REMELTING AND PURIFICATOIN OF Si-KERF FOR PV-WAFERS

M. Syvertsen[1], T. Halvorsen[2], K. Mørk[2], A. Nordmark[1], T. Kaden[3], A. Ulyashin[4]

[1]SINTEF, Material and Chemistry, Trondheim, Norway,
[2]ReSiTec AS, Setesdalsveien 110, NO-4617 Kristiansand, Norway,
[3]Fraunhofer THM, Am St.-Niclas-Schacht 13, 09599 Freiberg (Sachsen), Germany
[4]SINTEF, Material and Chemistry, Oslo, Norway

ABSTRACT: Kerf from slurry based wafer cutting has undergone several refining steps and remelted into ingots for PV-application. The ingots has been wafered and characterized and show promising quality.

1 INTRODUCTION

The CABRISS project is a European collaboration between 16 partners from 9 countries; 6 SMEs, 5 Industry and 5 RTO (Research Organization) [1]. The main vision of the project is to develop a circular economy mainly for the photovoltaic, but also for other industries such as electronic or metallurgy. It will consist in the implementation of recycling technologies to recover In, Ag and Si for the sustainable PV technology and others applications.

During production of silicon wafers in the step between silicon ingots to wafers, about 40 – 50 % of the material is lost due to the cutting technique. Due to the cutting technique, this silicon is in the form of particles with size from 1 – 100 µm. In addition, for slurry based cutting, the silicon particles are mixed with SiC-particles and PEG (Polyethylene glycol). The silicon in the slurry has to be separated from the SiC-particles and PEG. This is done in several steps, each step giving more and more pure silicon material. Finally, the material should be pure enough for directional solidification and production of new PV-wafers.

2 EXPERIMENTS

2.1 Input materials

The material used in the experiments presented here was delivered by ReSiTec. The material originates from cutting of silicon bricks into wafers by wire cutting. ReSiTec purify and dries the powder. The purity specification of the powder provided by ReSiTec is given in Table 1 and a sieve curve is shown in Figure 1.

Table 1: Purity specification of the tested material from ReSiTec.

Element	%
Si	> 99.7
Fe	≤ 0.04
Al	≤ 0.08
Ca	≤ 0.006
Cr, Cl, Ti	≤ 0.003

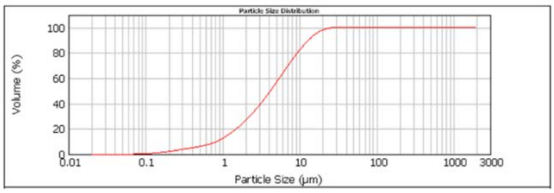

Figure 1: Size distribution of the silicon powder from Re-SiTec.

The silicon kerf was recycled in several step at an industrial scale. The kerf was removed from a highly diluted water slurry of app 0,5% solids. The silicon kerf was passivated to avoid degradation by oxidation. Contamination was to some extent removed by wet processing steps followed by drying. The recovery process is described in further detail [5].

2.2 First solidification in a Crystalox DS 250 furnace

The first melting tests were done by charging 8.9 kg of powder into a quartz crucible and performing a standard melting and crystallisation in the Crystalox DS250 furnace at SINTEF [2]. Normally 12 kg is used for these crystallisation.

Due to the nature of fine powder, it was not possible to charge such amount in the crucible. The idea was that solid inclusion will be pushed ahead of the solidification front during crystallisation. This principle has earlier been studied and verified [3,4].

A photo of the final ingot is shown in Figure 2. Visually, the produced ingot seemed successful; the bottom and sides of the ingot looked like solid silicon while a lump of porous oxides is concentrated on top.

Figure 2: Photo of the first crystallisation test of the provided powder from ReSiTec.

The ingot was cut with the intension of wafering a brick. A cut plane of the ingot is shown in Figure 3. After cutting of the ingot it became evident that a single directional solidification is not sufficient for separation of silicon and the inclusions.

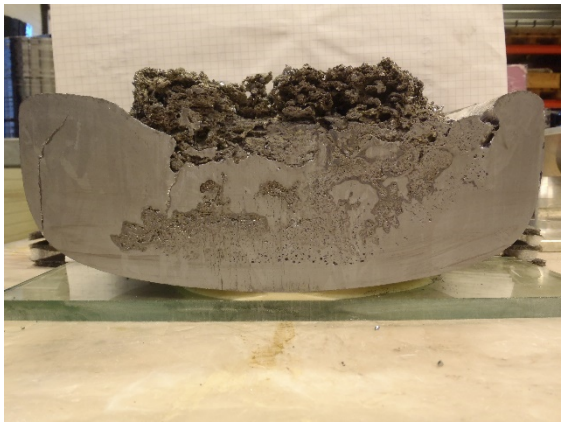

Figure 3: Cut plane of the first ingot. In addition to the particles on top, there are also large amounts of oxides embedded inside the ingot.

2.3 Separation of silicon and inclusions in semi-closed crucible

From the first two experiments, it was decided to do a separate inclusion removal step by melting and solidification. A schematic of this setup is shown in Figure 4. The crucible and lid are made of graphite. Argon gas is continuously flushing the chamber above the charge to minimize oxidation during melting. After melting, the silicon metal was poured into a silica crucible for solidification. As seen later, most of the inclusions were separated in this operation. Probably due to sticking between inclusions and the crucible wall.

Five batches of powder were melted and separated in this melting and tests in order to produce silicon for later crystallisation runs in the Crystalox furnace. The material yield in these melting tests were between 85 and 90 %. (Ratio of silicon tapped and powder fed into the crucible.)

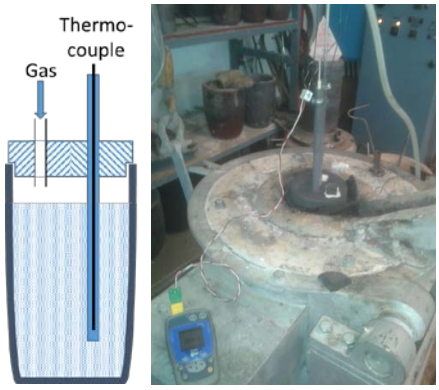

Figure 4: Schematic of the melting and separation setup on the left hand side and a photo of the experimental setup at the right. The inner diameter of the crucible is 150 mm and about 300 mm inner height.

After refining, solidification, and cooling, the material was etched to remove oxides from the surfaces.

2.4 Directional solidification of refined material

Two ingots were produced in the Crystalox DS 250 furace using refined material. One with 10% of refined material, and one with 100% refined material. Photos of these two ingots are shown in Figure 5 and Figure 6.

Figure 5: Photo of the ingot with 10 % refined material and 90 % poly-Si.

Figure 6: Photo of the ingot with 100 % refined material.

2.5 Cutting and analysis of cast material

The 10 % blended ingot even showed indications of crystal structure on top of the ingot. Also the ingot with 100 % refined material did not show much inclusions on top compared to the first ones. A brick was cut from each ingots for wafering. Photos of side cuts are shown in Figure 7 and Figure 8.

Figure 7: Side cut of the ingot with 10 % refined material.

Figure 8: Side cut of the ingot with 100 % refined material

The side cuts indicates that the ingot with 10 % refined material (Figure 7) had a planar solidification front, whereas the ingot with 100 % refined material (Figure 8) lost the planar solidification front. The latter due to too high amount of impurities in the material.

Samples have been taken from both start-material (before refining) and three different heights in both the 10 % and 100 % ingots and analysed by ICP-MS at NTNU. The results are given in Table 2. The results are somewhat inconclusive.

Table 2: ICP-MS analysis of material before refining and after directional solidification in Crystalox DS250 furnace. All values are given in ppm by mass.

	B	P	Al	Fe	Ca	Co	Na	K
Powder	0.3	9.6	3.4	2.8	46	0.02	9.8	18
10 % top	1.9	0.6	570	2	20	192	9.3	2
10 % mid	1.4	0	160	6.4	20	139	2	0
10 % bot	1.7	0	770	5.0	9	145	14	3
100 % top	10	4.4	840	5200	11	127	4.1	0
100 % mid	10	4.7	670	6600	6	111	1.6	0
100 % bot	8	4.8	260	3800	2	93	0	0

The most likely reason for the strange ICP-MS measurements are contamination from the graphite crucible used for melting and refining.

2.6 Resistivity and lifetime measurements

The bricks cut from the ingots with 10 % and 100 % refined material were sent to Fraunhofer THM for IR imaging, resistivity and lifetime mappining, and wafering. Even for the 10 % ingot, there were no IR transmission detected. Probably due to (still) too high level of impurities.

The resistivity measurements showed 0.1 – 0.2 Ωcm for the 10 % ingot (Figure 9) and 0.2 – 0.3 Ωcm for the 100 % ingot. This is somewhat lower than expected. For the 10% ingot, it was added boron to the 90 % poly-silicon so that the resistivity should have been about 1 Ωcm. This indicated that there are elements present in the refined material acting as dopants. This must be taken into consideration in later work.

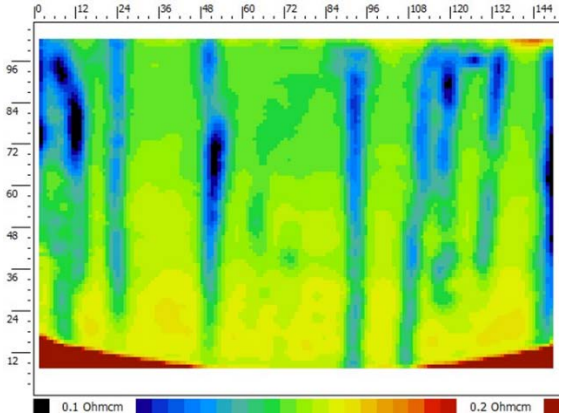

Figure 9: Resistivity mapping of a side of a square brick of the ingot with 10 % refined material.

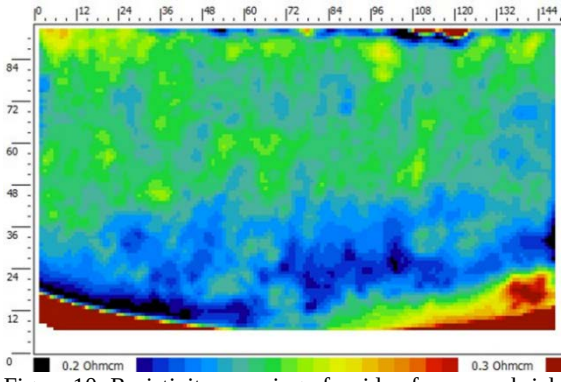

Figure 10: Resistivity mapping of a side of a square brick of the ingot with 100 % refined material.

The resistivity maps in Figure 9 and Figure 10 shows that the 10 % ingot has decreasing resistivity towards the top as expected for directional solidification, whereas the 100 % ingot did not obtain directional solidification.

Figure 11 shows a carrier lifetime mapping of the brick from the ingot with 10 % refined material. The maximum lifetime was less than 1 µs.

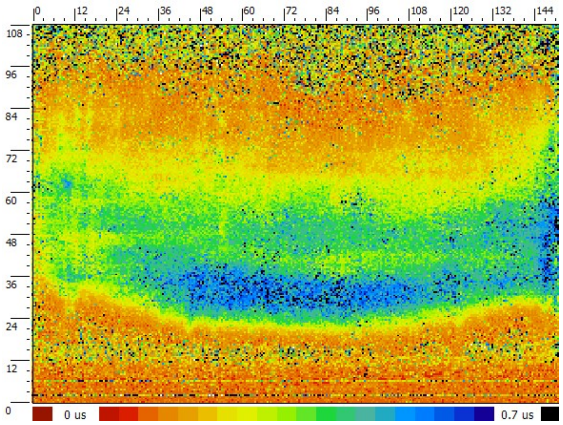

Figure 10: Lifetime mapping of the side of the 10 % ingot.

For the ingot with 100 % refined material, no lifetime was detectable. An explanation for this is that in this ingot, inclusions must be present in high concentrations.

3 CONCLUSIONS

Based on the experiments done so far, the following conclusions can be drawn:

- Refining of the powder by melting and separation of inclusions must be done if is should be used as feedstock for PV-material.
- By melting the powder in a graphite crucible and pouring it into an other crucible, the majority of inclusions will remain in the first crucible by sticking to the crucible walls.
- The refining process shown here gave 85 – 90 % material yield.
- With 10 % refined material, the ingot was still directionally solidified, whereas with 100 % refined material, the ingot was not.
- The quality of the material from the presented refining method is not high enough for ingots with 100 % refined material to be used as PV-material.

4 ACKNOWLEDGEMENTS

The project has received funding from the European Union's H2020 research and innovation programme under grant agreement N° 641972 with the consortium: CEA, SINTEF, IMEC, LOSER CHEMIE, SOLITEK, PYROGENESIS, RHP TECHNOLOGY, RESITEC, TU VIENNA, FERROATLANTICA I&D, SUNPLUGGED, THM FRAUNHOFER, PROJECT KOMPETENZ, PV CYCLE, INKRON, and ECM GREENTECH.

5 REFERENCES

[1] http://www.spire2030.eu/cabriss/

[2] Ø. Mjøs: *Directional solidification of silicon for solar cells.* Dr. Ing. Thesis NTNU 2006:109

[3] A.K. Søland: *Silicon for Solar Cells.* Dr. ing. Thesis NTNU 2004:140

[4] A. Çiftja: *Solar silicon refining; Inclusions, settling, filtration, wetting.* PhD thesis NTNU 2009:103

[5] T. Halvorsen, M.Moen, K.Mørk, D. Grosset-Bourbange, P. Rivat, H. Hajjaji, F. Coustier: Cabriss: Recycling of si-kerf, EU PVSEC 5EO.1.5, 2017.