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Recycling of p-type mc-Si top cuts into p-type mono c-Si solar cells

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Abstract

Solar cell results and material analysis are presented of 2 p-type Czochralski (Cz) ingots pulled from a charge consisting of 100% and 50% recycled multicrystalline silicon top cuts. The top cuts were pre-cleaned with a dedicated low energy consuming technology. No structure loss was observed in the bodies of the ingots. The performance of solar cells made from the 100% recycled Si ingot decreases towards the seed end of the ingot, which could be related to a non-optimal pulling process. Solar cells from the tail end of this ingot and from the 50% recycled Si ingot demonstrated an average solar cell efficiency of 18.6%. This is only 0.1% absolute lower than the efficiency of higher resistivity reference solar cells from commercially available wafers that were co-processed.

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1. Introduction

The availability of cheap, good quality solar grade silicon is one of the major cost factors in the production of solar cells. One of the most straightforward methods to reduce the costs and the energy payback time of solar cells is to recycle silicon scrap from the ingot and wafer production, such as the top, bottom and side parts that are usually cut off before the ingot is processed into wafers.

On average, 25% of the silicon in a mc-Si ingot is cut off in industry at the cropping step, where the sides, tops and bottoms are removed and the remaining bricks are sawn into wafers. The side cuts (about 18% of the silicon) are relatively clean and can be easily recycled back into the production process. The top and bottom cuts, about 7% of the total amount of silicon in a multicrystalline ingot, are normally considered to be too contaminated for recycling and are wasted. The company SiPro in Norway is specialized in recycling silicon off-cuts to feedstock for wafer producers. In the RESIM project [1] a low

energy consuming cleaning procedure, developed by SiPro, was tested to remove particles and surface contamination from the normally wasted multicrystalline silicon top cuts. Subsequently, these cleaned top-cuts were used as charge for a Czochralski ingot pulling process.

During the multicrystalline casting process, impurities are pushed to the top of the ingot by segregation. Due to high concentrations caused by segregation, at the end of the solidification process large SiC and SiN_x particles can form precipitates that are included in the top-cuts [2]. These precipitates do not dissolve during melting of the silicon charge and would be incorporated in a mc-Si ingot when recycled. Therefore, the top-cuts are usually wasted. A Czochralski mono c-Si process, however, has an advantage over a mc-Si casting process in recycling of top cuts. If the convection in the melt is kept low, the precipitates may sink to the bottom of the crucible, where they will remain while the monocrystal is pulled from the surface of the melt. A major fraction of the other impurities will segregate to the tail of the ingot, which is cut off, or remain in the pot-scrap.

Even though pulling of a Czochralski ingot is an energy intensive process, since the energy for refining of the silicon in the top-cuts was already invested at the step where the mc-Si ingot was grown, the embedded energy of the ingot charge is reduced by at least 50% when silicon is recycled in a direct route with a charge of 100% recycled top-cuts. In this work, the viability of this direct route is tested.

2. Experimental details

Randomly selected boron doped multicrystalline top-cuts from REC Solar were used as input material for this experiment. The top-cuts were cleaned by targeted removal of bad areas and a water based surface cleaning method developed by SiPro. After cleaning, the top cuts were stacked as piles of plates in the bottom of the crucible and the gaps in between the plates were filled with broken pieces. Two 200 mm diameter ingots were pulled in this manner: one from a charge consisting of 100% recycled silicon top-cuts (RESIM1) and one (RESIM2) from a charge consisting of 50% recycled top-cuts and 50% Elkem Solar Silicon[®] (ESS[™]). No structure loss was observed along the body of both ingots and therefore 156 × 156 mm² semi-square wafers were cut and processed into solar cells.

The resistivity profiles throughout the ingots were determined using the Sinton WCT120 PCD set-up. Interstitial oxygen and substitutional carbon concentrations were determined by a Perkin Elmer FTIR on polished 2 mm thick slugs cut from different positions on the ingot (for RESIM1) or on the wafers itself (RESIM2).

To process the wafers into solar cells, on all wafers a random pyramid texture was formed by an alkaline etch. A phosphorus 82 Ohm/□ emitter was formed by P-diffusion, with POCl₃ as precursor gas. After removing the PSG, the front side was coated with a 80 nm thick SiN_x anti-reflection and passivation coating. All cells were contacted by a screenprinted Ag grid at the front and had a screenprinted full area Al rear side. Seven commercially available p-type Cz wafers were co-processed in the same run as the RESIM wafers. These wafers were of industrial grade and should lead to >18.5% solar cells with the used solar cell process. The reference wafers were square and the RESIM wafers were semi-square, therefore different metallization screens had to be used, which might have caused minor FF differences.

The I-V parameters of the cells were determined by using a Wacom dual beam class AAA solar simulator according to IEC60904. The electroluminescence (EL) images were made with a wide range VIS-IR camera focused on the cell surface.

3. Results and discussion

3.1. Wafer analysis

In Fig. 1 the substitutional carbon concentration and the interstitial oxygen concentration, as measured by FTIR, are given against the position in the ingot. There is some discrepancy between the carbon concentration trends found on slugs of RESIM1 at different labs, but a slightly increasing trend towards the tail of the ingot is clear for both ingots, which is most likely due to the carbon rich top cuts in the charge. The carbon segregates towards the tail during ingot growth. For the RESIM2 ingots, the carbon concentration remains below 4 ppma, far below saturation of the melt, so no nucleation of SiC precipitates, causing structure loss, sawing wire breakage or lowered reverse breakdown voltage, is expected in this ingot and in a large part of the RESIM1 ingot.

The oxygen level is high in the top of both ingots and decreases towards the tail, which is a normal trend in Cz ingots, because the melt becomes less oxygen rich as the contact area between the melt and the crucible decreases. However, at least for RESIM1, the crucible rotation speed was kept higher than standard. This resulted in oxygen levels far above the commonly accepted specs level of ≥ 20 ppma, at least up to $\sim 60\%$ of the ingot length. In the RESIM2 ingot, the oxygen decrease is more steep and reaches values ≤ 20 ppma already at 20% ingot length, so close to the outer end of the wafered body of the ingot.

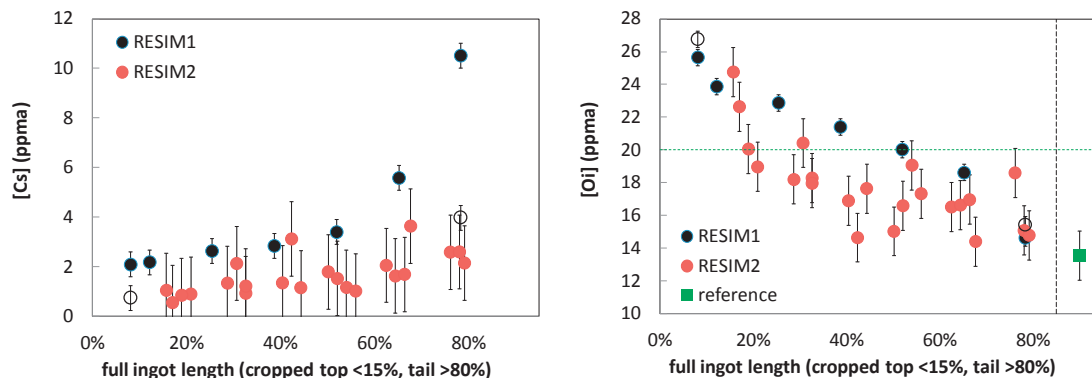


Fig. 1. Substitutional carbon (left) and interstitial oxygen (right) measurements for the two RESIM ingots as determined by FTIR. The ingot was cropped before wafering, i.e. the parts of the ingot below 15% ingot length and above 80% ingot length, the seed and shoulders and the pointy tail, were cut off. The values for RESIM1 were measured at different labs (open/closed symbols) on 2 mm thick slugs. The values for the RESIM2 ingot were measured on wafers. The green dashed line in the [O_i] graph indicates the maximum of 20 ppma that is included in common specs. [C_s] is normally zero in Cz wafers, but here it is increased by the carbon in the top-cuts.

The resistivity of the RESIM ingots is relatively low ($< 1.5 \Omega \text{ cm}$) compared to the reference ($\sim 2.7 \Omega \text{ cm}$). In commercial p-type Cz ingots, the target base resistivity is usually $> 2 \Omega \text{ cm}$. Although a lower base resistivity in theory leads to higher V_{OC} values, this effect is compensated by the combination of a high B and O level in low resistivity wafers which causes the formation of the recombination active B-O complex. The expected effect will therefore be a net decrease of the $J_{SC} \times V_{OC}$ product. The very flat resistivity trend in the RESIM2 ingot is most likely related to the level of compensation in the ESSTM. The resistivity trend in ingots from compensated material increases towards the end of the top, because phosphorus segregates faster than boron. When boron rich feedstock is added, this trend is flattened.

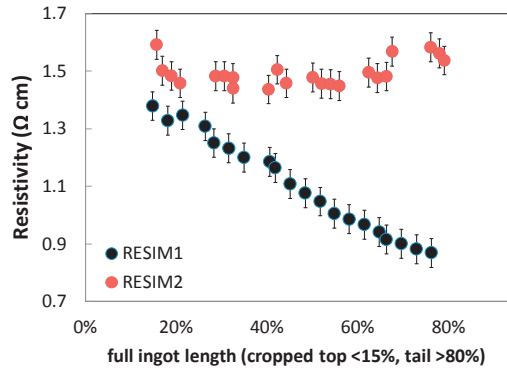


Fig. 2. Resistivity of the RESIM1 and RESIM2 wafers as measured with the Sinton WCT-120 tool. The resistivity of the reference wafers varied, because they were not stored in order (though from the same ingot). On average the resistivity of the reference wafers was $2.7 \pm 0.5 \Omega \text{ cm}$. This value is not indicated in the graph.

3.2. Solar cells

Fig. 3 shows the initial solar cell efficiency trend for the wafers from the two RESIM ingots. The reference solar cells have an average conversion efficiency of 18.73%, with a maximum of 18.76%. The initial efficiency of the cells from the RESIM2 ingot is less than 0.2% below the reference, with an average efficiency of 18.60% and a maximum of 18.72%. Above 60% ingot length, the RESIM1 ingot, made of 100% top-cuts, performs as good as RESIM2, but towards the seed end a steep decrease in solar cell efficiency is observed. The $J_{\text{SC}} \times V_{\text{OC}}$ plot confirms that the recombination level is somewhat increased compared to the reference cell, also in the best parts of the ingot.

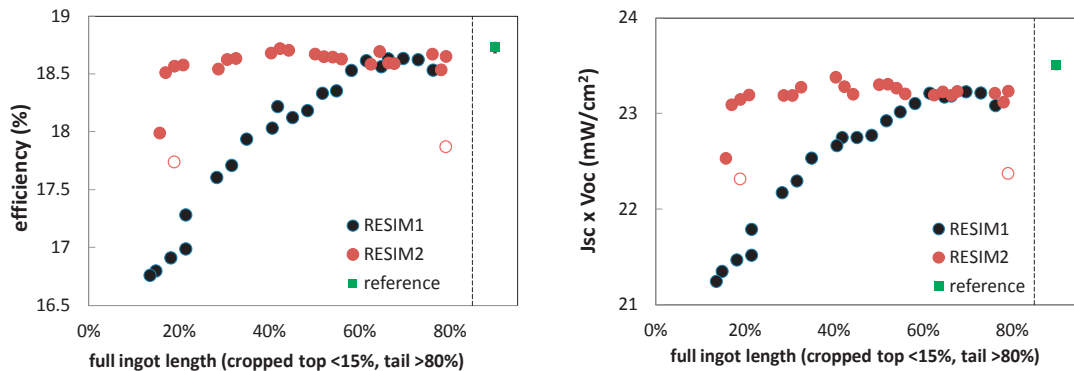


Fig. 3. Conversion efficiencies (left) and $J_{\text{SC}} \times V_{\text{OC}}$ product (right) of the solar cells made from the RESIM1 and RESIM2 ingots. The open symbols indicate the values for two of the RESIM2 cells after 300 minutes of LID for one cell with high oxygen level.

The open symbols in Fig. 3 indicate the efficiency and $J_{SC} \times V_{OC}$ of two cells after 300 minutes of light soaking at 1 sun. The efficiency decreases by $\sim 0.8\%$ absolute both at the seed and the tail end, which points out that the boron concentration should be strongly reduced to include cells from such ingots into a solar module. This could be achieved by blending the charge with some dopant free polysilicon feedstock.

The difference in $J_{SC} \times V_{OC}$ is slightly compensated by a positive difference of about 0.5% in FF between the RESIM ingots and the reference cells (Fig. 4). A possible reason for this difference is the use of different print screens for the square reference wafers and the semi-square RESIM wafers. Simple PC1D simulations of the cells with high and low resistivity, taking into account the approximate difference in lifetime due to the B-O complex formation, indicated that the difference in FF cannot be explained by the difference in resistivity only. Furthermore, the increased recombination in the RESIM1 ingot can also be observed in the FF, most likely due to the subtle effect of the increased recombination on the diode ideality [3].

The reverse current at -10V (right image in Fig. 4) is slightly increased in the RESIM ingots to a still acceptable value of $0.4 \pm 0.25A$ (except for one outlier), but no correlation (based on linear regression analysis) between the reverse current and the ingot position can be observed. A minor increase in reverse current of this magnitude is to be expected considering the low base resistivity of the wafers [4]. There is no indication that the reverse current is increased due to the presence of SiC precipitates or other impurities.

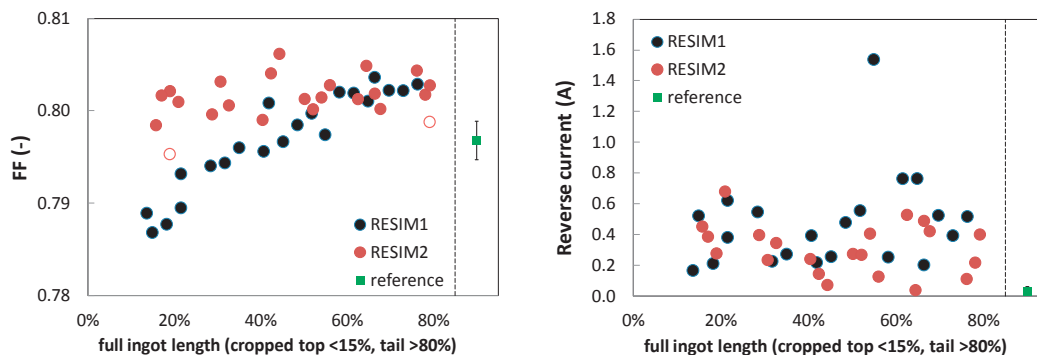


Fig. 4. Fill factor (left) and reverse current at -10V for the solar cells made from the RESIM1 and RESIM2 ingots.

In the left image of Fig. 5 an electroluminescence image is shown of the solar cell from 15% ingot length in the RESIM1 ingot. Similar images could be made for the other solar cells from the RESIM1 ingot below 60% ingot length. The occurrence of these patterns coincides with the region of the ingot at the seed end, where a steep decrease in solar cell efficiency was observed. Moreover, the intensity of the pattern, in particular that of the dark spot in the center, increases towards the seed end. The occurrence of such ring (striation) patterns is commonly attributed to a combination of instable ingot growth and a high oxygen concentration [5], which causes the formation of detrimental oxygen particles within the material. In the right image of Fig. 5 it is indeed demonstrated that there seems to be a strong correlation between the performance of the solar cells and the oxygen concentration in the ingot. Where the oxygen concentration exceeds the specs of 20 ppma, the solar cell efficiency is reduced. Additionally, Zhang et al. [6] demonstrated the presence of oxygen related defects close to the seed end of this ingot by applying a copper decoration etch on slug samples. Altogether, we can conclude that the decrease in cell efficiency towards the seed end of the RESIM1 ingot, was not related to the composition of the crucible charge that was used, but to pulling process related effects. In the RESIM2 ingot no ring patterns were observed.

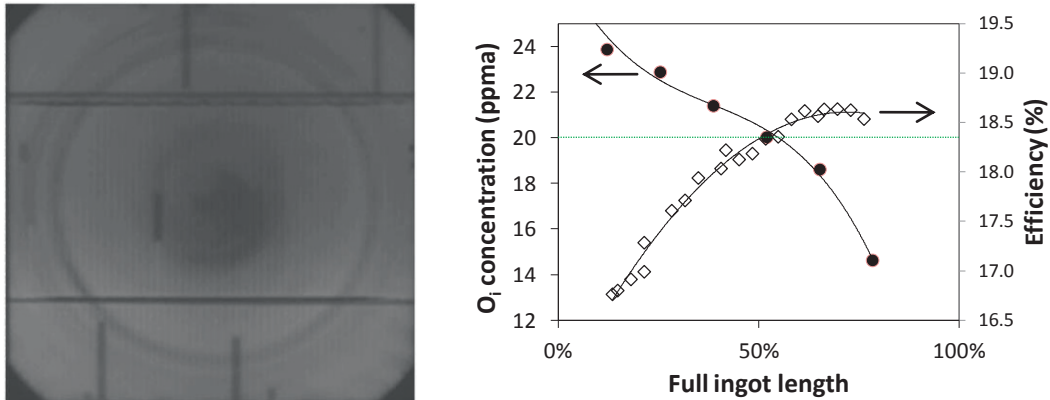


Fig. 5. (left) Ring pattern observed in an electroluminescence image of a solar cell from 15% full ingot length. (right) Efficiency and oxygen concentration in the RESIM1 ingot. The green line is the oxygen level of 20 ppma from common wafer specs.

4. Conclusions

The use of cleaned multicrystalline silicon top-cuts as (part of) the crucible charge for pulling of a p-type Czochralski silicon ingot leads to only a minor initial efficiency loss of less than 0.2% absolute on solar cell level. This was observed for wafers from 2 ingots: one pulled from a charge of 100% recycled top-cuts (good cells only at the tail end) and one made from a 50/50 blend of Elkem Solar Silicon® and recycled top cuts. In solar cells from the first ingot (100% top cuts), a decay of the efficiency was observed towards the seed end, which could be attributed to a non-optimal pulling process. Due to the high boron concentration in the charge and/or high oxygen incorporation during ingot manufacturing, a large decrease of 0.8% abs. in efficiency was observed after light soaking. For industrial application of this approach, the boron concentration should be lowered, e.g. by blending with undoped silicon.

Acknowledgements

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