see Fig. 1). The lower part of the cell is close to the crucible wall. *Left column:* cells of the block “SQ + SC” near the bottom region (c) and in the middle block height (a). *Right column:* cells of the block “SQ + 3× HC” in bottom (d) and in middle region (b).

Linescans of IQE maps from Fig. 4 as a function of distance to the crucible wall show the clear influence of the crucible for cells of block “SQ + SC” in bottom and middle height (see red squares in Fig. 5). This block shows a “red zone” of more than 50 mm in the bottom and of ~20 mm in the middle height. In the middle height of the block “SQ + 3× HC”, IQE values are almost at the same level over the two solar cells A<sub>a</sub> and A<sub>b</sub> close to the crucible wall, indicating an absence of the “red zone”. In bottom ingot height, the “red zone” is observed with a width of ~40 mm. To detect the presence of a “red zone”, we consider that all regions near the crucible wall with average IQE values (at 980 nm wavelength) less than 0.8 are affected by the influence of the “red zone”.

In the bottom region (see Fig. 5 (b)), it can also be seen that IQE values for “SQ + 3× HC” are higher than for “SQ + SC”. This indicates that although the width of the “red zone” of both blocks is nearly equal in the as-grown state ( $\mu\text{PCD}$  mapping of the blocks in the as-grown state are not shown here), the solar cell process can almost completely remove the deteriorated “red zone” for block “SQ + 3× HC”. The multiple coating of the crucible with a highly purified powder seems to considerably reduce in-diffusion of metallic impurities from the crucible into the silicon melt and the solidified silicon during crystallization.



**Figure 5:** Lineplots of IQE maps from Fig. 4 as a function of distance to the crucible wall. Depicted in (a) are the averages of linescans across the two solar cells A\_a and A\_b of the middle block height. (b) shows the averages of linescans across the two adjacent solar cells A\_a and A\_b or A\_c and A\_d with the same distance to the crucible in the bottom ingot height.

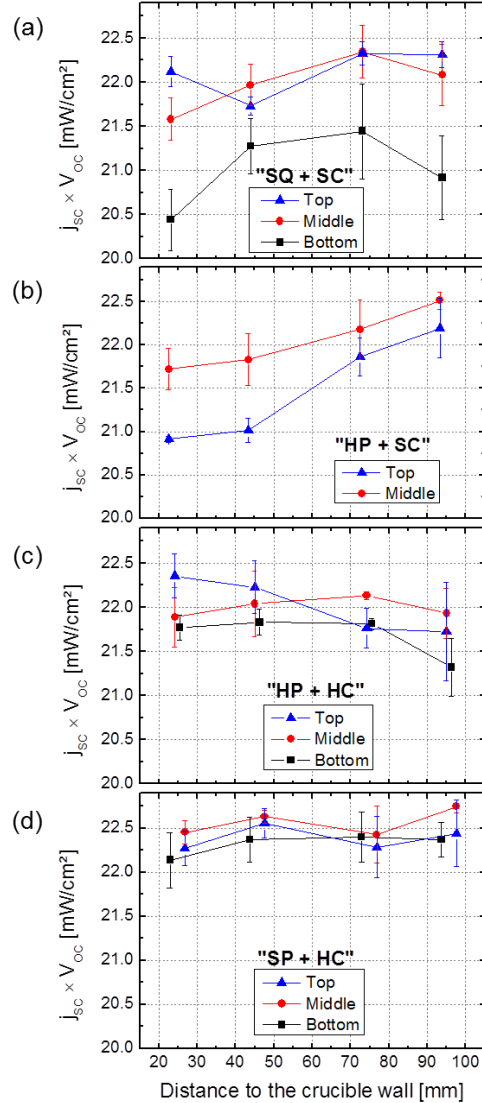
### 3.2 Effect of the crucible

#### IV parameters

To minimize the influence of a process induced variation of the fill factor, the pseudo power  $j_{sc} \times V_{oc}$  was chosen to compare all blocks. All IV data shown here refer to solar cells with a single anti-reflection coating layer of  $SiN_x:H$ . As can be seen from Fig. 6, the pseudo power  $j_{sc} \times V_{oc}$  increases from the edge towards the center of the ingot for blocks “SQ + SC” and “HP + SC”. Moreover, this behaviour seems to decrease with increasing ingot height for “SQ + SC”, indicating an influence of the crucible wall as extensively described above. For the block “HP + SC”,  $j_{sc} \times V_{oc}$  is higher in the middle than in the top region.

For block “HP + HC” (see Fig. 6 (c)),  $j_{sc} \times V_{oc}$  drops towards the ingot center for bottom and top block height. For middle block height, it is almost constant from edge to center of the ingot. This demonstrates that crucible and coating do not influence solar cell performance in areas close to the crucible wall more significantly than in areas in the centre of this block.

As can be seen in Fig. 6 (d), block “SP + HC” shows a slight increase of  $j_{sc} \times V_{oc}$  in the bottom region towards the ingot center. This is an indication of a possible existence of the “red zone” for this block height. The middle and top regions of this block do not show a large variation of  $j_{sc} \times V_{oc}$  depending on the distance to the crucible wall. For this block,  $j_{sc} \times V_{oc}$  values of all three ingot heights are approximately on the same level while they are higher than those of the other blocks.



**Figure 6:** Pseudo power  $j_{sc} \times V_{oc}$  as function of the distance to the crucible wall for three block heights. Values are averaged from 4-8 cells and standard deviations are given. For “HP + SC” no data for the bottom block height is available.

#### LBIC measurements

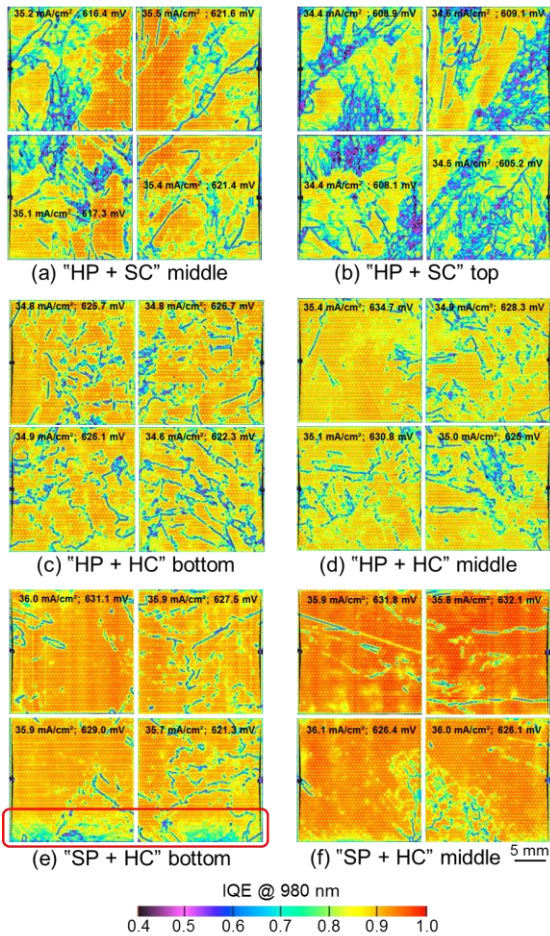
As can be seen in Fig. 7 (a) and (b), the strong increase of  $j_{sc} \times V_{oc}$  from the edge towards the center of the ingot for block “HP + SC” is not a clear and direct effect of the crucible and coating alone. Also the presence of many decorated grain boundaries and defect clusters distributed over the cells in the edge region has to be taken into account. Furthermore, there is a direct correlation between density of decorated grain boundaries and defect clusters with short circuit current density  $j_{sc}$  and also open circuit voltage  $V_{oc}$ .

Block “HP + HC” does not show a significant influence of the crucible wall. Solar cells from the edge region of this block show many decorated grain-boundaries randomly distributed over the cells, particularly in the bottom region.

IQE maps of the block “SP + HC” in the bottom region (see Fig. 7 (e)) indicate a slight effect of the “red

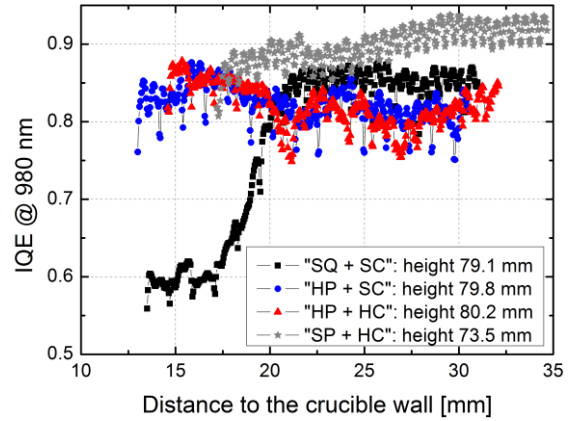
zone” (red framed area). However, solar cells from this block show relatively homogeneous regions with little decorated grain-boundaries and consequently have comparatively higher IQE values (see Fig. 8).

For the high purity quartz crucible (“HP”), the influence of the crucible and the coating seems to be independent of the coating quality (compare IQE maps of the blocks “HP + SC” and “HP + HC”). This is also visible in Fig. 8. Average IQE values for block “HP + SC” (blue dots) are on the same level as those for block “HP + HC” (red triangles). This indicates that the main source of impurities in the “red zone” is the crucible.



**Figure 7:** IQE topograms at 980 nm wavelength (with 50  $\mu\text{m}$  spatial resolution) of four solar cells A\_a, A\_b, A\_c and A\_d close the crucible wall (see Fig. 1) from different block heights. The lower part of the cell is close to the crucible wall.

Linescans of the IQE maps from Fig. 7 and Fig. 4 (a) as a function of distance to the crucible wall show the clear influence of the crucible for cells of block “SQ + SC” (see Fig. 8). This block shows a “red zone” of  $\sim 20$  mm in the middle height.



**Figure 8:** Linescans of IQE maps from Fig. 7 and Fig. 4 (a) as a function of distance to the crucible wall. Shown are averages of linescans across the two solar cells A\_a and A\_b of the middle block height.

#### 4 CONCLUSION

The use of a standard industrial crucible coated with standard powder (“SQ + SC”) during growth of mc-Si leads to a clear impact of the “red zone” on solar cell performance. This effect decreases with increasing ingot height. The coating of the standard crucible with a thick highly purified coating powder (block “SQ + 3 $\times$  HC”) shows a notable positive effect on the “red zone” on cell level. It seems to considerably reduce in-diffusion of metallic impurities from the crucible. Although the two blocks “SQ + SC” and “SQ + 3 $\times$  HC” have nearly the same thickness of the “red zone” in the as-grown state, the “red zone” was completely removed in the middle height of the “SQ + 3 $\times$  HC” block during solar cell processing.

Using a purified industrial crucible with a coating powder of very high purity (“SP + HC”) results in a considerable reduction of the effect of the “red zone” on solar cell level. Moreover, the use of a highly purified crucible (“HP”) shows no negative effect of the “red zone” on solar cell level up to a distance of  $\sim 12$  mm from the crucible wall. This is most probably due to the reduction of metallic contamination from the crucible during crystallization as shown by Schubert et al. [5]. No significant effect of the coating powder on the “red zone” for the blocks crystallized in the highly pure crucible was observed (compare Fig. 8: IQE values of “HP + SC” and “HP + HC”). However, for the standard crucible a thick high purity coating powder reduces notably the in-diffusion of the impurities. This means that the main source of contamination, resulting in the “red zone”, is the crucible. The coating has only a minor effect.

Using mc-Si material from a block crystallized with the highly purified crucible, efficiencies of up to 19.0% were achieved on 2 x 2  $\text{cm}^2$  solar cells after deposition of a second anti-reflection layer of  $\text{MgF}_2$ . For the standard crucible, efficiencies of up to 18.9% were obtained.

#### 5 ACKNOWLEDGEMENTS

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