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Recent developments on manufacturing and characterization of fused quartz crucibles for monocrystalline silicon for photovoltaic applications

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ABSTRACT

The dominating technology of solar cell production today is based on monocrystalline silicon, produced mostly by the Czochralski process. Recently, the solar cell industry, has started to move towards growing larger and better-performing ingots. This triggered a need for crucibles that can withstand longer runtimes with better mechanical properties of high purity to reduce the silicon melt contamination.

In this work we present the current state of fused quartz crucibles technology and a summary of the most important literature papers in this field. This review indicates that the characterization of fused quartz crucibles remains a challenge. The existing techniques are often not sufficient for fused quartz glass characterization without optimization.

Therefore, further work should be a combination of complementary characterization techniques to be able to assess the properties of the crucible and their interactions, which could result in assessing the best combination of crucible properties.

1. Introduction

In the recent years, the demand for Czochralski monocrystalline silicon based solar cells has increased drastically. This has resulted in the need of improving the process for increased yield. One of the means of increasing the process yield is to recharge the crucible with new feedstock material right after pulling of an ingot. In this way, the furnace does not need to be cooled down, and the crucible can last longer. However, there still exist limitations to how long the crucibles can withstand the high temperatures, meaning how many ingots one can pull out of the same crucible. Research in this field is of great industrial and scientific importance, as it can provide the necessary knowledge needed for improving the monocrystalline silicon production.

One challenge in this field is the variation in the nomenclature used by the authors, which makes finding literature difficult, since the terms "silica glass", "vitreous silica" and "quartz glass" are very often used interchangeably. There are no specific guidelines about these terms, however, as a general rule, some authors proposed to use the term "silica glass" when the glass is made from synthetic silica, while the term "quartz glass" is to be used when the glass was made from natural quartz sand. However, this is not standardized, leading to the mentioned difficulties and confusion. In this work, we are consequently using the term "fused quartz crucibles" as most of the crucibles used in the solar cell industry are made from natural quartz sand. If any other term is used, it is because the material discussed is not the standard crucible material, or the authors of the reviewed paper used another term.

In the literature available, the information about high purity quartz fused quartz crucibles and their properties, characterization and manufacturing is scattered. It is difficult to find any review paper which summarizes the developments in this area. However, this is a very crucial aspect of the PV industry whose development has been very fast in the recent years. This paper can therefore become a useful tool for anyone interested in the field of fused quartz crucibles, since it includes many important papers and developments in this research area. It also includes a description of the sand purification and manufacturing processes, as well as characterization techniques that can be used to assess the crucible properties.

2. Manufacturing of quartz crucibles

The purification process of natural quartz sand is not standardized, which means that the steps presented below are not kept the same

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among the quartz sand manufacturers. The sand purification processes described in this section are often used to achieve the highest possible sand purity. The processes utilize the difference between the properties of quartz and its impurities, such as their wettability, magnetic properties etc.

2.1. Pre-processing

For crucible production, the natural quartz sand must have a purity of at least 99.997%. The first step in the purification process is the pre-processing which involves optical sorting and crushing. In the optical sorting, the ore is divided (semi or fully automatically) according to its size and color, meaning that if they are too large, they would need to go through crushing, while if they are of a certain color, they must undergo further physical and chemical treatment in addition to crushing. Traditionally, the crushing has been done mechanically. In this type of processing the ore is fed into a jaw or a cone crusher. However, in the recent years there has been a development into techniques that lower the wear-related contamination coming from these traditional methods.

One of these techniques is the electrodynamic comminution, in which a voltage discharge is generated and directed at the quartz ore. The incoming electric shock will propagate along the grain boundaries, resulting in fracture. This results in no wear-related contamination; however, it is a quite expensive technique [1].

Another technique introducing less wear-related contamination than the traditional mechanical crushing, is the autogenous grinding. In this technique the quartz ore is placed in a container together with already purified quartz sand. In this way the purified quartz is grinding the ore, resulting in very little contamination [2].

2.2. Physical processing

The physical processing part consists of several steps that can be done in different order, depending on the manufacturer. It is, however, common to start with attrition. In this step the minerals on the quartz' surface are liberated and ready for further removal during the next processing steps [3].

Magnetic separation is a process in which the sand is passed through a magnetic field. This leads to the para- and ferromagnetic elements being taken away from the quartz, while the quartz will be repelled. In this way, many impurities, such as iron oxides are removed, and the quartz can, for instance, proceed to high tension separation.

The high-tension separation technique (often called also electrostatic separation) is useful for feldspar removal. It utilizes the difference in the surface conductance. The particles are moved through an electrostatic field which can be as high as 120 kV. It occurs in an electrostatic separator which consists of a heating chamber with electrodes. The separation happens at elevated temperatures which activates the electrically conductive species in the feed. As the particles pass, the conductive species are separated and removed from quartz.

The last technique that is often used during the physical processing is froth flotation. In this case one utilizes the difference in wettability of the quartz and its impurities. The sand enters a flotation cell which is filled with a water-based suspension to avoid sedimentation processes. Further, air is let in together with a frothing agent. This will make the hydrophobic impurities move up in the flotation cell together with air bubbles and combine with the froth on top, which can then be easily removed. This technique is useful for the removal of feldspar, mica and heavy minerals [2].

2.3. Chemical processing

Chemical processing is efficient in the removal of surface impurities that had not been removed during the various steps of physical processing. The three chemical processes that can be done are: i) acid washing, ii) leaching and iii) hot chlorination. This type of processing is effective towards alkaline impurities, such as sodium and potassium.

Acid washing and leaching are similar techniques, in which the sand is washed in an acid. The difference between those is the type of acids used. While for acid washing usually less strong acids are used, such as hydrochloric or sulfuric acid, the leaching process uses the strong hydrofluoric acid at elevated temperatures. These techniques are especially efficient in the removal of concentrated impurities, or the ones located at grain boundaries or dislocations, as acids increase the dissolution rate.

As mentioned before, alkaline impurities are efficiently removed by the hot chlorination process. The sand is heated to temperatures around 1200–1300 °C in HCl. At these temperatures, the impurities react with HCl and form volatile chlorides [2].

2.4. Thermal processing

Calcination is a form of thermal processing done on quartz sand. It is done to improve the melting behavior of quartz. In this process the quartz sand is heated up to 1200 °C, in which most of the fluid inclusions are removed. During calcination, the OH-content in the sand will be reduced. In some cases, by varying the pressure and temperature parameters, this process has also been effective to reduce the number of bubbles in glass after fusion [2].

2.5. Crucible manufacturing process

The most used process for crucible manufacturing is the fusion process in electric arc furnaces (EAF). The description that will be provided is meant to be an overview of the general steps, as its details are kept confidential by the manufacturers. The existing knowledge about this process comes from the open patents, which gives a general overview of the process.

The mold in which the sand is going to be fused into a crucible, is made of graphite. This is because graphite is one of the few materials that can withstand the temperatures reached in this process, which is around 2000 °C inside the mold. In addition, it has a high heat capacity, and it is a relatively inexpensive material. The first step of the fusion process is to pour the high purity quartz (HPQ) sand inside the graphite mold. Already at this step, there are differences in the process, depending on the manufacturer, and they can for instance regard the size distribution of the HPQ sand. Generally, there are two options: HPQ sand of the same particle size is used for both the bubble free and the bubble containing layer, or there are two different HPQ sand particle sizes, where the finer sand is used for the inner bubble free (BF) layer and the coarser sand for bubble containing (BC) layer. The latter would result in a crucible containing less bubbles overall [4,5]. There is also another option, in which sands of different purities are mixed. In this case, the sand with the lowest purity will be used for the formation of BC-layer, while the sand with the highest purity will be used for the formation of the BF-layer.

After the sand is placed in the mold, a spatula is used to distribute an even layer around the mold's walls. Now, a centrifugal force around the mold's vertical axis is applied, which makes the sand stay in its designated place so that it will not fall to the bottom of the mold. At this point, the temperature is raised to above 1650 °C by the electrodes, which can be seen in Fig. 1. The temperature gradient is thus moving from the inside of the system and outwards, resulting in the crucible fusing in this direction. In the first part of the process, in which the inner part of the crucible is fusing, a vacuum is applied through the gas outlets, also marked in Fig. 1. This is done to remove the gas entrapped in between sand particles. This is a crucial step in order to form a bubble free layer on the inside of the crucible. The gas outlets are drilled in the surrounding graphite mold. There is also a graphite plug on top of the outlets to ensure that the sand is not sucked into the outlets while the vacuum is being introduced [4].

When the BF-layer has reached the desired thickness, the vacuum is

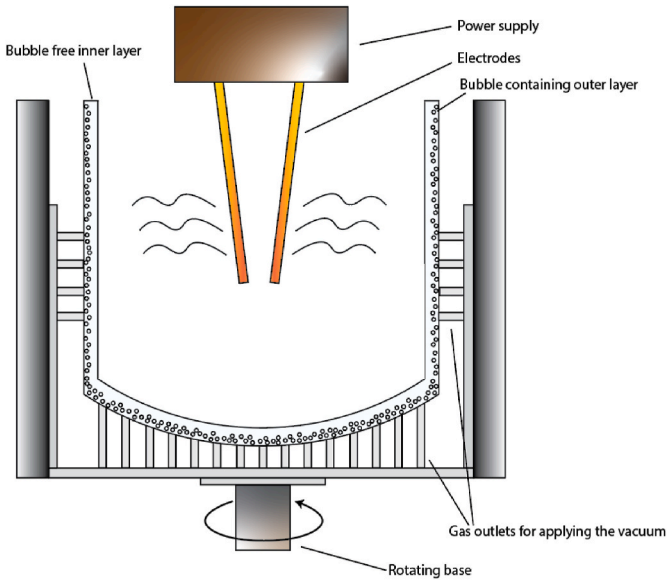

Fig. 1. Schematic illustration of the fusion process where the most important elements are marked.

either reduced or turned off and as the fusion process continues, the bubble containing layer is formed. At the end of the process, the heat supply is switched off and the electrodes are removed. The finished crucible is removed by applying compressed air flow through the gas outlets [4].

3. Properties of quartz crucibles

This section is devoted to introducing some of the important properties of quartz crucibles, including both mechanical and chemical properties, starting with bubbles role in the crucible, and moving on to discuss other properties, such as viscosity, impurity content etc.

3.1. The two crucible layers and bubble content

The product of the fusion process is a quartz crucible with two distinct layers: one bubble free inner layer and one bubble containing outer layer. The difference between the two layers can be observed by the naked eye, and it is presented in Fig. 2. Since the main difference between them is the bubble content, they will exhibit different properties; while the BC-layer containing many bubbles is needed for its mechanical properties, the BF-layer is needed for its purity [6].

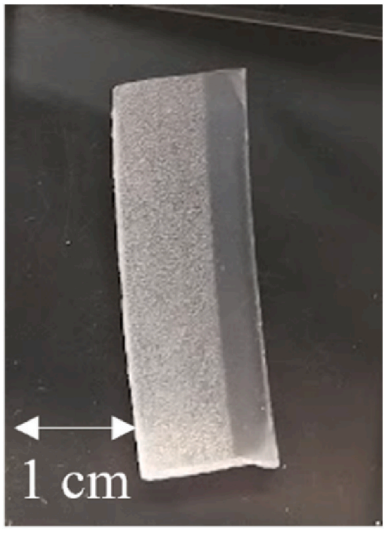

Fig. 2. Cross section of a fused quartz crucible wall, consisting of a bubble containing (to the left) and a bubble free (to the right) layer.

The BF-layer will be in contact with the silicon melt during the whole crystal pulling process, and it will be slowly dissolving into the melt by the following reaction:

$$Si + SiO_2 \rightleftharpoons 2\,SiO \quad (1)$$

The dissolution process is the reason for why this layer should contain as little bubbles as possible. The existence of bubbles so close to the melt could lead to several undesired consequences. One of them is the risk of bubbles entering the melt, which, in worst case, could result in structure loss or defects in the growing ingot. Another important reason is that the presence of bubbles lowers the viscosity of the crucible, leading to sagging and deformation, which is unwanted [7,8]. The effect of bubbles is dependent on their size and concentration.

In contrast to the inner layer, the outer one contains many bubbles. Firstly, the bubbles increase the crucible's heat resistance by lowering its heat capacity and weight, giving a better heat transfer. This is important since temperatures inside the Czochralski furnace are kept at above 1450 °C for several hours. The presence of bubbles will help the crucible withstand the heat. At the same time, as it was already mentioned, the bubbles would lower the viscosity of the crucible, which in the case of outer layer is desirable, as the crucible would end up sagging and deforming, but it will not crack [7–9]. In addition, having bubbles in the outer layer, which is not in direct contact with the melt can contribute to the overall weight reduction of the crucible.

Another aspect concerning the presence of bubbles is their growth during Czochralski process. As the bubbles get larger, they propose even a greater risk of lowering crucible's viscosity. This effect was studied by Huang et al. [9]. One of the main conclusions was that the bubbles do not move spatially. This means that bubbles that are not entrapped near the contact surface with the melt, are not likely to travel there from the inside of the crucible. At the same time, they reported that almost all the bubbles had grown during a controlled heat treatment mimicking the Czochralski process temperatures. The bubble expansion occurred in both natural and synthetic quartz glass samples [9].

Minami et al. [10] studied the growth of bubbles at the silica-melt interface. This study is deviating from the others presented in this section, as it deals with the bubbles forming at the crucible wall, and not the ones already existing inside the crucible structure. It is, however, important to present the results of this work in the context of the risks associated with bubbles in general. They have found that the bubbles at the interface originate at cavities in the crucible wall and they are mostly filled with the argon gas, which is present during Czochralski process. They suggested that the detached bubbles are the source to the pinhole defects in the crystal. The effect of the bubbles entering the melt during crucible dissolution can surely be of similar significance [10].

Paulsen et al. [11] investigated the characterization of bubble content, distribution, and expansion of bubbles before and after heat treatment for a dry and a wet sample set. They reported that there was no significant difference between the wet and dry samples. Further, the applied heat treatment resulted in bubble expansion for all samples. It was suggested that the presence of carbon can be one of the influencing factors affecting bubble expansion, as the bubbles contained CO_2 [11].

Two recent studies by Hirsch et al. [6,12] focused on bubble distribution and factors influencing bubble growth. In the first study they investigated samples originating from different positions in the crucible in different temperature, pressure and times. The results of this work showed that while the position in the crucible does not necessarily have a significant influence on the bubble growth, the Czochralski (or heat treatment) process parameters have a great effect on this phenomenon. They also distinguished between two mechanisms: bubble growth at low bubble densities, resulting in higher areal bubble density (number of detected bubbles per evaluated area) after heat treatment, and bubble

consumption at certain bubble densities, resulting in lower bubble density after heat treatment. This was linked to the different process parameters, suggesting that bubble growth can be controlled by controlling the process parameters [6]. The same group has recently published another article, concerning factors influencing the bubble growth as well as the cristobalite formation. The latter will be further described in the section on cristobalite formation. In this work they investigated four different types of crucibles, with the inner layer consisting of synthetic SiO_2. They concluded that bubbles in synthetic BF-layer grow slower than in the natural one. The bubble growth was increasing with increasing time and temperature [12].

The combination of the two layers is a good compromise between mechanical stability, heat resistance and high purity, allowing growth of high purity ingots. Understanding the behavior of each of the layers alone, as well as when they are fused together, is crucial for further improvement of fused quartz crucibles.

3.2. Viscosity

Viscosity is one of the most important crucible properties, which is related to the mechanical strength. In general, it can be described as the material's resistance to withstand deformation at a given rate. Already with this simple definition, it becomes apparent that for the case of quartz crucibles there is a need for high viscosity material which would be able to withstand deformation at high temperatures during Czochralski process.

Doremus [13] compared and investigated possible mechanisms of viscous flow in silica based on the experimental findings of various authors [14–20]. He found that the viscous flow is most probably a result of motion of line defects composed of SiO molecules. He concluded that viscosity must be a kinetic property that is determined by the concentration of defects, which again is determined by the structure and bonding of the silica network [13].

In addition to bubble content, the OH-content is also affecting the viscosity. Both Kikuchi et al. [21] and Zandian et al. [22] have found that increasing OH-content would result in lower viscosity by investigating samples with different OH content [21,22]. In addition, we also know that viscosity will decrease while the crucible is held at high temperature during the solidification process, hence having a crucible able to withstand it, would require high viscosity. Viscosity measurements are quite challenging from the technical point of view, especially at materials with high viscosity which do not deform easily, even at high temperatures.

3.3. OH-content

In addition to the hydroxyl (OH) groups present in the sand, they are also introduced into the crucible during the fusion process. The OH groups will weaken the silica structure, as they reduce the number of bridging oxygen atoms [23].

The behavior of hydroxyl groups in silica was studied by Plotnichenko et al. [24], who studied that these groups usually do not interact with each other and are mostly present in the matrix as single groups. They were also able to distinguish four different positions which the OH-groups can occupy in the silica matrix [24].

There also exist OH-groups that bind to the surface. Gee et al. [25] found that these are almost fully removed if the glass is submitted to a heat treatment above 1000 °C, so that they do not pose a risk of lowering crucible viscosity at even higher temperatures [25]. A study of Yongzheng and Zhenan [26] focused on the removal of the OH-groups in silica matrix. They performed several different heat treatments to the same type of glass, and later measured the OH-content. The samples were 20 mm long, 10 mm wide and 1 mm thick. They reported that the effectiveness of OH-removal is greatly dependent on the temperatures used, and that almost 90% of all hydroxyl groups can be removed even at relatively short time of 1 h at 1000 °C [26]. These results suggest that heat treatment of quartz crucibles can significantly reduce the influence of OH-groups on the crucible viscosity. It is, however, worth to mention that these results were obtained for relatively thin samples, and it is therefore possible that they could differ for thicker samples and/or crucibles, since the removal rate is dependent on the sample thickness.

3.4. Particle size

The particle size used for crucible manufacturing has been linked to the size and number of bubbles in the final product by the authors of a patent proposing a method of manufacturing of a crucible with reduced bubble content. They suggest that using a finer particle size of the quartz sand for the inner crucible layer would result in less bubbles [5].

Besides the patent literature, there has been little investigation on the effect of particle size on the final crucible properties. However, this topic was covered by Stensvold [27] who worked on the effect of sand treatment on the crucible properties. He investigated different types of crucibles, including some with refined particle size. His results suggest that the reduction of particle size not only affects the bubble size, but it also reduces the OH-content compared to the standard particle size. Reducing the particle size can thus have an indirect positive influence on the final crucible properties [27].

3.5. Impurity content

Impurity content is another important property of the crucibles, as they can have a direct influence on its mechanical properties, such as viscosity. Crucibles should be as free of impurities as possible. It is common to distinguish between the following three groups of metallic impurities in the crucibles: alkali metals, transition metals and boron [28,29].

The alkali metals such as Na, K and Li have been found to affect the cristobalite formation in the crucible inner wall [7]. They are also influencing the thermal stability of the crucible, which could lead to a faster dissolution of the BF-layer [28]. They have also been found to reduce the mechanical properties of silica, such as strength [30]. However, as it was mentioned in the section on chemical treatment, the alkali metals content can be reduced by the hot chlorination process of quartz sand.

Boron is another impurity whose presence can be detrimental, not necessarily for the crucible quality, but the quality of the growing silicon crystal. As boron is often used as a doping element in silicon, its concentration in the melt must be controlled strictly. However, if this element would be present in the crucible, it could result in its concentration being higher in the melt, while the crucible is dissolving. In addition, boron is also difficult to remove from the sand by the conventional purification steps [28].

Further, the transition metals propose a similar risk of affecting the growing ingot's properties if present in the crucible. They are known to degrade the silicon's electrical properties; hence it is highly unwanted that they would enter the melt [28].

In addition to the three main groups, it is also important to discuss the presence of aluminum in the crucible matrix and its effect on the crucible viscosity. Its effect was studied by, among others, Liu et al. [31]. They found that the addition of small amounts of Al would result in a higher viscosity of the silica glass. It has been generally established before that Al would negatively affect the viscosity by disturbing the silica network, even if earlier papers showed results similar to theirs [32]. Liu et al. argue that a small Al content would immobilize the diffusivity of oxygen atoms in the structure in addition to the increase in viscosity. Adding higher Al-concentrations, however, would lead to disturbance of SiO_2 molecular structure, resulting in lower viscosity [31].

The effect of impurities on the final crucible properties has not been researched in great details. However, while the transition metals, would be unwanted in the crucible structure, Al can be a good addition to

strengthen the mechanical properties of the crucibles.

3.6. Cristobalite formation

Cristobalite is one of the quartz phase transformations. The formation of cristobalite during crystal pulling is inevitable and irreversible.

The growth of cristobalite on the crucible surface was studied by Liu and Carlberg [33]. In their study they investigated the cristobalite in both small crucibles and sealed silica ampoules on which they performed a heat treatment. They proposed that the cristobalite formation is strongly dependent on the oxygen concentration (and hence also crucible dissolution) inside the melt. They also found that this phase transformation proceeds by lateral growth and in order to proceed, the contact with silicon melt is necessary [33].

In situ observations of the formation of brownish cristobalite rings were performed by Huang et al. [34]. In contrast, to the earlier study described above, the authors found that the growth of cristobalite is only dependent on the crucible dissolution to a small degree when it is above a critical value. They argue that it is mostly temperature that controls the cristobalite formation and propose two mechanisms of growth: i) cristobalite forms in the central region of the interfacial (between Si-melt and silica glass) phase; ii) the periphery of the interfacial phase is thicker than the middle, and only part of the periphery region remains after passing through the triple junction of Si-melt, Ar-gas, and silica glass [34].

Schnurre and Schmid-Fetzer [35] investigated the interfacial phase (or "reaction zone", as they call it) in various quartz glass samples. They showed that its morphology is varying a lot between the samples, but that it mostly consists of cristobalite and silica glass, supporting the theory proposed by Huang et al. They propose a solution-precipitation mechanism, which consists of the original glass-phase to dissolve and precipitate as a reaction zone in this super-saturated part of the melt. At the same time, they claim that pure cristobalite formation is hindered by kinetic growth constraints. The formation of this type of cristobalite "islands" is a rather undesired effect during Czochralski pulling as they could cause structure losses if they detach from the crucible wall [7,35].

Hirsch et al. [6] confirmed the presence of two different forms of cristobalite. While the white (or pure) cristobalite is formed due to the devitrification (crystallization of glass) process of the crucible, the brownish cristobalite rings are the result of crucible dissolution. They observed that the devitrification would be the main mechanism of cristobalite formation if no Si is present, while the other form is dominating in the case of contact with the Si-melt [6].

Although the presence of the so-called cristobalite islands is not desirable, the white form of cristobalite can actually be beneficial for the crucible mechanical properties. This is because cristobalite has superior mechanical properties, such as increased viscosity at high temperatures, as well as it is more resistant to dissolution compared to quartz. However, the cristobalite formed due to devitrification of glass is the main reason for why the crucibles can only be used once, as they become brittle upon cooling. Therefore, it could be beneficial to use the crucible for as long as possible, which can be achieved by recharging, with a sort of cristobalite "shield", protecting the crucible from collapsing [7].

Huang et al. [36] investigated the effect of Ba-doping of the crucible on the cristobalite formation. They used Ba as the doping element, as it would increase the devitrification of the crucible, and thus improve the formation of a uniform cristobalite shield [37]. To achieve this, they used a Ba-doped silica powder for crucible manufacturing. During CZ-pulling, a uniform layer of cristobalite was formed on the crucible inner surface, effectively stopping the formation of the brownish cristobalite islands, which was a very important result of this work [36].

Today, many manufacturers use either dip or spray coating for the surface treatment of crucibles to achieve doping with a devitrification agent that promotes the uniform formation of the cristobalite phase. Alternatively, the silica powder doping with Ba can be performed to achieve this effect. An illustration of the different coating/doping processes is presented in Fig. 3.

The dip coating process consists of four main steps. It starts with a controlled dipping of the crucible and holding it in the solution (for the case of crucibles, it would be a solution containing some sort of devitrification agent) for some time, before lifting it carefully. Further, the crucible is left so that the excess solvent can evaporate. In this case, a layer of the coating is formed on the crucible's inner surface [7].

Spray coating is the most used technique in the case of quartz crucibles. The devitrification agent is atomized in a nozzle and sprayed on the crucible surface, which is heated during the whole spraying process in order to increase the adherence of the coating [7,38].

As discussed by Huang et al., the doping technique for incorporating of a devitrification, must be done during the crucible manufacturing. It is the silica powder which is doped with Ba or other agents that is added during manufacturing process for the construction of the crucible wall. This means that the doping will be introduced directly inside the crucible. This technique is not used often in the crucible manufacturing industry due to quite high costs. It is, however, superior compared to the other techniques, as the cristobalite layer formed using this technique is uniform and thick, whereas for the other two cases it can be hard to control the cristobalite layer's thickness [7,39].

The cristobalite phase transformation is inevitable, and if controlled to form a shield rather than islands, it can prove to be quite beneficial, as it can both slow down the dissolution rate, and strengthen the mechanical properties. Therefore, research on the optimization of this transformation would probably be of industrial interest.

4. Characterization techniques- state of art and new developments

The last section of this literature review includes a short introduction into several characterization techniques that can be used for characterization of quartz crucible's properties, described in the previous section.

4.1. Viscosity measurements

i) Indentation method

The indentation method of measuring viscosity is a commonly used technique to assess this property of glass. In this technique, a glass sample is put inside a furnace, heated up, while a load is applied on the sample. A schematic illustration of the experimental setup is presented in Fig. 4.

Sakai and Shimizu [40] investigated several types of indenters (the part which is in contact with the sample during the measurement) in order to evaluate the relationship between the geometry of the indenter and the calculated viscosity. They relate the viscosity to the penetration depth, the load, time and the radius of an indenter. If a flat cylindrical indenter is used, the viscosity can be calculated from the following formula:

$$\eta = \frac{P_0/8R}{dh/dt}, \tag{2}$$

where P_0 is the applied load, R is the radius of the indenter, h is the penetration depth and t is the time [40].

This technique is quite challenging, as it requires approaching temperatures close to the glass transition or softening temperature, which in the case of fused quartz glass, are very high (above 1500 °C) [41]. The need for this temperature is also explained by the use of the indenter- in order to be able to use this technique, the glass needs to become soft enough for the indenter to be able to penetrate the sample. Another requirement is that the indenter is made of a material which is able to withstand these temperatures without experiencing any sort of deformation. Further, a transducer monitoring the voltage changes needs to

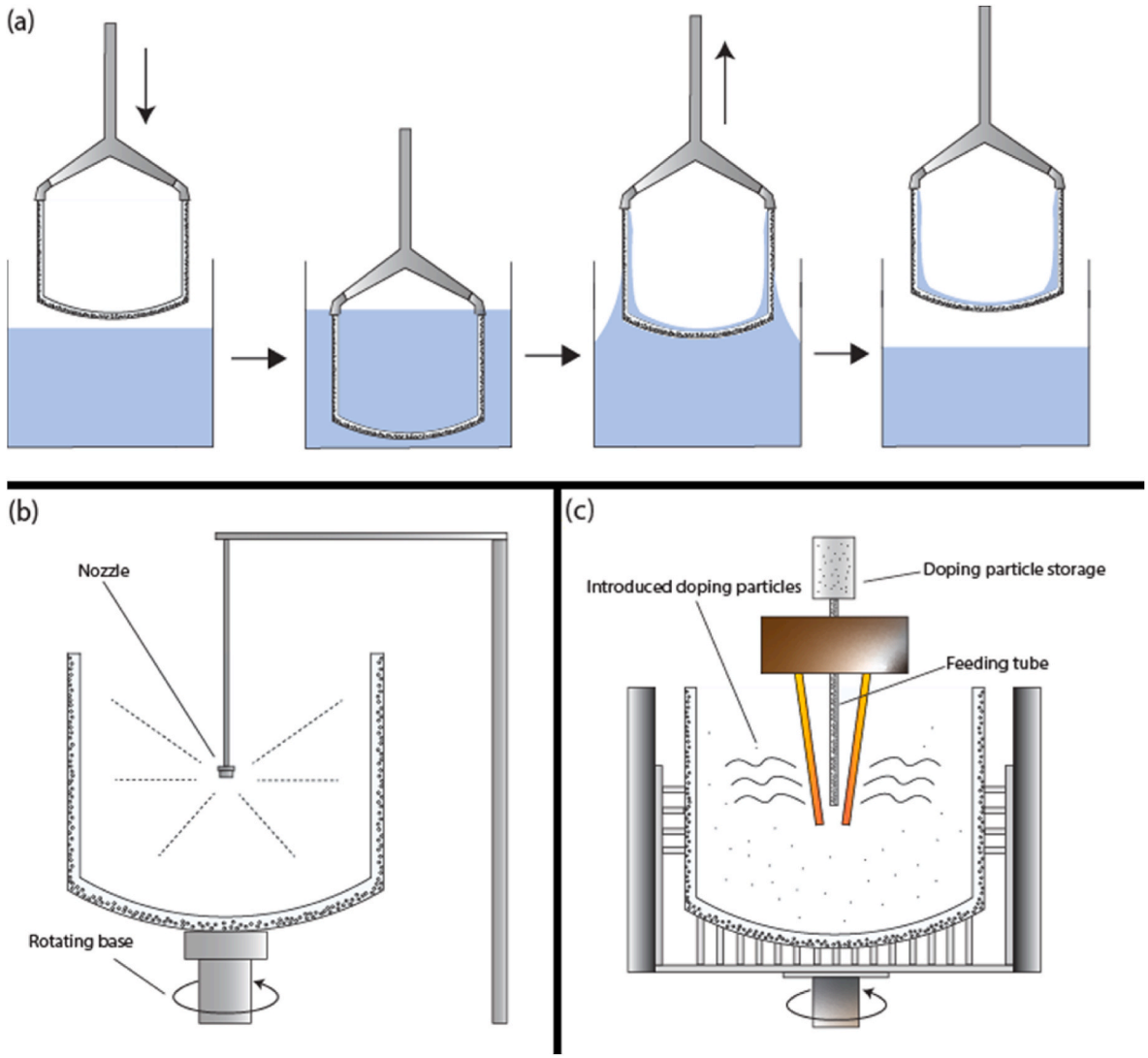

Fig. 3. A schematic illustration of the different coating and doping processes: (a) dip coating, (b) spray coating and (c) doping setup.

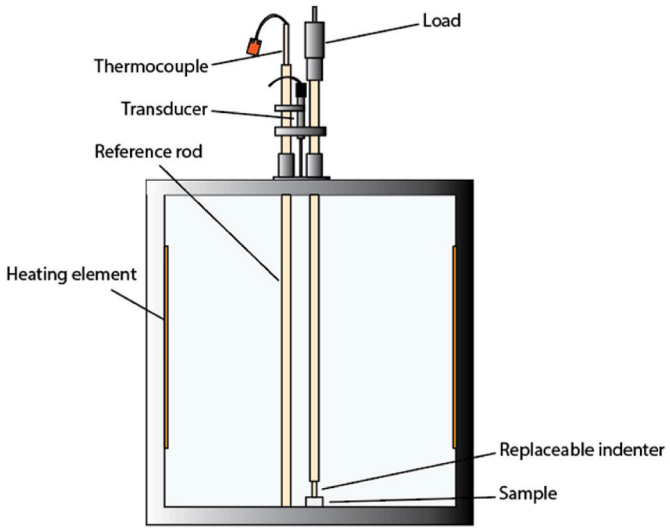

Fig. 4. Schematic illustration of the experiment setup for measuring viscosity by the indentation method.

be used, which can then be translated to the penetration depth, which can cause some problems related to sensitivity etc. As a result, this technique is not commonly used for measuring the viscosity of fused quartz.

The measurements performed by these techniques are quite time consuming, since the penetration in quartz, even at elevated temperatures can take several hours, resulting in long measurements time. It is also worth mentioning that the actual temperature in the sample may differ from the one in the furnace. That is why it is recommended to measure the temperature as close to the sample as possible. The sample preparation needed to perform this measurement is rather simple: the samples need to be ground down to achieve a flat surface to avoid the indenter from sliding of a non-flat surface, and cleaning in ultrasonic bath. Another positive aspect of this technique is that the measured penetration depth in the sample can be validated by the use of optical microscopy.

Overall, this technique is promising for assessing the viscosity of quartz glass, if its main challenges related to the equipment sensitivity and stability are overcome.

ii) Natural bending method

First, it should be noted that ”natural bending method” is not the scientific term that is commonly used. This method has been given this

name by the authors of this review in order to make it easier to understand the differences between this and the method described in the section above.

The natural bending method was proposed by Kikuchi et al. in their work focusing on the OH-groups' influence on the viscosity of silica [21]. Fig. 5 is an illustration of this method.

In this technique, a long and thin silica/quartz glass sample is placed on an alumina block with a track, which is covered in with another alumina block that holds the sample in place, as illustrated, and put in a furnace. The temperature is raised to 1100, 1200 or 1300 °C (or even higher temperature) and kept in the oven for some time. Then, the furnace is cooled down and the bending of the sample is measured. The viscosity can be calculated by the following equation:

$$\eta = \frac{\rho g L^4 \Delta t}{2a^2 h}, \tag{3}$$

where ρ is the density of glass, g is the gravity constant equal to 9.81 m/s^2, L is the length of the whole sample, Δt is the time at the maximum temperature, a is the sample thickness and h is the bending. This method of viscosity measurement is much easier to implement compared to the indentation method, as it does not require much of equipment besides a furnace. However, there still exist some challenges, like an accurate measurement of the bending and the fact that the sample must be hold in place, and it must be placed exactly in the same place between each sample.

Another advantage of this method is that the same samples can be used in other techniques, such as FTIR, described in the next chapter. If this is to be done, the sample preparation is quite time consuming, as described in the next chapter. If, however, the sample is only going to be used in this technique, only cleaning in ultrasonic bath is required before the measurement.

Similarly to the other viscosity measurement method, this is a time consuming technique, since the deformation in quartz glass, even at elevated temperatures, requires some time. There is, however, a possibility of measuring several samples at the same time, if the furnace is large enough, which could be a huge advantage if there is a need for systematical or statistical analysis. However, in order to measure several samples at the same time, the temperature in the furnace should be uniform, which practically can be hard to achieve, hence it should be taken into account during quantification. The fact that the same sample can be used for several characterization techniques is a huge advantage over the other measurement method.

4.2. FTIR

Fourier Transform Infrared Spectroscopy (FTIR) is a well-known characterization technique used in many fields to, for instance, assess impurity concentration in a material. In the case of fused quartz crucibles, it is mainly used for measuring the OH-content. This technique uses an infrared light source and sends it through the sample to obtain infrared spectra, which include peaks at the positions which are characteristic to specific impurities in a given material. The working principle of the instrument is as follows: the IR light is passed through an interferometer consisting of a moving mirror, a beam splitter and a stationary mirror. Then the beam is passed through the sample, and an interferogram is recorded, which is then translated to an absorption spectrum by the Fourier transform [42].

The absorption peak associated with OH in quartz glass is located at 3200–3800 cm^{-1}. To quantify OH-content, the height of the peak, the thickness of the sample, and some material constants are needed. The quantification of OH is done by the following formulas:

$$factor = \frac{M_{OH} \bullet 10000}{e_{OH} \bullet \rho}, \tag{4}$$

$$\beta = \frac{1}{d} \log\left(\frac{T_{max}}{T_{min}}\right), \tag{5}$$

$$OH = factor \bullet \beta, \tag{6}$$

where M_{OH} is the molar mass of OH, e_{OH} is the absorption coefficient, ρ is the density of silica glass, d is the thickness of the sample and $T_{\max}$ and T_{min} are the lowest and highest value of the measured transmission [43].

The sample preparation for this method consists of mechanical grinding of the sample on both sides to achieve a surface without any defects or scratches. This usually involves grinding with many steps up to a very fine (2000 or 4000 grit) SiC paper. A defect- and scratch-free surface is important because of the nature of this measurement, as any defects could lead to wrong measurements as they may reflect or scatter the incoming infrared beam.

The measurement itself is relatively fast and accurate, so that many measurements can be done throughout the day, and the detection limit is in the ppma range. As it can be seen in Equation (5), the sample thickness is an important parameter in the OH-quantification. To achieve reliable results, the sample thickness should be in the range 1.5–3 mm, with the optimum thickness of 2 mm.

4.3. ICP-MS

ICP-MS stands for Inductively Coupled Plasma Mass Spectrometry. It is used to detect metals and some non-metals even at low concentrations. For the case of fused quartz, it can be used to find the content of, for instance Fe, Na and K, which can be detrimental for the properties of quartz, as it was described in section on impurities [44].

As for other mass spectroscopy instruments, this technique utilizes the difference of mass to charge ratio to differentiate between different ions. The ions are generated by inductively coupled plasma, which are then separated and analyzed based on their mass to charge ratio. The impurity concentration can be quantified based on the signal. It is a superior mass spectrometry technique, allowing for high precision even

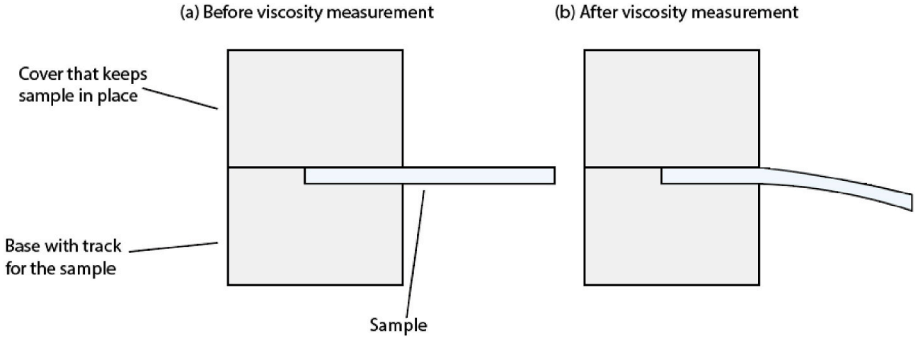

Fig. 5. Illustration of the experiment setup for measuring the viscosity natural bending method: (a) before the measurement and (b) after the measurement. This setup is put in a furnace.

at low concentrations (the detection limit is ppt) [45].

The ICP-MS technique requires that the sample is dissolved for analysis. In the case of glass samples, it would mean that the sample first must be crushed and further dissolved in, for instance, hydrofluoric acid. The measurement is relatively fast and precise, meaning it is a very potent technique for fused quartz measurements that usually have very low impurity concentration.

4.4. Optical microscopy

Optical or light microscopy is one of the most used characterization techniques in the field of materials science. In the case of fused quartz, optical microscopy is a quite interesting and powerful technique, which can be used to analyze the bubble content, as well as the cristobalite layer.

The basics of optical microscopy are generally well-known, hence they are only going to be presented briefly. A usual light microscope consists of a set of lenses, a light source, and a set of objectives. The specimen can be evaluated in different magnifications and focuses. The most popular way of using a light microscope is to observe the sample in brightfield. In this mode, the light is focused on the sample through a condenser lens, and the transmitted light enters the objective lens directly, forming an image.

However, for the case of certain materials, such as ceramics, there is a possibility of using the light microscope in the darkfield mode, which reveals new features. In this mode, the light is partially blocked, so that only some light is passed through the condenser lens onto the sample. The light that enters the objective lens in this case, is not the transmitted light, but the light that is scattered on to the sample surface. In this technique, the background appears dark (or a different color), while the object of interest appears white, which is the opposite of the bright field [46].

The use of dark field in the case of fused quartz, allows for better imaging of bubbles inside the sample, which is of great interest. As it can be seen in Fig. 6, darkfield illumination exposes some bubbles that are deeper within the sample structure, that are lost in the brightfield illumination. Fig. 6 (a) is an image obtained in the brightfield image, where only three bubbles are present in the image. However, changing the settings to darkfield, in Fig. 6 (b) revealed the existence of other bubbles. Using different focus settings in Fig. 6 (c) allowed observation of bubbles laying even more deep inside the structure.

In addition to this, dark field can also reveal some new interesting features of the crucible structure, such as the propagation of the cristobalite phase transformation inside the sample, which can be seen in Fig. 7, where the cristobalite phase is marked with 1. Number 3 on the figure is the inside of the sample, while number 2 is the region in between the two. It can be observed that number 2 looks differently than 1 and 3, and it was observed that the phase was brittle, which suggests that this region can already be affected by the cristobalite phase transformation.

The sample preparation for this characterization technique is similar to the one for FTIR. First, the samples must be ground up to 2000 grit SiC sandpaper. If the sample is only going to be analyzed under darkfield illumination, there is no need for further preparation. However, if the sample is going to be investigated under brightfield illumination, additional polishing steps should be performed, finishing at 1 μm fineness.

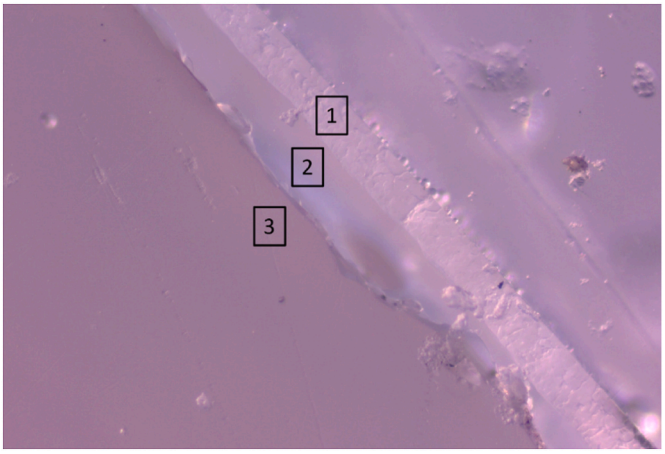

Fig. 7. The image shows: 1. cristobalite phase, 2. region affected by cristobalite phase transformation, 3. the inside of the sample not affected by the transformation. The picture was taken with magnification of 5×.

4.5. X-ray μ-CT

X-ray micro-computed tomography allows of imaging of the inside of the samples, meaning their structure or internal damages. Interestingly, this technique is frequently used in medicine to produce images of e.g., fractured bones. In the case of fused quartz crucibles, this technique can be used to obtain images of the bubble distribution in the sample [11,47].

In this technique, the sample is put on a rotating stage between an X-ray source and a beam detector. A set of radiographies is recorded. The radiographies are generated while the sample is rotating, which allows to generate a large set of the scans. These are later used to generate a 3D-image of the inside of the sample using a reconstruction software.

This technique can be quite a helpful tool to obtain 3D-images of the fused quartz samples. While light microscopy has the disadvantage of only being able to observe the surface and very little in-depth imaging, this technique does not depend on a light that can be scattered/reflected or transmitted, allowing minimal sample preparation and quality images.

4.6. X-ray diffraction

X-ray diffraction is a well-established and widely used characterization technique. In materials science it can be used to identify the

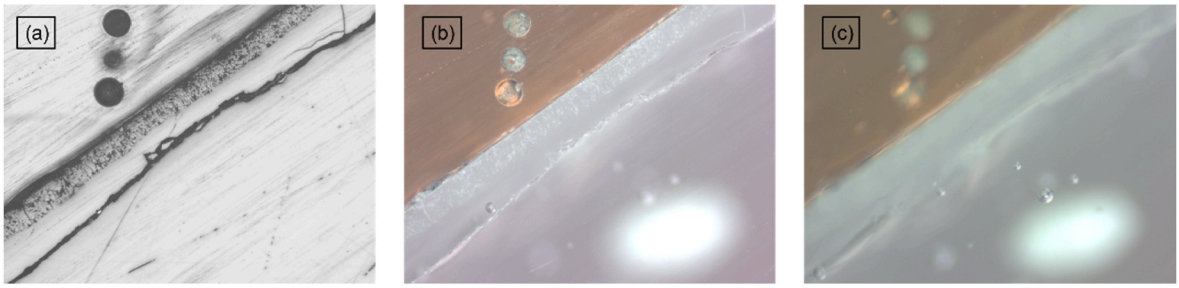

Fig. 6. Sample surface captured in: (a) brightfield, revealing three bubbles, (b) darkfield, revealing new bubbles, (c) darkfield using different focus settings, revealing bubbles located deeper inside the sample. The quartz sample is casted in epoxy, which can be recognized by its brownish color on the darkfield images. The pictures were taken with magnification of 5×. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

crystal structure of the studied material, as well as identify which phases are present. In the case of fused quartz glass, this technique can be used to identify which phases of quartz are present in the material. It is particularly useful to find the presence of cristobalite.

In this technique, the X-rays from the source are directed onto the sample. They are then scattered and interfere constructively and are then captured by a detector. The resulting diffractogram contains peaks which are distinct for each phase, making it able to identify the phases that are present in the material [48].

This characterization technique is a very fast and precise technique for phase identification in fused quartz. The main disadvantage of this method would be the sample preparation which involves having a flat sample surface, which can be difficult to achieve for heat treated fused quartz samples because of their brittle behavior. However, X-ray diffraction can pick up the signal even if there are trace amounts of any phase.

4.7. Raman spectroscopy

Another technique that is especially useful for phase identification is Raman spectroscopy. It is a very well-known technique used in materials science, which utilizes the fact that different phases have distinct position at the Raman spectrum.

In Raman spectroscopy the sample is illuminated by a strong light source, such as a laser. The light that is scattered by the sample is then captured by a detector. The resulting spectrograph is displayed with distinct peaks. In addition to the phase identification, it is also possible to get information about the structure of the studied material.

In the case of fused quartz, this technique is useful to identify which phases are present in the material. Since the technique does not require any advanced sample preparation, it makes it possible to study even the brittle heat-treated samples. Another advantage is that Raman spectroscopy can be combined with light microscopy imaging at the same time, meaning that it is possible to identify where exactly the phases are located [49].

5. Conclusion

This literature review is an overview of the most important aspects of PV high purity fused quartz crucibles, such as purification processes of quartz sand, crucible manufacturing, and some of the most important crucible properties and characterization methods.

One of major conclusions of this work is that many of the crucible's properties are dependent on and influenced by each other. Investigating their direct and indirect interactions can be a key-element to understanding their role during Czochralski pulling of silicon ingots. This review clearly shows that characterization of quartz glass crucibles properties is a challenging task due to their superior properties, which can be hard to quantify by the commonly used techniques used on inferior materials. However, it is because of this challenge that the techniques can be developed further to be used in characterization of different materials, not only fused quartz. Further development of the characterization equipment can become useful in testing of new concepts, such as doping of the sand or coating of the crucible.

Research on fused quartz crucibles is a crucial part of the development of the solar cell technologies based on Czochralski grown silicon, but it seems to get far less focus compared to the other aspects of the PV industry. As of now, the cost of production of quartz crucibles is a substantial part of the total cost of production of monocrystalline silicon ingots. Understanding their behavior, properties and (perhaps most importantly) having the necessary equipment for the characterization, can in the long run prove to be beneficial in the means of reducing the production cost and/or optimization of the crucibles' properties. This again, could make the energy produced by solar cells, become more affordable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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