INVESTIGATION OF NEW READY-TO-USE SOLAR CRUCIBLE® FOR CRYSTALLISATION OF MULTICRYSTALLINE SILICON INGOTS

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ABSTRACT: A new crucible concept has been investigated where silica crucibles used for directional solidification of multicrystalline silicon are coated with a high purity silicon oxide layer on top of the standard silicon nitride coating. The purpose is to create a mechanical resistant coating interface which will dissolve in the melt. Two solidification experiments using this Ready-to-Use (RTU) crucible have been conducted in addition to a reference experiment using a crucible coated with only silicon nitride. A considerable increase in scratch resistance was observed for the RTU crucibles in addition to excellent releasing properties and no contact areas between crucible and ingot. Higher oxygen levels were found in the ingots solidified in RTU crucibles due to dissolution of silica coating into the melt. The minority carrier lifetime was satisfactory but seemed to be lower than in the reference material. The efficient diffusion length was highest close to the bottom of the ingots and decreased towards the top. This trend can not be explained by the oxygen, indicating that other factors must influence the solar cell performance. Further investigations are needed to determine the optimal thickness of the silica layer to obtain a mechanical resistant coating combined with low oxygen levels in the solidified ingots.
Keywords: Multi-crystalline, Crystallisation, Crucible

1 INTRODUCTION

By contributing to about 53% of the solar cell market [1], multicrystalline silicon made by directional solidification has the position as the leading cell technology material. The main concerns during solidification of multicrystalline silicon are to avoid impurities entering the silicon, and to minimise the stresses that are created during solidification and subsequent cooling which generate dislocations in the material. It is well known that structural defects (e.g. dislocations and grain boundaries), impurities and the interaction between these will have a negative impact on the solar cell performance [2, 3].

When silicon is solidified in directional solidification furnaces, impurities are introduced from the raw material, furnace atmosphere, crucible and the crucible coating. Most of the impurities entering the melt will be located in the top of the solidified ingot as the element solubility in the liquid silicon is considerably higher than in the solid. However, impurities diffusing into the solid silicon are more difficult to remove, making the crucible and the coating important contamination sources.

Multicrystalline silicon is solidified in silica crucibles coated with silicon nitride. The aims of the coating are to prevent a chemical reaction between the silica crucible and the silicon, which may cause cracking of the solidified ingot and also crucible failure, and to reduce the diffusion of impurities from the crucible into the silicon. The crucibles are fired before use to remove organic compounds in the coating. The coating will then become brittle and easily cracks when the surface is scratched, making the charging of the crucibles difficult.

In this work a new crucible concept is tested where a silicon oxide layer is added on top of the silicon nitride coating, facing the melt. The purpose of the silica layer is to create a mechanical resistant coating interface which will later dissolve in the melt. This allows the crucibles to be delivered to the ingot producers in an already coated and fired state and also simplifies the charging of the crucibles. This patented Ready-to-Use (RTU) crucible concept is developed by Vesuvius and laboratory crucibles were tested in a pilot scale furnace at the Norwegian University of Science and Technology. The impact of the silica layer on the oxygen concentration in the RTU ingots has been investigated in addition to determine the minority carrier lifetime and the solar cell performance.

2 EXPERIMENTAL

2.1 Solidification experiments

Before the solidification experiments a scratch resistance test was performed on a ready to process silicon nitride coating and a RTU type. The measurements were conducted using a tungsten carbide probe applied at pressures from 0.1 to 1 N according to ISO standard 1518 [5].

Three solidification experiments were conducted; one reference experiment (Ref), where the crucible was coated with silicon nitride produced by UBE, and two experiments using RTU crucibles (RTU1 and RTU2). The crucibles in the latter experiments were coated with a patented oxygen enriched silicon nitride to improve the mechanical resistance and the adhesion to the crucible wall after firing, and thereafter a high purity silicon oxide layer.

For comparison of solar cell results a block of silicon from a previous experiment solidified in a crucible with higher impurity content (e.g. four times more iron) coated with purified silicon nitride from UBE (e.g. about twenty times less iron than normal) was used (Ingot4) [4]. An overview of the crucibles and coatings used in the experiments is given in Table I.

The solidification experiments were conducted in a Crystalox DS 250 pilot scale furnace where multicrystalline silicon was grown by the directional solidification method. During solidification heat was extracted through the bottom of the crucible by

controlled exposure to a water-cooled copper plate below the crucible simultaneously as the crucible was slowly pulled out of the heating zone. The crucible was rotated during the experiments to achieve complete symmetry.

The produced ingots weighted 12 kg and had a diameter of 250 mm and a height of 105 mm. The boron concentration in the middle of the ingots was determined by resistivity measurements to be 1.3×10^{16} cm^{-3}. The feedstock used was high purity solar grade silicon and the temperature histories were the same for all experiments.

The interfaces of the RTU crucibles were studied by scanning electron microscope after the experiments to explain the releasing mechanism.

Table I: Overview of coatings and crucibles used. "UBE pure" is Si_3N_4 cleaned in acid solution [4]. "O added" is patented oxygen enriched silicon nitride. NS: New standard, low iron grade. PS: Previous standard.

		Si_3N_4		***Silica***	***Crucible***	
	UBE	UBE pure	O added	***coating***	NS	PS
RTU1			X	X	X	
RTU2			X	X	X	
Ref	X				X	
Ingot4		X				X

2.2 Sample preparations and characterization

After solidification, the ingots RTU1, RTU2 and Ref were cut as shown in Figure 1 for further investigation. Characterization measurements were performed vertically close to the centreline.

Samples for oxygen measurements were ground and polished on both sides from 80 grit SiC-paper to 1 μm diamond abrasives on a polishing cloth. The interstitial oxygen concentration was measured using a Thermo Nicolet Nexus FT-IR Spectrometer with a float zone sample low in oxygen as reference. The measurements and interstitial oxygen calculations were performed according to ASTM standard F 1188-931 [6].

The minority carrier lifetime was measured using Quasi Steady State Photoconductance (QSSPC). The thickness of the samples was 10 mm and the surface was ground using 80 to 1200 grit SiC-paper. The instrument used for the measurements was a WCT-100 photoconductance tool from Sinton Consulting Inc [7] which averages the lifetime over an area of 2.3 cm^2. Unpassivated samples were radiated with 1000 nm light which enables the light to penetrate deep into the sample. The measured lifetime readings were performed at an injection level of 1×10^{15} cm^{-3}, and the effective lifetimes were calculated using PC1D-simulations by assuming a high surface recombination velocity.

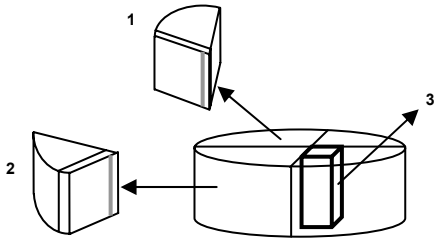

Figure 1: Measurements were performed along the grey lines. 1: Oxygen measurements (FT-IR). 2: Minority carrier lifetime measurements (QSSPC). 3: Block for wafering and solar cell processing (RTU1 and Ingot4).

Blocks of dimensions 50×50 mm were selected close to the centre of RTU1 and Ingot4 (see Figure 1) for wafering and further solar cell processing. Except for the crucible and coating (see Table I for details), the ingots were solidified under same conditions with the same feedstock, doping concentration and temperature profile. The blocks were only slightly polished on all sides before wafering, making it possible to determine the solar cell properties over the whole ingot height. The wafers were cut to a thickness of 220 μm at Fraunhofer ISE.

2.3 Solar cell processing and cell measurements

Solar cells were processed at the Energy research Centre of the Netherlands using an adaptation of the standard industrial p-type cell process. Sets of wafers from bottom to top of each ingot were used. The wafers were isotextured before diffusing phosphorous into the wafers in a belt furnace. Afterwards the wafers were coated with silicon nitride using plasma-enhanced chemical vapour deposition (PECVD) which passivates both the bulk and the surface of the wafers. The screen-printed metallization and firing-through SiN_x:H were performed in the end.

The spectral response and reflectivity were measured for all the solar cells from which the Internal Quantum Efficiency (IQE) and effective diffusion length were derived.

3 RESULTS

3.1 Coating characteristics

From the scratch resistance testing it was found that a load of 0.1 N was sufficient to damage the surface of the conventional silicon nitride coating while a load of 1 N was required for the RTU coating.

The releasing mechanism of the RTU crucibles were studied after the experiments on a crucible piece which had not been in contact with silicon (Figure 2a), in the meniscus line (Figure 2b) and on crucible piece which had been in contact with silicon (Figure 2c).

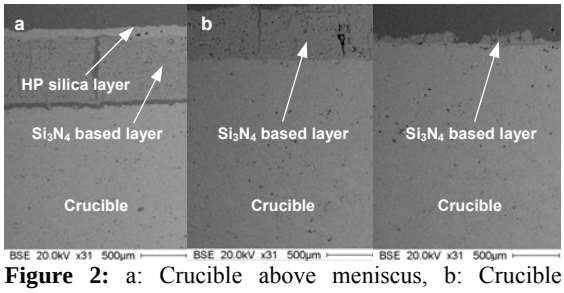

Figure 2: a: Crucible above meniscus, b: Crucible located in the meniscus, c: Crucible under meniscus.

For areas on the crucibles that had not been in contact with silicon during the experiments, the coating was almost identical to its origin where silicon oxide was covering the silicon nitride layer. In the meniscus area the silica layer had been completely dissolved. The silicon nitride layer was nevertheless intact and prevented silicon from reacting with the crucible walls. For crucible parts which had been in contact with the silicon, only silicon nitride remnants could be observed on the crucible walls as most of the coating attached to the ingot when it was removed from the crucible.

3.2 Oxygen concentration

The oxygen distribution in multicrystalline silicon ingots is generally highest close to the bottom as a consequence of solid state in-diffusion from the crucible at the long holding times for this part of the ingot, and decreases towards top where removal of oxygen to the atmosphere dominates.

The interstitial oxygen concentration vertically in the ingots is shown in Figure 3 where 0% is the bottom and 100% the top. Only minor contact areas ("pitting") between crucible and ingot were observed for the reference ingot which resulted in an interstitial oxygen concentration below 2×10^{17} cm^{-3}. The oxygen levels were increased in the RTU ingots.

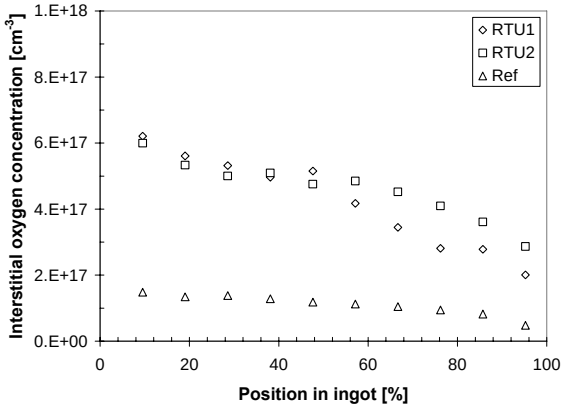

Figure 3: Interstitial oxygen concentration in the ingots.

3.3 Minority carrier lifetime

The minority carrier lifetime was comparable in the two RTU ingots with a maximum of about 10 µs (Figure 4). Areas with minority carrier trapping were frequently observed where the trapping became more apparent with increasing ingot height as shown in Figure 5. Bias light was used to correct the lifetime readings for the trapping effects [8]. The maximum measured lifetime in the reference was 47 µs and no trapping was observed in this material. Lifetime measurements for Ingot4 are included in Figure 4 which shows values similar to the reference.

The minority carrier lifetime was also measured on wafers from ingot RTU1 which had been surface passivated using silicon nitride (not shown). No trapping was observed for these wafers except from wafers located very close to the ingot top, indicating that the passivation had the capability to suppress the trapping.

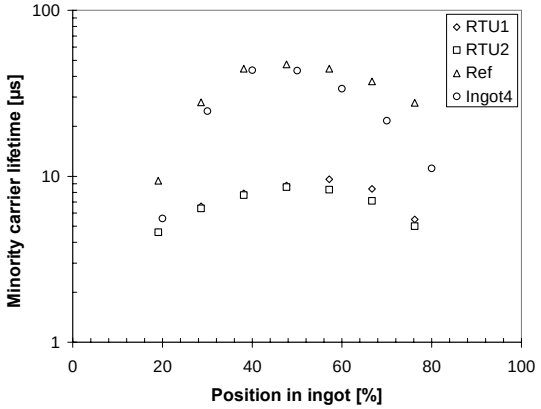

Figure 4: Minority carrier lifetime in the silicon ingots.

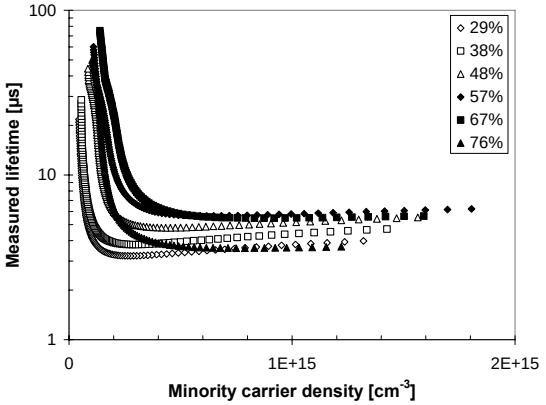

Figure 5: Measured lifetime (not corrected for surface recombination) versus minority carrier density in RTU1. The legend shows the vertical position in the ingot.

3.4 Solar cell performance

The main parameter for interpreting the quality of the material on solar cell level is the diffusion length. The effective diffusion length, L_{Deff}, has been determined from the IQE. By using the diffusion length many parameters such as reflectance, front surface and emitter recombination are removed which would otherwise obscure the results.

The effective diffusion lengths are shown in Figure 6. The values are highest close to the bottom and decreases towards top, showing about 310 and 440 µm in the middle of RTU1 and Ingot4 respectively.

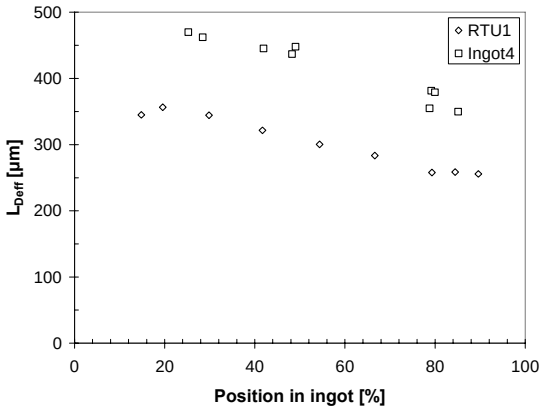

Figure 6: Effective diffusion lengths for RTU1 and Ingot4.

The solar cell efficiency values are shown in Figure 7. Due to irregular wafer edges the fill factor was somewhat reduced. The short circuit current (J_{sc}) times open circuit voltage (V_{oc}) is therefore more representative for solar cell performance and the $J_{sc}\times V_{oc}$ products are shown in Figure 8.

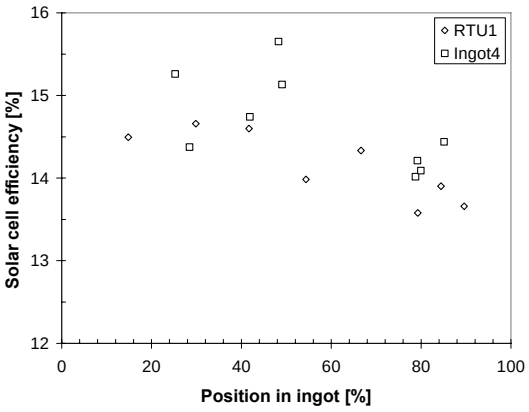

Figure 7: Solar cell efficiencies for RTU1 and Ingot4.

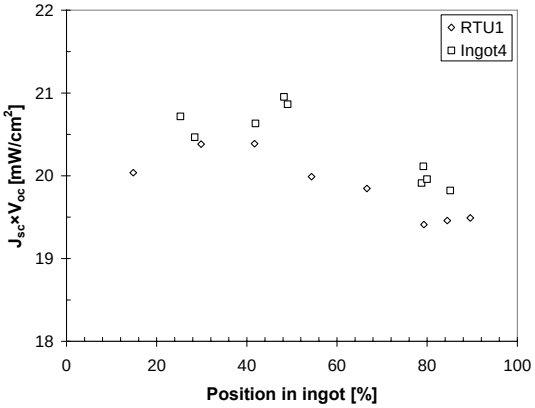

Figure 8: $J_{sc} \times V_{oc}$ for solar cells made from ingot RTU1 and Ingot4.

4 DISCUSSION

Care should be taken when comparing the RTU ingots and Ref/Ingot4. As different silicon nitride has been used, and also for Ingot4 different crucible, these conditions need to be taken into consideration when relating changes in material properties and solar cell performance. Also, thermal donors/new donors created by interstitial/precipitated oxygen have not been taken into consideration. As described by Bothe et. al [9] the thermal donor concentration can be as high as 10^{16} cm^{-3} in regions with high interstitial concentrations, and care should be taken when interpreting lifetime measurements on samples which have not been annealed to annihilate these donors. As a consequence of the higher oxygen content in the silicon solidified in RTU crucibles, the solar cell performance could be improved by adjusting the cell process to reduce the effect of thermal donors.

The interstitial oxygen concentration in bottom of the RTU ingots was more than three times the concentration in the reference material. The oxygen levels observed in the RTU ingots are however not abnormally high and are often found in monocrystalline silicon where the values are typically in the range of $5\text{-}10\times10^{17}$ cm^{-3} [10]. It should be noted that the ratio of the crucible surface area in contact with the melt/solidified silicon to the volume of the silicon will be lower in industrial scale furnaces. The oxygen concentration should therefore not reach the high concentration levels as observed in this investigation.

The higher oxygen concentrations in the RTU ingots may be a combination of silica coating dissolving into the melt, resulting in a high oxygen content in the first silicon solidifying as the distribution coefficient for oxygen in silicon is higher than 1.0 (e.g. [11]), and solid state in-diffusion from undissolved silica coating/oxygen in the silicon nitride coating. The oxygen concentration was also measured horizontally from the sidewall to the centre of the ingots and the concentration was not found to increase closer to the edges. This indicates that the dissolution of silica into the melt plays the major role for increasing the oxygen content.

The minority carrier lifetimes found in the reference ingot are comparable to values measured on ingots solidified in high purity electronic grade crucibles containing 0.5 ppm wt Fe compared to 30 ppm wt Fe as for crucibles used in this work [12]. This indicates that an efficient coating which prohibits direct contact between crucible and ingot is vital for achieving high quality silicon material.

Minority carrier trapping was frequently observed in the RTU ingots, indicating higher defect densities. The trapping effects were increasing with ingot height, a trend which is opposite to the trend of the oxygen concentration. Also, the effective diffusion length was highest close to the bottom of RTU1 and Ingot4. The decreasing material quality towards the top of the ingots can therefore not be directly related to the oxygen. The trend of the effective diffusion length could be related to an increasing dislocation density with increasing ingot height which is often observed in silicon ingots (e.g. [13]) in combination with higher impurity concentrations towards the top as a result of segregation.

Despite the large difference in the initial lifetime between RTU1 and Ingot4, the difference in solar cell performance is considerably reduced. This can be explained by the gettering and hydrogenation properties of the solar cell process which is able to reduce the minority carrier recombination.

5 CONCLUSION

A new crucible concept has been investigated (Ready-to-Use crucible) where the crucibles were coated with oxygen doped silicon nitride and thereafter with a high purity silica layer. This has resulted in a considerable increase of the mechanical strength of the coating, allowing the coated crucibles to be shipped without damage and be used as received, while at the same time showing excellent releasing properties and no contact areas between the crucible and ingot.

The dissolution of the silica coating into the melt resulted in higher oxygen concentrations in the RTU ingots. The minority carrier lifetimes showed satisfactory values, however, compared to values measured in material solidified in a standard coated crucible the lifetime is not as high as expected.

50×50 mm solar cells were made of silicon solidified in a RTU crucible and effective diffusion lengths of about 300 µm were measured in these cells. The gettering and hydrogenation properties of the solar cell process have considerably reduced the initial differences in material quality.

The solar cell performance was highest on solar cells located close to the bottom of the ingot where the oxygen

concentration was highest, indicating that the oxygen concentration is not the reason for the decreasing solar cell performance towards the top of the ingot.

The results show that RTU is a promising concept in relation to the mechanical properties of the coating and acceptable solar cells are produced from silicon solidified in RTU crucibles. More investigations are needed to determine the optimal thickness of the silica coating to reduce the oxygen concentration and to further improve the minority carrier lifetime. Also, the influence of metallic impurities, particularly in relation to the quality of the silicon nitride, is needed.

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