IMPACT OF IRON, NICKEL AND CHROMIUM IN FEEDSTOCK ON MULTICRYSTALLINE SILICON SOLAR CELL PROPERTIES

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ABSTRACT: The effect of metal contamination in multicrystalline silicon ingots on solar cell performance is investigated. Metal impurities have been added to the silicon feedstock and the solar cell performance has been compared to a reference uncontaminated ingot. A larger crystal defect density is observed in the top and in the bottom of the contaminated ingots with respect to the reference. Adding 50 ppmw of iron or 40 ppmw of nickel or chromium to the silicon feedstock in p-type ingots, the solar cell performances are comparable to the reference in the range of 40 to 70% ingot height. Addition of Fe, Ni or Cr does not only have a direct impact on the diffusion length, but also on the crystal growth and shunting behaviour.

Keywords: metal impurities, feedstock, multicrystalline, Fe, Ni, Cr

1 INTRODUCTION

Understanding the role of impurities on the solar cell efficiency is a key issue for the definition of solar-grade silicon. We present results achieved within the CrystalClear Integrated Project and Foxy project, cofinanced by the EU commission, that enlighten the impact of contamination by metal impurities on the solar cell performance. The relevance of this work is in the method to intentionally contaminate in a controlled way prime quality polysilicon before crystallisation. The impact of impurities is analysed in multicrystalline directionally solidified ingots, along the entire process chain from feedstock to solar cells. In this way the added impurities undergo all high temperature steps, including gettering and bulk passivation.

2 EXPERIMENT

Several pilot scale 12 kg multicrystalline silicon ingots were grown in a Crystalox DS 250 furnace [1] that was designed to solidify mc-Si ingots using a Bridgman type directional solidification method. For these experiments, the used polysilicon feedstock was intentionally contaminated by a predetermined amount of the element under investigation. Prime quality polysilicon, high purity crucibles (with a spherical bottom) and purified Si3N4 lining were used, to keep unintentional contamination as low as possible. The amounts of dopants and impurities that were introduced in the feedstock charge are given in table 1.

Also, an additional ingot was grown using the same materials and crystallization parameters but without intentional contamination, which was used as a baseline reference for the entire manufacturing chain, from crystallisation to solar cell manufacturing. A full description of the crystallisation and solar cell process and characterisation can be found in refs.1 and 2.

From each ingot a centre block of 125×125 mm2 was cut and sliced into 200-240 μ m thick wafers, of which 20 representative wafers were processed into solar cells using a state of the art industrial P diffusion, full aluminium Back Surface Field and SiNx:H firing through, to determine the effect of impurity level on cell characteristics [2].

Besides solar cell processing, also as-grown wafers and wafers that were taken out after selected cell processing steps, were characterised by lifetime measurements (QSS-PC) to relate the intended impurity levels to electronic properties. In the following, the ingots contaminated with Fe (Ni or Cr) will be referred to as [impurity] [impurity concentration in ppmw], for example Fe 50 will be the name of the ingot contaminated with 50 ppmw of Fe.

| Label | resistivity (Ω×cm) | contamination (ppm |
|-------|--------------------|--------------------|
| | p-type | wt) |
| Ref | 0.9-1.1 | Reference |
| Fe 50 | 0.9-1.1 | 53.0 |
| Ni 40 | 0.9-1.2 | 40.4 |
| Cr 40 | 1.0-1.2 | 36.7 |

Table 1: impurity concentrations

3 RESULTS AND DISCUSSION

In figure 1, the efficiencies of the cells produced from wafers of the contaminated ingots are given as a function of ingot height. For all three ingots, produced from feedstock with 50 ppmw of Fe or 40 ppmw of Ni or Cr, the solar cell performances are comparable to the reference cells in the range of 40-70% ingot height (Fig.1). Roughly, the efficiency results of the test ingots can be divided into 3 regions: a bottom region up to 40% where the efficiency is lowered, a middle region from about 40 to 70% where the performance is comparable to the reference, and a top region above 70% ingot height where again the efficiency decreases towards the top. In the rest of this extended abstract, possible explanations for this decrease in efficiency in the bottom and top regions of the three contaminated ingots are discussed.



Figure 1: Conversion efficiency as a function of ingot height for all three contaminated ingots and the reference

In figure 2a the minority carrier lifetime of the Fe 50 ingot is given as a function of ingot position, measured before and after the gettering and hydrogenation steps, thus after all the high temperature processes. The trend as a function of ingot position correlates well with the inverse of the interstitial Fe concentration both before and after solar cell processing (figure 2b) as described in [2]. In the middle of the ingot, the solar cell process is able to getter the interstitial Fe, increasing the lifetime from as low as $1 \square$ s on the as-cut material to above 60 \Box s. However, in the bottom and top regions the lifetime increases, but remains at or below 10
s, even after gettering and hydrogenation. This lack of effective gettering has a direct impact on the recombination rate of minority carriers $(\sim 1/\Box)$ and therefore on the performance of the solar cells from the bottom and the top of the Fe 50 ingot.

More insight on this lack of gettering effect in the top and bottom regions of the ingot can be gained by making diffusion length maps of the cells at different ingot heights, as presented in figure 3 [3, 4]. Ld maps, by a combination of LBIC and reflectance measurements, qualitatively represent the grain structure, i.e. grainboundaries and higly dislocated areas give a relatively low LBIC signal and short Ld. There is a clear difference between the crystal structure development of the Fe 50 ingot and that of the reference. In the top and in the bottom of the Fe contaminated ingot a larger crystal defect density (e.g. grain boundaries and highly dislocated areas) is observed, as reported in [2].

In the bottom of the ingot, the high concentration of Fe in the silicon melt may have initiated or enhanced a disturbance of nucleation and growth during the early solidification phase. The increasing defect concentration in the top of the Fe doped ingots may be related to the increasing iron concentration in the melt (due to segregation), that affects the growth process.

The increased crystal defect concentration in the top and bottom of the ingots contributes considerably to the solar cell performance degradation and possibly complicates the gettering of Fe.



Figure 2: a) Minority carrier lifetime values before and after gettering and hydrogenation, measured by QSS-PC on wafers from the Fe 50 ingot. b) Interstitial Fe concentration before and after gettering and hydrogenation.



Figure 3: Effective diffusion length maps, obtained combining LBIC and reflectance measurements, of the cells from the three test ingots at 4 different ingot positions. To the left also such maps are given for the reference ingots. A clear correlation between low diffusion length and grain boundaries/highly dislocated areas is visible.

For the Cr 40 ingot, the impact in the bottom on the amount of crystal structure defects is much less severe than for the Fe contaminated ingot, but it increases towards the top. This is reflected by the IQE trend at 1000 nm, given in figure 4 [3, 4], which suggests an increase in bulk recombination towards the top.



Figure 4: Internal quantum efficiency (IQE) as a function of ingot height at two wavelengths of the incoming light for the three test ingots Fe 50 (a), Cr 40 (b) and Ni 40 (c). 400 nm photons are absorbed at the front side of the cell, i.e. in the emitter region. 1000 nm photons have a lower absorption coefficient, therefore the IQE at long wavelengths represents current generation in the bulk of the wafer.

The nickel contaminated ingot, however, hardly displays any sign of increased extended defects, in the top of the ingot. Also, the long wavelength IQE trend for this ingot is relatively flat. Although Ni, as opposed to the other two impurities, does not seem to influence the diffusion length, represented by the long wavelength IQE, it does have a large effect on the short wavelength IQE, especially in the top. This increase in recombination in the emitter region might be due to the much higher diffusivity of Ni, compared to the other two impurities. Ni possibly migrates to the wafer surface (e.g. during the emitter formation), where it can affect the emitter region. To prove this hypothesis, more tests are required.

The performance in the top of the ingot seems dominated by a mechanism which is governed by the Scheil segregation of impurities, as reported in [2]. However, we cannot rule out other possible relevant mechanisms, like for example back diffusion. Also, although the effects in the bottom and top regions can be reasonably explained by increased recombination, either in the bulk or in the emitter region, the large effect of the impurities in the bottom and in the very top is not yet completely accounted for. A large decrease in fill factor in the bottom (figure 5) and in the very top, mainly due to shunts, is an indication that other mechanisms play a large role in the (further) decrease of the solar cell performance.

The cause of these shunts is not well understood. It can be, for example, that the impact of the mechanism behind this shunt, is aggravated by the geometry of the small lab scale furnace that was used to cast the ingots and by the use of crucibles with a spherical bottom. Circular areas in the diffusion length maps (fig. 3) with increased crystal defect, that are centred on the original ingot centre within every wafer, point in this direction. Solving these issues will need a dedicated study and most likely adaptation of the crystallisation process.



Figure 5: A strong decrease in fill factor is observed in the bottom of all three test ingots and above ~85% ingot height.

4 CONCLUSIONS

The effect of metal contamination in multicrystalline silicon ingots is investigated by intentional contamination of the feedstock with Fe, Cr or Ni.

For all three contaminated ingots the solar cell performance is comparable to the reference in the ingot height range of 40-70%.

The decrease in performance in the top is most likely related to the segregation of impurities through the ingot. For the Fe 50 and Cr 40 ingots this effect is visible in the long wavelength IQE and for the Ni 40 ingot it is observed in the short wavelength IQE, which is associated with an increase in bulk recombination and emitter region defects, respectively.

In the bottom of the Fe 50 ingot, at least part of the efficiency reduction is explained by a reduced gettering effectiveness and an increased crystal defect density, which might be correlated. Here, the impact of impurities does not only cause a reduction of diffusion length due to interstitial point defects, but the presence of a high amount of Fe in feedstock, also seems to adversely affect the crystallisation process, which contributes to a further reduction of the performance of the solar cells [2].

For the Cr 40 and Ni 40 ingots, no significant decrease in IQE was observed in the bottom. However, the performance of the cells is heavily decreased in this region. For all three ingots, a large FF reduction is observed, both in the very top and bottom region. Although unexplained in itself, this effect is responsible for large decreases in cell efficiency and the dominant effect in the bottom of the Cr and Ni contaminated ingots.

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