

Quartz Glass Crucible For Producing Silicon Crystals And Process For Producing Quartz Glass Crucible

The invention relates to a fused quartz crucible for crystal pulling, having a crucible wall. The invention further relates to a technique for pulling a crystal, using this
5 crucible, by the Czochralski process.

Fused quartz crucibles are used, for example, for holding the metal melt in the pulling of single crystals according to the process known as the Czochralski process. In this process, a seed crystal with predetermined orientation is immersed into the melt and then slowly pulled upward. During this procedure, the seed crystal and the melt rotate
10 in opposite directions. As a result of the surface tension between the seed crystal and the melt, melt is pulled off with the seed crystal as well, and this melt gradually cools and so solidifies to form a continually further-growing single crystal.

The ingots that have been pulled can be used for cutting into semiconductor wafers by mechanical methods such as a wire saw, for example. After subsequent polishing, the
15 wafers obtained in this way, after an optional step of epitaxy, can be used for the fabrication of electronic components.

In the course of the crystal pulling operation, the fused quartz crucible is subject over several hours to high mechanical, chemical, and thermal loads, which it has to withstand without significant plastic deformation. The larger the crucible and hence
20 the greater the volume of melt to be accommodated in it, the longer, in general, are the melting times.

In order to increase the thermal stability of the fused quartz crucible, a proposal is made in **EP 07 48 885 A1** that said crucible be provided with a surface layer of cristobalite. The melting point of cristobalite, at about 1720°C, is markedly above the
25 melting temperatures of typical semiconductor materials (in the case of a silicon melt, for example, the melting temperature is around 1420°C). To generate the cristobalite surface layer, the glassy outer wall of a standard commercial crucible of opaque fused quartz, containing bubbles, is treated with a chemical solution comprising substances which promote the devitrification of fused quartz, to form cristobalite ("crystallization
30 promoters"). Recommended crystallization promoters are essentially compounds of

boron, of alkaline earth metals, and of phosphorus; preference is given to using barium hydroxide. When the fused quartz crucible is heated to a temperature above 1420°C – during service in the crystal pulling operation, for example – the pretreated crucible wall undergoes superficial crystallization to form cristobalite, and this
5 contributes to a greater mechanical and thermal strength on the part of the fused quartz crucible.

The specification **EP 1 497 484 A1** describes a fused quartz crucible for crystal pulling, having a crucible wall, comprising an outer layer of opaque fused quartz and an inner layer, where the outer layer has an internal region and an external region
10 which is provided with a crystallization promoter which, on heating of the fused quartz crucible in the course of its designated use in crystal pulling, produces a crystallization of fused quartz to form cristobalite. Said crystallization promoter comprises a first component which act as a network former in fused quartz – in addition to silicon – and/or which acts as a network modifier in fused quartz, and a second component,
15 which acts as a separating-point former in fused quartz and which is free from alkali metal.

The patent specification **US 2019 145 019 A1** describes the thickness of the crystallization accelerator-containing coating films as being preferably 0.3 to 100 micrometers. Accordingly, the barium concentration applied thereto is controlled
20 by changing the thickness of the crystallization accelerator-containing coating films. It should be borne in mind that elements which are able to act as crystallization accelerators are not intentionally added to the fused quartz crucible body, and if the crucible body consists, for example, of natural quartz flour, it is preferential for the barium concentration to be less than 0.10 ppm, the magnesium concentration less
25 than 0.10 ppm, and the calcium concentration less than 2.0 ppm. Where synthetic quartz flour is used as a raw material for the internal surface of the crucible body, it is preferential for the concentrations both of magnesium and of calcium in the crucible body to be less than 0.02 ppm.

The inventors have recognized that the use of the crucibles produced according to the
30 present state of the art continues to be impacted by disadvantages. In particular, the pulling of a number of crystals from a crucible frequently involves damage, since the crystals have an increased dislocation rate and can therefore not be used, or can be

used only partially, for the semiconductor industry. The inventors have also recognized that the long time for which a crucible is subject to high temperatures leads to dislocations. This is the case especially with large diameters and high weighed inputs. Precisely under such conditions, however, it would be particularly attractive from an economic standpoint to be able to use crucibles which did not exhibit the stated disadvantages.

It is found, moreover, that crystals pulled in succession from a crucible exhibit significant differences in quality. For example, there is a drop in the characteristic mean free path length of the minority charge carriers of the crystals, as the number of crystals already pulled from a crucible goes up. These differences in quality according to the number of crystals already pulled from a crucible is unacceptable for the semiconductor industry.

The problems described were the basis for the objective of the invention, namely to provide quartz crucibles which do not develop the stated disadvantages in crystal pulling. A further object is to provide methods for producing suitable quartz crucibles.

The object of the invention is achieved by means of the methods and products described in the claims.

The features that are stated with regard to the above-detailed embodiments of the method of the invention can be transposed correspondingly to the product according to the invention. Conversely, the features stated with regard to the above-detailed embodiments of the product according to the invention can be transposed correspondingly to the method of the invention. These and other features of the embodiments of the invention are elucidated in the description of the figures and in the claims. The individual features may be realized either separately or in combination as embodiments of the invention. Additionally they may describe advantageous implementations which have independent capacity for protection.

Brief description of the figures

Figure 1 shows a minimum and maximum concentration C , in accordance with the invention, of the synthetically obtained SiO_2 , as a function of the distance d from the internal surface of the quartz crucible. The preferred concentration profile is located between curve 1 and curve 2, and the particularly preferred concentration profile is located between curve 3 and curve 4.

An empirical imaging protocol for the respective limits was developed from experimental data.

Curve **1**, accordingly, may be mathematically described with the imaging protocol $C [\%] \leq 100 - (d [\text{mm}] - 0.25) \times 30$, and curve **2** with the imaging protocol $C [\%] \geq 100 - (d [\text{mm}] + 0.25) \times 80$.

The inventors have recognized that even greater effect can be found in the region between curve **3** and curve **4**. These curves **3** and **4** can be well described using the respective mathematical protocols $C [\%] \geq 100 - (d [\text{mm}] - 0.05) \times 36$ and $C [\%] \leq 100 - (d [\text{mm}] + 0.1) \times 80$.

The graphs in **Figures 2, 3 and 4** illustrate results of measurements obtained when pulling a number of crystals (abscissa) from a crucible.

The ordinates designated “**SPV**” convey the characteristic mean free path length of the minority charge carriers (SPV) of the respective crystal (abscissa) in relative units based on the maximum value.

The ordinates designated “**L**” convey the length of the dislocation-free portion of the respective crystal (abscissa).

Crystals for which data is shown in figures **2a** and **2b** were pulled using a crucible which – as described in the prior art – was produced from naturally obtained SiO_2 , and whose inside was coated with a barium-containing component.

While it is found that the length of the dislocation-free portion of the crystals remains high, there is nevertheless a considerable drop apparent in the mean free path length. The mean free path length, then, drops on average to 70% of the initial value. There is therefore no assurance that crystals of uniform quality can be produced with a crucible.

Crystals for which data is shown in figures **3a** and **3b** were pulled using a crucible which – as described in the prior art – was produced from synthetically obtained SiO_2 , and whose inside was coated with a barium-containing component.

The normalized values (figure **3a**) for the free path length show a significantly increased scatter. Even the first crystal from the crucible used shows a mean free path length which is smaller by an average of 10%. Crystals of this quality are inadequate for the semiconductor industry. The length of the dislocation-free portion of the crystals as well (figure **3b**) exhibits an unacceptable scatter and would result economic damage for a corresponding.

Figures **4a** and **4b** show the results for crystals pulled with a crucible produced in accordance with the invention.

It is clearly apparent that not only the mean free path length (figure **4a**) but also the portion of the dislocation-free length of the crystals (figure **4b**) exhibit no more than minimum (zero) scatter. Both in terms of quality and economics, the crucibles of the invention are optimal.

Detailed description of exemplary embodiments of the invention

A plurality of crystals were pulled in each case from a crucible by means of the Czochralski pulling method and measurements were made both of the mean free path length of the minority charge carriers (SPV) and of the length of the undislocated crystal. The length of the undislocated portion of the crystal was placed in relation to the theoretically attainable overall length.

Similarly, the characteristic mean free path length of the minority charge carriers was placed in relation to the measured maximum mean free path length measured. This

statistic is used below as a quality criterion for any impurities that might be present in the crystal that to adversely affect the components subsequently fabricated on the silicon. It would also be possible theoretically to use other statistics for the quality of the crystals. Examples of such include a μ PCD lifetime measurement or else a
5 chemical analysis of the resulting silicon by ICP-MS. A number of suitable methods are available here to the skilled person.

The inventors have identified the above-described measurement techniques as being the most suitable and, in particular, readily accessible.

The inventors here have recognized that the use of crucibles manufactured according
10 to the prior art is subject to distinct disadvantages when a crucible is used to pull a number of crystals in succession according to the Czochralski technique. Moreover, crystal pulling appeared to be more difficult the longer the pulling process lasted.

The results of the studies are conveyed in **figure 2** and **figure 3**.

Crystals for which data is shown in figures **2a** and **2b** were pulled using a crucible
15 which – as described in the prior art – was produced from naturally obtained SiO_2 , and whose inside was coated with a barium-containing component.

While it is found that the length of the dislocation-free portion of the crystals remains high, there is nevertheless a considerable drop apparent in the mean free path length. The mean free path length, then, drops on average to 70% of the initial value. There is
20 therefore no assurance that crystals of uniform quality can be produced with a crucible.

Crystals for which data is shown in figures **3a** and **3b** were pulled using a crucible which – as described in the prior art – was produced from synthetically obtained SiO_2 , and whose inside was coated with a barium-containing component.

25 The normalized values (figure **3a**) for the free path length show a significantly increased scatter. Even the first crystal from the crucible used shows a mean free path length which is smaller by an average of 10%. Crystals of this quality are inadequate for the semiconductor industry. The length of the dislocation-free portion

of the crystals as well (figure **3b**) exhibits an unacceptable scatter and would result economic damage for a corresponding.

The inventors have identified crucible material as being a cause of the measured deficiencies and have undertaken extensive trials to eliminate the deficiencies.

- 5 It is known from the literature that β -cristobalite has a higher melting temperature than quartz. It is also known that there are certain crystallization promoters which sometimes favor the generation of β -cristobalite.

- Another piece of knowledge is that quartz crucibles made from synthetically obtained SiO_2 differ in their properties from those quartz crucibles made from naturally obtained SiO_2 . The results of the experiments are shown for example in figures **2** and **3**.

- Surprisingly, the inventors found that a fused quartz crucible having an inner side located on which there is an inner layer of fused quartz that forms a surface, the inner layer being provided with a crystallization promoter, exhibits positive properties in relation to the multiple pulling of crystals from a crucible, specifically when the concentration C of synthetically obtained SiO_2 at one distance from the surface is greater than the concentration of synthetically obtained SiO_2 at another distance from the surface.

Acting crystallization promoters here with particular preference are the substances barium or strontium, with barium being especially preferred.

- 20 The inventors have recognized that it is preferential if the concentration C of synthetically obtained SiO_2 is greater than 90% when the distance to the surface is less than 0.4 mm.

Further trials revealed, unexpectedly, that if the concentration of synthetically obtained SiO_2 as a function of the distance d is subject to the following relationships:

- 25 $C [\%] \leq 100 - (d [\text{mm}] - 0.25) \times 30$ and
 $C [\%] \geq 100 - (d [\text{mm}] + 0.25) \times 80$

there are advantages in relation both to the quality (SPV) and to the portion of dislocation-free length of the crystal. The range just described is depicted in figure 1, and relates to the shaded region between curve 1 and curve 2.

Results are depicted, for example, in figures 4a and 4b.

- 5 The inventors were able to narrow down the region somewhat, through further experiments, and found that, when the concentration of synthetically obtained SiO₂ as a function of the distance d is subject to the following relationships

$$C [\%] \leq 100 - (d [\text{mm}] + 0.1) \times 80$$

$$\text{and } C [\%] \geq 100 - (d [\text{mm}] - 0.05) \times 36,$$

- 10 there are further advantages in relation both to the quality (SPV) and to the portion of dislocation-free length of the crystal.

This region described is also illustrated in figure 1, and relates to the shaded region between curve 3 and curve 4.

- 15 With particular preference the concentration of the crystal promoter here is less than 1 ppba and greater than 0.05 ppba, based on silicon.

- Preferred for producing the fused quartz crucibles of the invention, comprising a crystallization promoter, is a method which involves producing a crucible base body having an inner side and comprising naturally obtained SiO₂, and coating the inner side with a layer comprising synthetically obtained SiO₂, the concentration C of the synthetically obtained SiO₂ increasing with increasing layer thickness.
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It is particularly preferred here if the crystallization promoter is added during the actual production of the crucible base body.

- For the method it is preferable if the material intended for the coating is mixed continuously in a mixing vessel in order to prevent separation. The proportions of synthetically obtained and naturally obtained SiO₂ in the mixing vessel here are altered over time. At the same time, material for the coating is withdrawn from the
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mixing vessel. The fraction of the synthetically obtained material in the vessel is ideally increased over time.

It has proven to be particularly advantageous for a crystallization promoter to be added during the actual coating of the inner side.

- 5 It is particularly preferred if, subsequent to the coating, the crucible is filled with polysilicon and is heated to above 1400°C in order to melt the polysilicon.

It is especially preferred for the polysilicon to be admixed additionally with a crystallization promoter, preferably comprising barium, with a concentration of greater than 0.5 ppba and less than 10 ppba, based on the polysilicon.

Patent claims

1. A fused quartz crucible for pulling a single crystal of silicon according to the Czochralski technique,
 having an inner side on which there is located an inner layer of fused quartz that
 5 forms a surface,
 the inner layer being provided with a crystallization promoter which on heating of
 the fused quartz crucible in the context of its designated use, in crystal pulling,
 brings about crystallization of fused quartz to form β -cristobalite,
 characterized in that the concentration C of synthetically obtained SiO_2 at a
 10 distance d from the surface is greater than the concentration of synthetically
 obtained SiO_2 at a distance d2 from the surface, where d2 is greater than d.
2. The fused quartz crucible as claimed in claim 1, characterized in that said
 crystallization promoter comprises barium or strontium.
3. The fused quartz crucible as claimed in claim 1 or claim 2, characterized in that the
 15 concentration C of synthetically obtained SiO_2 is greater than 90% when the
 distance d to the surface is less than 0.4 mm.
4. The fused quartz crucible as claimed in any of claims 1 to 3, characterized in that
 the concentration C of synthetically obtained SiO_2 as a function of the distance d is
 subject to the following relationships:
 20 $C [\%] \leq 100 - (d [\text{mm}] - 0.25) \times 30$ and
 $C [\%] \geq 100 - (d [\text{mm}] + 0.25) \times 80$.
5. The fused quartz crucible as claimed in any of claims 1 to 3, characterized in that
 the concentration C of synthetically obtained SiO_2 as a function of the distance d is
 subject to the following relationships:
 25 $C [\%] \leq 100 - (d [\text{mm}] + 0.1) \times 80$
 and $C [\%] \geq 100 - (d [\text{mm}] - 0.05) \times 36$.
6. The fused quartz crucible as claimed in any of claims 1 to 5, characterized in that
 the concentration of the crystal promoter is less than 1 ppba and greater than
 0.05 ppba, based on silicon in the fused quartz crucible.

7. The fused quartz crucible as claimed in any of claims 1 to 5, characterized in that the crystal promoter comprises barium.
8. A method for producing a fused quartz crucible comprising a crystallization promoter,
5 by producing a crucible base body which has an inner side and comprises naturally obtained SiO_2 ,
and coating the inner side with a layer comprising synthetically obtained SiO_2 , the concentration C of the synthetically obtained SiO_2 increasing with increasing layer thickness.
- 10 9. The method as claimed in claim 8, characterized in that the crystallization promoter is added during the production of the crucible base body.
10. The method as claimed in claim 8 or claim 9, characterized in that the material intended for the coating is mixed continuously in a mixing vessel in order to prevent separation, with the fractions of synthetically obtained and naturally
15 obtained SiO_2 in the mixing vessel being altered over time and at the same time material being withdrawn therefrom for the coating.
11. The method as claimed in any of claims 8 to 10, characterized in that during said coating of the inner side, a crystallization promoter is added.
12. The method as claimed in any of claims 8 to 11, characterized in that subsequent
20 to the coating, the crucible is filled with polysilicon and is heated to above 1400°C in order to melt the polysilicon.
13. The method as claimed in claim 12, characterized in that the polysilicon is additionally admixed with a crystallization promoter having a concentration greater than 0.5 ppba and less than 10 ppba, based on the polysilicon.
- 25 14. The method as claimed in any of claims 8 to 13, characterized in that the crystallization promoter comprises barium.
15. A method for producing semiconductor wafers, characterized in that an ingot is pulled in a crystal pulling unit, using a fused quartz crucible as claimed in any of

claims 1 to 7, the ingot is cut into wafers by means of a wire saw, the wafers are polished, and optionally they are subjected to epitaxy.