Cristobalite Formation in Fused Quartz Crucibles for Czochralski Silicon Production in Different Conditions

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Abstract. Cristobalite is one of the quartz crystalline polymorphs that forms at above 1470 °C in its pure form and above 1000 °C for quartz glass. Its formation during the Czochralski process is therefore inevitable, and is usually controlled by doping the quartz sand with barium or barium-based coatings. The formation of cristobalite can lead to significant structural defects in silicon ingots. In this work, we studied the influence of various materials (graphite, silicon carbide and alumina) on the formation and properties of the cristobalite layer. In our study we investigated glass samples extracted from a commercially produced fused quartz crucible. The samples were heat-treated in different furnaces with different contact materials: alumina, silicon carbide and graphite. The furnace with alumina as contact material was an open-air furnace, while the two others were purged with argon. All of the heat treatment experiments lasted for 3 hours at a temperature of 1500 °C, which is the approximate temperature of the Czochralski process. After the heat treatment, the samples were investigated by light microscopy and X-ray diffraction. The results showed that the contact material is the most determining factor for the cristobalite layer's thickness and morphology. The enhancement of cristobalite formation is the greatest by using graphite as the contact material, followed by alumina. Results indicate a retardation in phase transformation in comparison to other materials. These findings are an important step to further understanding of the cristobalite formation kinetics in fused quartz crucibles during the Czochralski process.

Keywords: Czochralski Process, Fused Quartz Crucibles, Cristobalite.

1. Introduction

Monocrystalline silicon is the most common material used for solar cell manufacturing today [1]. Because of the high demand for this material in the recent years, there is a need to explore the different properties of fused quartz crucibles that contain the molten silicon during the Czochralski process. The formation of cristobalite is inevitable during the process, as according to the phase diagram of silica, it is the stable crystalline silica polymorph at temperatures above 1470 °C for pure quartz [2]. For quartz glass, the temperature for cristobalite phase transformation is lower, around 1000 °C. Since its formation is inevitable, it is important that the manufacturers are able to control its growth on the inside of the crucible to avoid cristobalite chipping, which would affect the properties of the silicon melt and in the worst case, could lead to structure loss in the growing crystal [3], [4], [5]. To control cristobalite growth, the crucibles

are either coated with barium-based coatings or doped with barium to provide many nucleation sites for cristobalite, ensuring a uniform cristobalite layer on the inside of the crucible [3], [6], [7], [8]. However, the growth of cristobalite on the outside of the crucible will affect the crucibles mechanical properties. Therefore, this study focused on the possibility of controlling the cristobalite growth on the outside of the crucible.

There are many studies focusing on the cristobalite phase transformation, both in crystalline quartz and glasses [9], [10], [11], [12], [13], [14], [15], [16]. Most of the glasses investigated in the previous studies were synthetically produced. Consequently, their behavior is different than that of the material studied in this work as they do share the same treatment history as natural sand. Some of the most important findings of the previous studies were that: i) cristobalite formation and growth is enhanced in quartz with increased alkali and alkaline earth impurities content [9], ii) it is dependent on the atmosphere and furnace impurities [12], [13], as well as on the particle size of the quartz powder used to manufacture the crucible [11]. Moreover, also addition of impurities or dopants was found to have an effect, where Brown and Kistler [15] found that alumina would lead to a more rapid devitrification. Generally, it was established that the nucleation of cristobalite occurs at the surface and proceeds inwards into the glass, however, Wagstaff found that cristobalite can also nucleate inside the glass, independent of the cristobalite phase transformation happening on the surface [14].

Hirsch et al. conducted, to our knowledge, the only study that analyzed the crucible material and the evolution of cristobalite, while simulating the conditions of the Czochralski pulling process [17]. They investigated the difference in the cristobalite formation with and without the presence of silicon. Two different types of cristobalite formed based on the contact with silicon: i) brownish rings when the crucible is in contact with silicon, and ii) white cristobalite in the case of no contact with silicon. Most of the previous studies confirmed that increasing the holding time at elevated temperatures resulted in formation of a thicker cristobalite layer, and that the thickness increased also with temperature. Thus, for this study we decided to use the same holding time and temperature in all experiments. To the best of our knowledge, ours is the first study which analyzed cristobalite formation in the crucible material under different atmospheres and by using different contact materials, which can be the next step to understand whether the formation and growth of cristobalite can be controlled by tailoring the wetting conditions at the surface.

2. Materials and methods

Pieces of fused quartz crucible were extracted from commercially produced crucibles by NTNU glass workshop. An overview of the samples investigated in this study is given in Table 1. The round-shaped samples had a height equal to the crucible wall thickness (around 1 cm) and a diameter of 2.5 cm. The long samples were approximately 5 cm long, 0.2 cm thick and their width was equal to the thickness of the crucible wall (around 1 cm). Sample shapes are visualized in Figure 1.

Table 1. Samples' details and conditions. The notation "-" means that the samples were untreated.

Sample name	Shape	Contact material	Heat treatment atmosphere	Analysis
1	Round	-	-	OM
2	Round	Silicon Carbide	Argon	OM
3	Round	Alumina	Air	OM
4	Long	Graphite	Argon	OM
5	Long	Alumina	Air	XRD
6	Long	Alumina	Air	XRD
7	Long	-	-	XRD

Three different furnaces were used in this study: the ENTECH-SFX/17 furnace with alumina support, and two custom-made furnaces developed at NTNU. The two custom-made furnaces will be further referred to as the blue furnace (with graphite crucible) and the red furnace (with silicon carbide crucible). The commercially produced furnace was an open-air furnace, while the two others had the possibility of controlling the atmosphere during the heat treatment, which in the case of our study was argon. The only difference between the two custom-made furnaces is the size and the type of the crucible used for sample storage during the heat treatment, as indicated above. All the heat treatment experiments were conducted with a similar heating profile. First, the temperature was raised to 1500 °C with the following heating rates: 400 °C/h for open-air furnace, and around 500 °C/h for the other furnaces. In the case of the custom-made furnaces the temperature was controlled manually, meaning that the actual heating rate could have deviated slightly from target. However, the next step was identical in all heat treatment experiments, and it was keeping the temperature of 1500 °C for three hours. The cooling rate was around 400 °C/h, similar in all furnaces.

Samples 1 and 7 have undergone a similar sample preparation, consisting of grinding and polishing. However, Sample 1 was first cast in epoxy and then, cut in half with an automatic cutting machine using a diamond blade and water cooling. The reason for epoxy casting was to ensure that the glass would not break during the cutting. The grinding sequence was as follows: 500, 800, 1200, 2400 grit sandpaper sheets. Two sheets of each sandpaper quality were used for 3 minutes. This is due to the hardness of quartz that results in sandpaper wear. The polishing consisted of 12.5-minute-long steps at 3 µm and 1 µm polishing discs with a diamond-based polishing. The samples were then cleaned in ultrasonic bath.

The heat treated round Samples (2 and 3) and Sample 4 followed the same sample preparation procedure as Sample 1 with casting in epoxy and cutting before the grinding and polishing steps. Sample 5 had not undergone any sample preparation after heat treatment and was handled with extra care, because of the brittleness of the formed cristobalite layer. In the case of Sample 6, the brittle cristobalite layer was carefully removed using a flat metal tool on both sides of the sample in order to expose the untransformed glass below. The heat-treated samples were not polished due to their high brittleness.

For optical microscopy analysis a Zeiss Axio Vert.A1 Inverted light microscope was used in the bright field mode. To measure the thickness of the cristobalite layer, the ZEN core software provided by Zeiss was used. The thickness was measured in 10 different positions in each investigated sample and the reported thickness, in Table 2, is the average of those measurements.
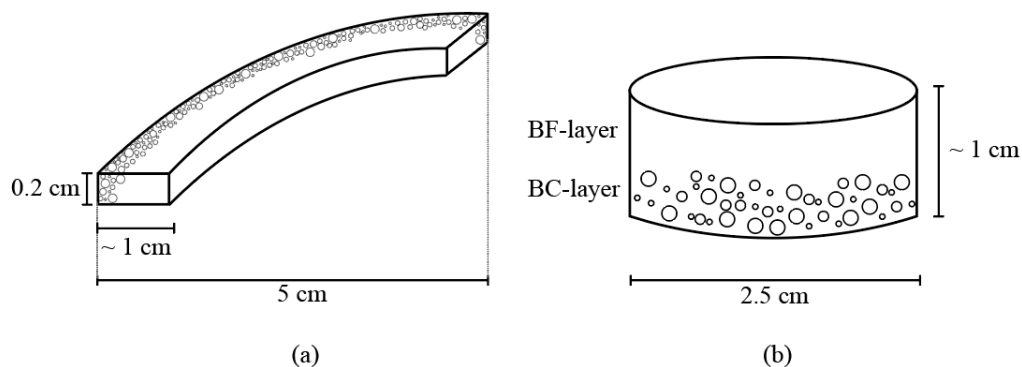

Figure 1. *A schematic illustration of the shape and dimensions of (a) the long samples and (b) the round samples. BF stands for "bubble free", while BC stands for "bubble containing".*

The XRD analysis was performed with Bruker D8 ADVANCE DaVinci X-ray diffractometer with the following settings: 2theta range 5-75 degrees, V6 slit, 0.045-degree step size. The collected data was analyzed using the Bruker DIFFRAC.EVA software.

3. Results and discussion

Figure 2 shows a photograph of both the untreated (Figure 2 (c)) and the two round heat-treated samples. The difference in the cristobalite formation between the two heat-treated samples is visible with a naked eye. Sample 3 (Figure 2 (a)) has a thick white layer of cristobalite with visible grains, where some of them visibly chipped off. Sample 2 (Figure 2 (b)) has only a hint of white color on the surface and two whiter spots on top where there was no contact with silicon carbide, however, the cristobalite grains are not visible and the surface is not chipping off.
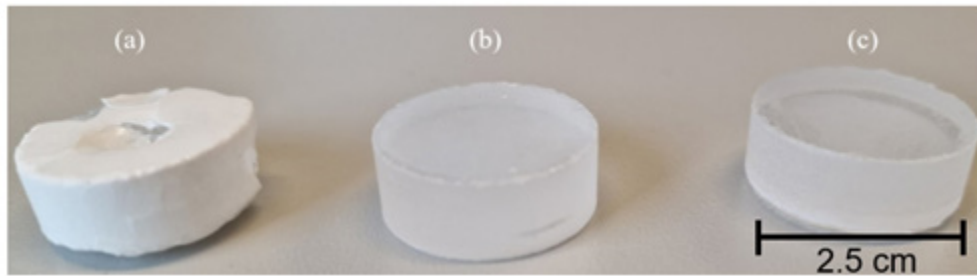

Figure 2. *A photograph of (a) Sample 3 with a thick white and brittle cristobalite layer after heat treatment with Al_2O_3 as contact material, (b) Sample 2 with a thin cristobalite layer after heat treatment with SiC as contact material, (c) Sample 1 with no cristobalite layer.*

These samples were then investigated with the light microscope in bright field mode (Figure 3). In addition to the three samples, Sample 4 was also investigated with the light microscope, as the cristobalite formed there seemed to be a very thick layer. A summary of the different thicknesses of the cristobalite layer is presented in Table 2.
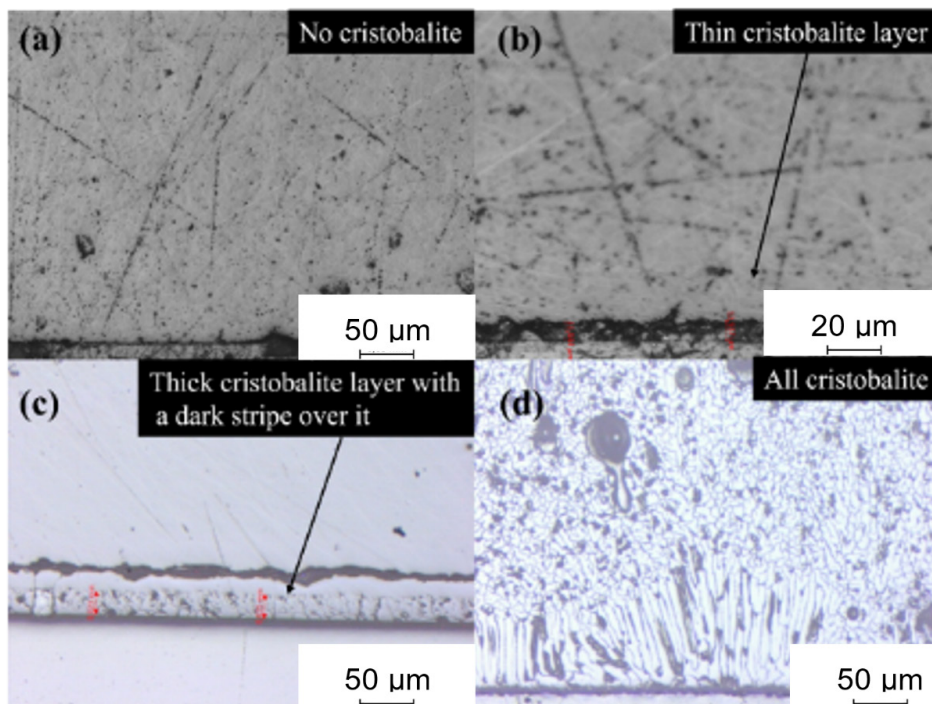

Figure 3. *Micrographs of the cristobalite layers in: (a) untreated Sample 1, (b) Sample 2 with SiC as contact material, (c) Sample 3 with Al_2O_3 as contact material, (d) Sample 4 with graphite as contact material.*

The micrographs show clear differences in the cristobalite layer morphology in the different samples. From the micrograph of Sample 4, it is worth noting the elongated grains close to the surface that was in contact with the graphite crucible. The micrographs suggest that the cristobalite nucleates there and propagates into the glass structure, as described in the Introduction section. The grains deeper inside the bulk are smaller, and similar to the grains formed in Sample 3. Sample 3 shows a uniform cristobalite layer formed at the surface, followed by an amorphous phase and a dark stripe over it, segregating the seemingly untransformed amorphous phase from the bulk of the glass. It is well known that the cristobalite phase leads to a volume change, leading to cracking, as it is a displacive transformation [18]. Therefore, we suggest that the dark stripe is a border between the unaffected bulk and the region affected by the phase transformation. This means that even though the cristobalite layer stops forming, the amorphous phase in the vicinity of it will also become brittle and crack, until it reaches the dark stripe, which is where the unaffected glass starts. A similar mechanism is described elsewhere [3].

Sample 2 displays the thinnest cristobalite layer, at 0.012 mm on average. The layer is also completely different in morphology than the rest of the samples. This suggests that silicon carbide has a restraining influence on the cristobalite nucleation, in contrast to graphite and alumina, which both appeared to enhance the formation. Li et observed that phenolic resin-derived pyrolysis carbon was restraining the nucleation of cristobalite, as it was restraining the reaction of oxygen vacancies with the air molecules in the atmosphere. This reaction was thought to be the reason for nucleation and growth of cristobalite [12]. In our case, the silicon carbide could act as their pyrolysis carbon in the argon atmosphere. However, we have not observed an analogous inhibition of cristobalite formation in Sample 4, which was heat-treated in the same atmosphere. Therefore, the mechanisms behind the phenomenon observed here are most likely different, and not related to the atmosphere used.
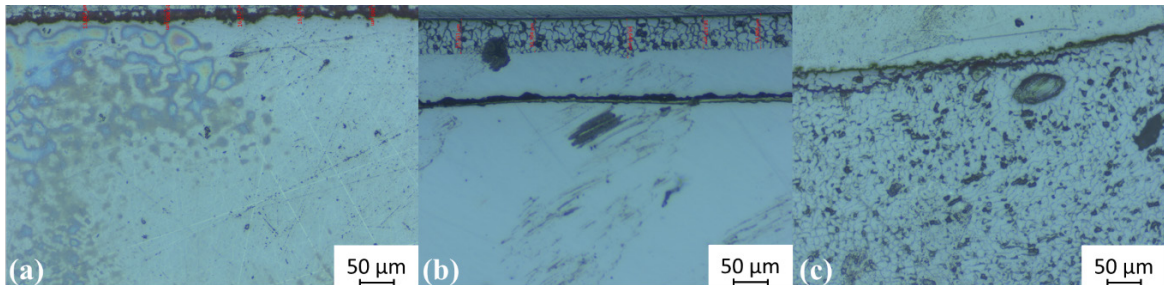

Figure 4. *Micrographs of the cristobalite layers formed at the top of: (a) Sample 2 with SiC as contact material, (b) Sample 3 with Al$_2$O$_3$ as contact material, (c) Sample 4 with graphite as contact material.*

Figure 4 shows the cristobalite layer formed at the top of the samples, which were exposed to furnace atmosphere. As can be seen, the morphologies here are similar to the ones presented in Figure 3, however, they are thinner for the case of SiC and Al$_2$O$_3$, and the grains in Sample 4 are smaller at the top, compared to the bottom surface. Therefore, we can conclude that the heat treatment atmosphere does not impact the cristobalite phase transformation greatly.

These results show that the kinetics of cristobalite phase transformation are clearly affected by the contact material, and that it is the most determining factor for the morphology and thickness of the cristobalite layer. Previous studies [12] indicated that a reducing atmosphere restrained cristobalite formation and growth. However, this was not observed in this work, as the thickest layer was produced in the argon atmosphere in the case of Sample 4, while Sample 2 that was heat treated in the same atmosphere, did not produce this type of cristobalite.

Table 2. *Average thickness of the cristobalite layer in Samples 1, 2, 3 and 4. The notation "-" means that the samples were untreated.*

Sample name	Thickness of the cristobalite layer	Contact material	Heat treatment atmosphere
1	0	-	-
2	0.012 mm	Silicon Carbide	Argon
3	0.024 mm	Alumina	Air
4	10 mm	Graphite	Argon

The results of the XRD measurements are presented in Figure 5. As described in the Materials and methods section, Sample 5 was fully covered in a brittle and quite thick cristobalite layer that formed very uniformly on the sample surface. Hence, the XRD shows the typical cristobalite diffraction pattern. Sample 6 had also formed the same type of cristobalite layer. The layer was removed before the XRD measurement to expose the seemingly unaffected glass structure. However, even after the removal of the surface cristobalite, the diffractogram shows characteristic reflections of cristobalite with low intensity. The diffractogram is dominated by a signal from a disordered structure. The diffractogram of Sample 6 is very similar to the one of the untreated Sample 7, which shows only the pattern of a disordered, amorphous structure.
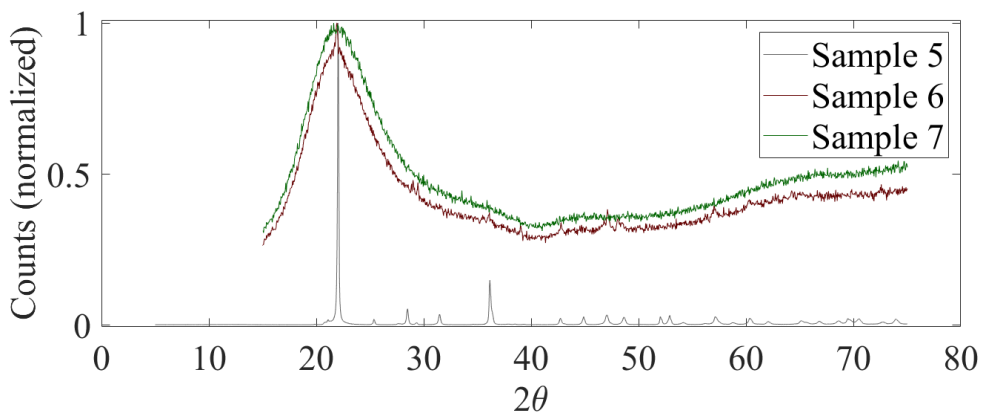

Figure 5. *Diffractogram of Samples 5, 6 and 7. The diffractograms are normalized to each their respective maximum intensity in order to highlight the details in the diffractograms of Samples 6 and 7 that in reality are much less intense than the diffractogram of Sample 5.*

The observation of reflections from cristobalite on an amorphous background even after physical removal of the cristobalite layer, suggests that during the heat treatment experiment, cristobalite does not only form on the sample surface, but also inside of the glass structure, in accordance with the study of Wagstaff [14]. Some possible nucleation sites for this phase transformation would be potential impurities, inclusions or even bubbles.

4. Conclusions

In this study, we investigated how different contact materials and atmospheres affect the growth of cristobalite in fused quartz crucibles for Czochralski ingots. The choice of contact material had a significant influence on the cristobalite formation, where graphite is a strong enhancer, alumina is a moderate enhancer, while silicon carbide retarded the phase transformation. The influence of the different atmospheres on the nucleation and growth of cristobalite was found to be much less than the influence of the contact material.

The morphology of the cristobalite layers was different depending on the contact material. Long and elongated grains were observed near the surface in the sample heat-treated in the graphite crucible, in contrast to smaller grains observed in samples heat-treated in contact with alumina. The morphology of the cristobalite layer in the sample heat-treated in contact with silicon carbide consisted of unclear and small grains that did not resemble any of the other morphologies.

The XRD analysis suggested that some cristobalite domains nucleated inside the glass, and not only on the sample surface. This can be concluded because of the existence of some cristobalite peaks in the sample where visible surface cristobalite was fully removed.

In summary, this study confirms that the contact material is one of the most important factors influencing the nucleation and growth of cristobalite. These results could be useful to the Czochralski silicon ingot manufacturers, as they prove one can either enhance or retard the phase transformation depending on the material choice.

Data availability statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

G.K.W.: Conceptualization, Investigation, Data Curation, Writing – Original Draft, Visualization, Methodology, B.A.G.: Conceptualization, Resources, Writing – Review & Editing, Supervision, M.J.: Conceptualization, Writing – Review Editing, Project administration, Supervision, A.E.: Writing – Review & Editing, Supervision, M.D.S.: Conceptualization, Supervision, Project Administration, Writing – Review & Editing.

Competing interests

The authors declare that they have no competing interests.

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