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Fused Quartz Crucibles for PV Applications: The Role of Czochralski Process Parameters and Sand Quality on the Bubble Formation and Growth

Marisa Di Sabatino[1,*], Sebastian H. Hansen[1], Gabriela K. Warden[1], Bartlomiej A. Gawel[2], and Mari Juel[3]

[1]Dept. of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), Norway
[2]The Quart Corp, Norway
[3]SINTEF Industry, Norway
*Correspondence: Marisa Di Sabatino, marisa.di.sabatino@ntnu.no

Abstract. Monocrystalline silicon ingots are grown in a Czochralski (Cz) furnace by melting high purity silicon feedstock in a fused quartz crucible. As the standard solar cell size is getting larger, silicon ingots manufacturers have increased their demands on crucibles size and properties. Among other factors, the formation of bubbles and their growth affect the crucible`s properties and performance, which in turn are affected by the process parameters. The mechanisms of these bubbles formation and growth are still not well understood.

In this study, we investigate the bubble formation and growth in three different types of crucibles before and after use in a Cz process. The crucibles have different sand qualities, -size and -chemistries. The content of hydroxyl (OH) is measured by Fourier Transform Infrared Spectroscopy (FTIR), while bubble size and distribution are measured by X-ray tomography and optical microscopy, respectively. The results indicate that a reduction in OH content correlates with increasing bubble growth. The reference crucible, which has coarse particle size distribution and standard chemistry, has the largest variation in bubble content and the largest average bubble growth for the samples investigated. The crucible with the finest particle size distribution and high purity seems to be the best choice for silicon ingot production as it experiences, on average, the lowest bubble growth in the bubble free (BF) layer. The results also show that the crucible quality (e.g. the manufacturing process and chemistry) affect the bubble content as well as the OH level.

Keywords: Quartz Crucibles, Czochralski Process, Bubble Evolution, Silicon Solar Cells

1. Introduction

Due to the increased demand for monocrystalline silicon ingots in the last decade, there is a need for investigations of the different parameters and materials used in the silicon ingot manufacturing [1,2]. In recent years, more focus is being placed on the role of the crucible used for the molten silicon during the Czochralski process, as its lifetime is a limiting factor for the final number of ingots produced. This crucible is made of fused quartz sand, and it consists of two layers: an outer layer which shows the presence of gas bubbles, called *bubble containing* (BC) layer, and an inner layer with very low or no presence of these bubbles called *bubble free* (BF) layer, which is in contact with the silicon melt. While the BC-layer provides mechanical stability and better thermal properties, the BF-layer is needed to keep the silicon melt pure and bubble free, as the incorporation of bubbles in the melt could potentially result in the loss of the monocrystalline structure of the growing ingot [3, 4].

One of the most important crucible properties is its viscosity, which is an indication of the crucible strength. As a result of being kept at high temperatures for long times, the crucible's viscosity will decrease, as the glass becomes softer, leading to deformation and sagging [2]. During the Cz process, the crucible experiences a phase transformation to cristobalite, which can increase the crucible's viscosity, if the cristobalite is uniform. This depends on the glass structure, doping, furnace atmosphere and possible coating, among other things [5, 6, 7, 8, 9]. The effect of cristobalite is, however, not enough to avoid the sagging of the crucible. The crucible's viscosity is also significantly deteriorated by the evolution of the gas bubbles.

Previous studies have shown that bubbles present in the crucible grow with increasing holding time and temperature [3, 10, 11] by studying the samples before and after heat treatment mimicking the Cz process. In the present study, we investigated samples originating from crucibles manufactured from three different sand types, both before and after being used in an industrial Cz process to grow one monocrystalline silicon ingot. The techniques used for bubble evolution investigations were optical microscopy and micro-computed tomography (μ-CT). In addition, we studied the OH-content and its reduction during the Cz process by Fourier Transform Infrared Spectroscopy (FTIR), to investigate whether the OH content has an effect on the bubble evolution.

2. Samples and Methodology

We studied three different types of crucibles made from sand of different qualities, chemistry and particles size. The samples from these crucibles are referred to as STD, A, and B, and Table 1 shows their details. The sand size is measured by particle size distribution (PSD) technique. Coarse sand size means that d_{50} is 176 μm, while the fine sand has d_{50} of 100 μm. Crucibles A and B present a higher purity in terms of key elements such as K, Ca and Fe, where their concentrations were 69%, 72% and 87% lower, respectively, compared to STD crucible (according to the inductively coupled plasma mass spectrometry, ICP-MS, measurements provided by the manufacturer).

Table 1. *Overview of the sand size and chemistry for the three crucibles.*

Crucible	Sand size	Chemistry
STD	Coarse (d_{50}=176 μm)	Standard
A	Coarse (d_{50}=176 μm)	Higher purity
B	Fine (d_{50}=100 μm)	Higher purity

Crucibles from type A and B were also coated with barium nitrite. Therefore, for crucibles A and B we had two samples: one coated (C) and one uncoated (NC). Crucible STD came in the coated version only. The thickness of the coating in the investigated coated crucibles is approximately the same and is below 100 microns. We tested each type of crucibles as received, thus new (N), and after being used for one ingot in an industrial Czochralski (Cz) puller (U). Therefore, all the used samples came from crucibles that have been used under the same temperature, pressure and Ar gas flow conditions, even though we cannot give the details of the industrial parameters. The main difference is the dwell time during the Cz process, which in the case of crucible A was 40% shorter than the others.

In order to assess the bubble size and density, samples from each crucible were cut and analyzed by optical microscopy and micro-computed tomography (μ-CT). The samples for the μ-CT analysis were cut 12 cm below the top of the crucible in a cubic shape with dimension of 1 cm x 1 cm x 1 cm. The μ-CT of the samples was done in a Nikon XT H 225 ST X-ray computed tomography scanner. Each quartz cube was placed on a sample holder about 5 cm from the X-ray source with the BC layer facing downwards. The Wolfram X-ray source generated X-rays at 180 kV and 110 µA.

After the µ-CT analysis, the samples were polished for the optical microscopy. They were first embodied into an Epofix resin to be able to do automatic polishing and to prevent crack formation and cristobalite flake-off. The polishing sequence was: 2 min for each SiC paper of grit 120, 320 and 500, respectively, followed by 4 min in 1200 and 2400 grit. Furthermore, from the same crucibles, 2 mm thick samples were cut for Fourier Transform Infrared Spectroscopy (FTIR) from the same position as the cubes to measure the OH content.

3. Results and Discussion

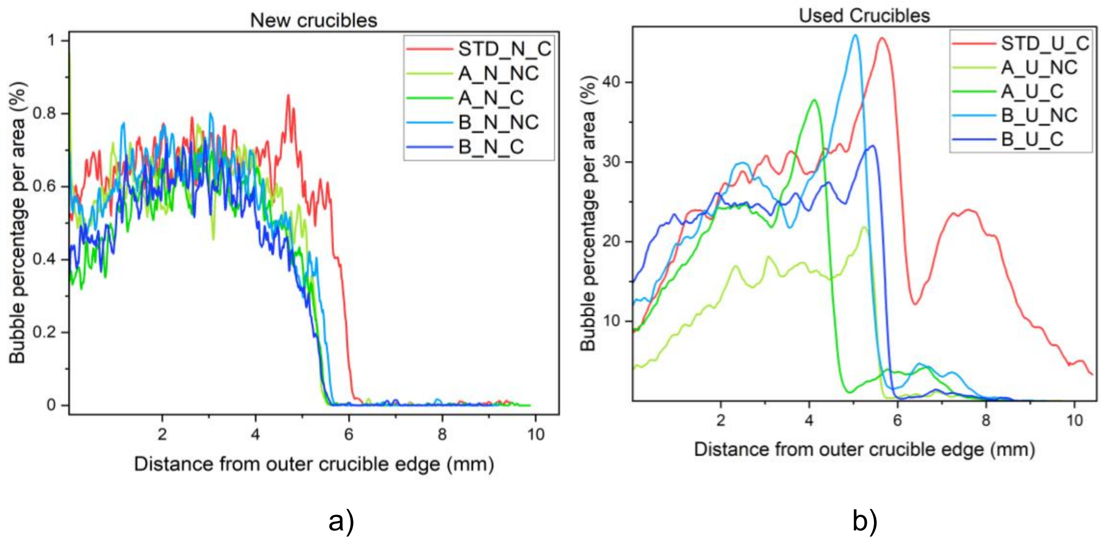


***Figure 1**. Mean plot of bubble percentage per area as a function of position (from the crucible external wall at 0 mm towards the inner wall) for a) all three new crucibles, and b) for the used crucibles.*

Figure 1 shows the bubble percentage per area along the sample cross section for new (N) and used (U) crucibles for the three types (STD, A and B) both coated (C) and uncoated (NC). In these graphs, 0 mm refers to the external wall of the crucibles, which is not in touch with the silicon melt during the Cz process, and the samples are then measured from the outer wall (BC layer) towards the inner wall (BF layer), which is in touch with the melt. Figure 2 gives the optical micrographs showing the bubbles distribution in the cross sections (from the BF layer to the left to the BC layer to the right) of all the coated STD, A and B crucibles both used and unused. Similar maps were made also for all the uncoated samples and were reported in [12].

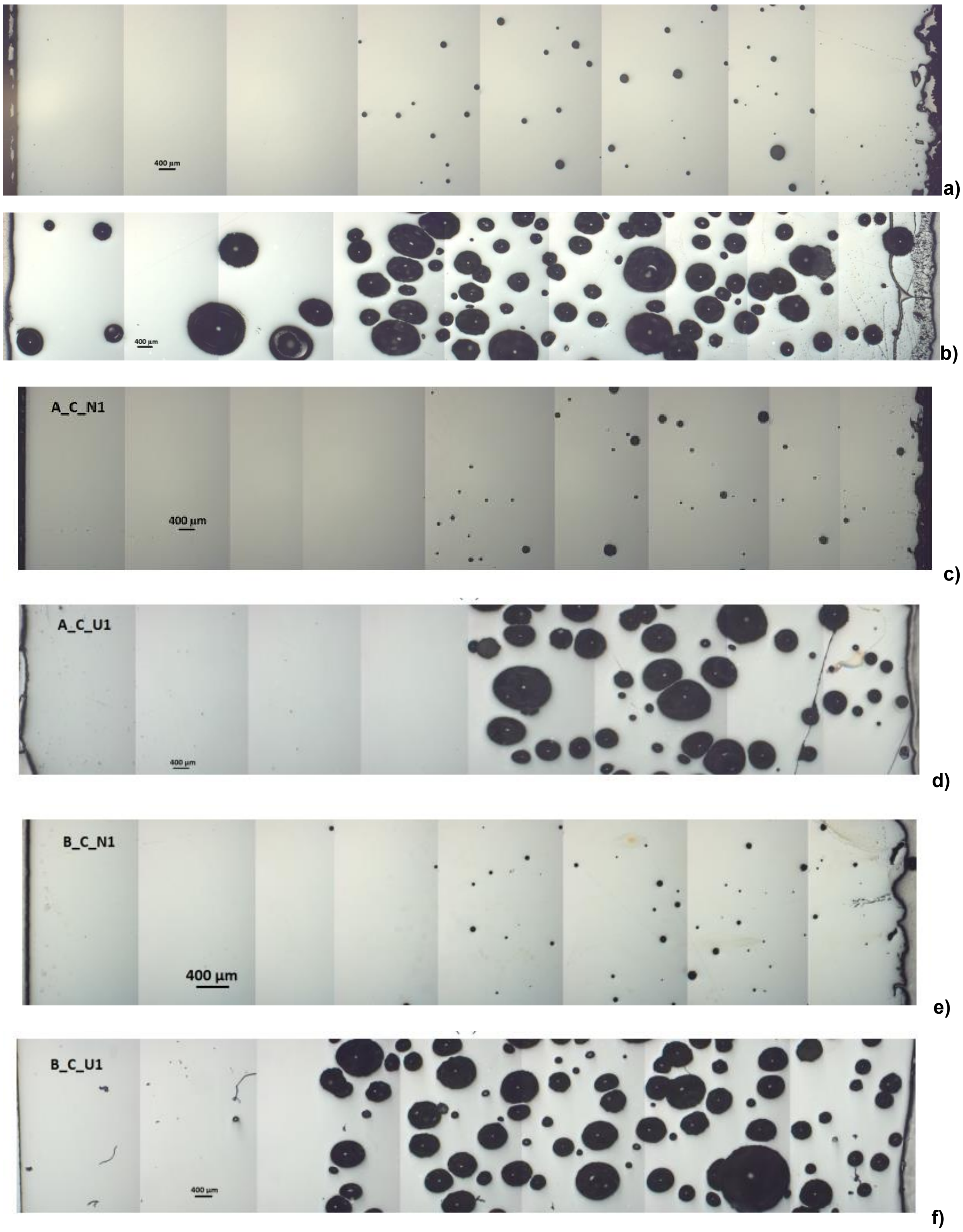
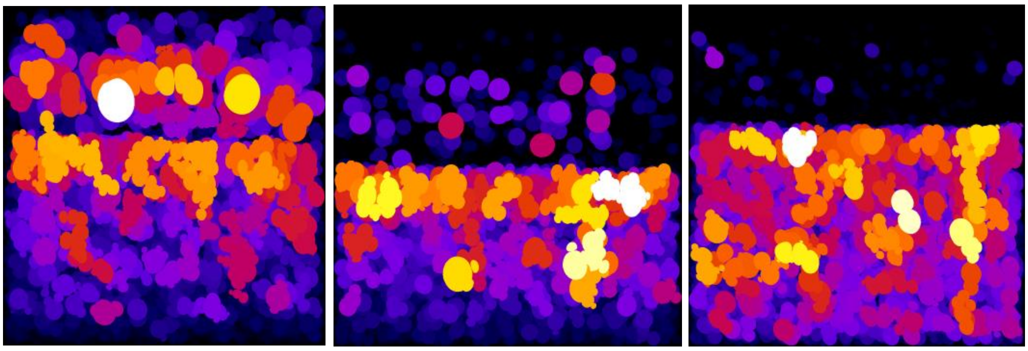


Figure 2. *Optical micrographs of cross sections (left BF- and right BC layers) of samples from a) STD_N_C, and b) STD_U_C; c) A_N_C, and d) A_U_C; e) B_N_C, and f) B_U_C.*

Figure 3 shows the micro-computed tomography (μ-CT) scans of the used samples, where the brighter the color, the bigger the bubbles. It is worth noting that these micrographs are presented in each their own color scale, so that the same shade of color does not mean the same actual size of the bubble between the different samples.

Table 2 gives an overview of the FTIR measurements of the used and unused crucible samples. The samples extracted from the BC-layer in the used crucibles have not been measured due to their low transparency. The details on the OH quantification method were provided in [12].



a) b) c)

Figure 3. *μ-CT micrographs of used crucibles samples from a) STD_U_C, b) A_U_C, and c) B_U_C. Each of the micrographs is in its own color scale, but in all the brighter the color, the larger the bubble. Scale: 1 cm x 1 cm.*

Table 2. *Average OH content (in ppm weight) in the BC and BF layers of coated unused (N) and used (U) crucible samples.*

Crucible	BC AVG OH	BF AVG OH
STD-N	38	64
A-N	167	92
B-N	72	63
STD-U	-	20
A-U	-	31
B-U	-	36

The bubble content distribution across the crucible wall for the case of new crucibles follows mostly the same trend, where only the standard crucible shows a clear peak between the BC- and BF-layer. The same peak in the bubble content is, however, visible in all used crucibles. This peak is most likely related to the manufacturing conditions: during the crucible fusion process the vacuum is switched off after the BC-layer is formed [2]. This has been previously discussed in [13] in relation to the OH-groups distribution in the crucibles. As shown in Figures 1 (b), 2 and 3, the bubbles growth during the Czochralski process is very significant, and it happens for all the samples. However, there is a clear difference between the three crucible types, where the standard crucible exhibits the highest increase in both the number of bubbles and their size. In addition, it is also the only crucible that experiences significant bubble growth also in the BF-layer. It should be mentioned that the A_U_NC crucible was used for only around 40% of the holding time of the other crucibles, which explains why this crucible has a significantly lower bubble content. There also seems to be a correlation between the coating and bubble growth, such that the coated crucibles have smaller bubbles after used than their uncoated counterparts. It should also be noted that some of the bubbles might not be captured by the μ-CT measurements due to the detection limit of the instrument which, for the specific samples geometry that we have used, is 9 μm.

All crucibles experience a significant removal of OH-groups during the Czochralski process, which is in accordance with the previous study of Yongeng and Zhenan [14]. In a recent study, it was proposed that the bubbles grow mainly due to the dihydroxylation, and that molecular oxygen is the main contributor to the bubble growth [15]. That means that higher OH content would result in increased bubble growth. This seems to be the case for the samples investigated in this work. Here, crucibles A and STD with a relatively high OH content followed by significant removal of the OH-groups showed increased bubble growth, while crucible B with a lower OH content resulted in a small OH-groups removal and a lower bubble growth.

Since high OH content [16] and bubble growth have a negative effect on crucible viscosity during the Czochralski process, it is beneficial to use crucibles with low OH-groups content. Therefore, the coated crucible B seems to exhibit the best set of properties of all investigated crucibles, as it has both lower OH content, promotes cristobalite formation, which both in turn contribute to lower bubble growth. This will lead to higher viscosity of the crucible, increasing its lifetime.

4. Conclusions

In this study we have compared three types of crucibles and analysed their bubbles density and distribution as well as the OH content before and after their use in an industrial Cz process. The results indicate that bubbles grow with increasing temperature and their density increases during the Cz process. Crucibles with higher purity and finer sand size have lower OH content. Among the three crucibles investigated, STD shows the largest variation in bubble content and the largest average bubbles density. The FTIR results show that a reduction in OH content is correlated with increasing bubble growth.

Crucible B, which has finest particle size distribution and high purity, gives lower OH content and lower bubbles growth, which both contribute to higher viscosity, meaning that the crucible can be used for longer times. Therefore, based on these results, this type of crucibles seems to be the best choice for Cz silicon ingots.

Data availability statement

Data will be made available on reasonable request.

Underlying and related material

https://ntnuopen.ntnu.no/ntnu-xmlui/bitstream/handle/11250/2460374/16824_COVER.pdf?sequence=2&isAllowed=y

Author contributions

M. D. S.: Writing – Original Draft, Writing – Review & Editing, Visualization, Supervision, Conceptualization, Resources; S. H.: Writing – Review & Editing, Formal Analysis, Investigation, Conceptualization, Data Curation, Visualization; G. K. W.: Writing – Original Draft, Writing – Review & Editing, Visualization; M. J.: Writing – Review & Editing, Conceptualization, Supervision; B. A. G.: Writing – Review & Editing, Resources.

Competing interests

The authors declare that they have no competing interests.

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