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SPECIFICATION

159159

TITLE OF THE INVENTION

Quartz glass crucible for pulling up single silicon crystal and production method therefor

TECHNICAL FIELD

The present invention relates to a quartz glass crucible for use in pulling up single silicon crystal that is used in producing semiconductors, and to a production method therefor.

BACKGROUND OF ART

Hitherto, so-called Czochralski (CZ) method is widely employed as the production method for single silicon crystals. The CZ method comprises melting poly-

crystalline silicon in a crucible made of quartz glass, immersing a seed crystal of single silicon crystal into the silicon melt, gradually pulling up the seed crystal while rotating the crucible, and thereby growing the single silicon crystal from the seed crystal as core. The single crystal that is produced in said CZ method should be of high purity and capable of producing silicon wafers at high yield; as the quartz glass crucible for use in the production, employed is a double-structured quartz glass crucible comprising an inner layer free from pores and an opaque outer layer containing pores.

With recent tendency of consuming longer time for the operation of pulling up single silicon crystals with increasing diameter of single silicon crystals, quartz glass crucibles with higher purity are required. Accordingly, the present applicants have proposed a

quartz glass crucible having a double structure comprising a transparent inner layer and an opaque outer layer, in which the inner layer is formed with synthetic silica grain (for instance, Patent No. 2811290 and Patent No. 2933404, etc.). A quartz glass crucible having an inner layer made from synthetic quartz glass grain is advantageous in that it is extremely low in impurity content, suffers very low generation of surface roughening or cristobalite spots on the inner surface during pulling up single silicon crystals, enables operation for a long time, and increases the yield of pulling up single crystals.

However, in case of melting polycrystalline silicon, when compared with crucibles made from natural quartz glass, the crucibles above having inner layers made of synthetic quartz glass tends to cause oscillation on the surface of the melt. In particular, such surface oscillation is frequently observed in the initial pulling up stages such as nucleation, formation of shoulders, and former stages of producing single crystal body part; and is disadvantageous in that it lowers productivity, due to increased time for nucleation, the generation of disordering in the crystals, causing re-melting, i.e., the so-called melt-back, and the like. In the light of such circumstances, the present inventors have proposed a multi-layer structured crucible having an opaque synthetic quartz glass intermediate layer interposed between a transparent inner layer made of synthetic quartz glass and an opaque bulk layer made of natural quartz glass (Japanese Patent Laid-Open No. 2001-348294). However, since multi-layer structured crucible uses expensive synthetic grain in large quantities, it

suffered a disadvantage as such that it results expensive.

In the light of the aforementioned circumstances, the present inventors have extensively conducted studies, and as a result, it has been found that the surface vibration generated on the surface of the silicon melt is deeply related with the inner surface of the straight shell part, and that the yield of pulling up single crystals is significantly related with the inner surface of the bottom part. Furthermore, by using natural quartz glass or a mixture of natural and synthetic quartz glasses for a specified range of the shell part of the quartz glass crucible that is used for pulling up single silicon crystals, it has been found that the generation of vibration on the surface of the silicon melt can be suppressed, and that it enables long stabilized operation using the crucible while suppressing the generation of surface roughening and cristobalite spots on the inner surface of the crucible by forming a specified range of the inner layer in the vicinity of the bottom part of the crucible with synthetic quartz glass. The present invention has been accomplished based on these findings enabling pulling up of single silicon crystal at high yield. More specifically:

An object of the present invention is to provide a quartz glass crucible capable of pulling up single silicon crystal stably at high yield by suppressing the generation of vibration on the surface of silicon melt, without generating surface roughening and cristobalite spots on the inner surface of the crucible even for long operation.

Further object of the present invention is to provide

a method for producing the quartz glass crucible above.

DISCLOSURE OF THE INVENTION

In order to achieve the objects above, the present invention relates to a quartz glass crucible for pulling up single silicon crystal comprising a crucible base body having a bottom part and a straight shell part with an inner layer provided to the inner surface thereof, in which the quartz glass crucible is characterized by that said inner layer comprises a synthetic quartz glass layer of at least up to a height of $0.25H$; a natural quartz glass layer or a mixed quartz glass layer of natural quartz glass and synthetic quartz glass extended over a range of from at least $0.5H$ to $0.8H$; and one selected from a synthetic quartz glass layer, a natural quartz glass layer, and a mixed quartz glass layer of natural and synthetic quartz glass for the rest of the inner layer; wherein H represents the height from the lowest end of the bottom part to the upper end plane of the shell part with respect to the crucible body.

Brief Description of the Drawings

Fig. 1 shows a schematically drawn cross section view of the quartz glass crucible of the present invention.

Fig. 2 is a schematic drawing of an apparatus for producing quartz glass crucible of the present invention.

Best Mode for Carrying out an Invention

The quartz glass crucible according to the present invention is a quartz glass crucible for pulling up single silicon crystal comprising a crucible base body with an inner layer provided to the inner surface

thereof, in which said inner layer comprises, with respect to the height (H) from the lowest end of the bottom part to the upper end plane of the shell part, a synthetic quartz glass layer of at least up to a height of $0.25H$; a natural quartz glass layer or a mixed quartz glass layer of natural quartz glass and synthetic quartz glass extended over a range of at least from $0.5H$ to $0.8H$; and one selected from a synthetic quartz glass layer, a natural quartz glass layer, and a mixed quartz glass layer of natural quartz glass and synthetic quartz glass for the rest of the inner layer. By forming an inner layer made of natural quartz glass or synthetic glass containing natural glass (i.e., a natural glass mixed with synthetic glass) on the inner surface of the crucible base body, the vibration in silicon melt can be suppressed. The thickness of the inner layer made of natural quartz glass or of natural glass mixed with synthetic glass above is preferably in a range of from 0.3 to 3 mm. In case the thickness is less than 0.3 mm, only small effect of suppressing the vibration of silicon melt can be expected; an inner layer formed at a thickness exceeding 3 mm is not preferred because there is no improvement in the effect of suppressing the vibration of the melt.

On the other hand, the yield of the single silicon crystal depends on whether the single crystal contains dislocations or not. However, most of the dislocations generate due to the surface roughening or to the generation of cristobalite spots in the later stage of the pulling up process, i.e., within a height of $0.25 H$ of the crucible that is brought into contact with the silicon melt for a long duration of time. Accordingly,

in the quartz glass crucible according to the present invention, the inner layer up to a height of at least 0.25 H is formed with synthetic quartz glass that is less affected by surface roughening or generation of cristobalite spots. The thickness of the inner layer is preferably in a range of from 0.5 to 5 mm. In case the thickness of the inner layer becomes less than 0.5 mm, the effect of suppressing surface roughening and cristobalite spots becomes small as to result in low yield. An inner layer exceeding 5 mm in thickness is also not preferred, because it increases the production cost.

The grain of natural silica mixed with synthetic silica for forming the inner layer of the quartz glass crucible above preferably contains 30 % or more of natural silica grain.

The structure of the quartz glass crucible according to the present invention is shown in Fig. 1. In Fig. 1 are shown a quartz glass crucible 1, bottom part 2 of the crucible, straight shell part 3, inner layer 4, a synthetic quartz glass inner layer 5, and an inner layer 6 made of natural quartz glass or natural glass mixed with synthetic glass. Fig. 2 shows an embodiment of an apparatus for producing quartz glass crucible. In Fig. 2 are shown a rotating mold 7, a crucible base body 8, a silica grain supply means 9, a plate-like lid body 10, a flow control valve 11, a silica grain supply 12, an arc electrode 13, a silica grain supply nozzle 14, and high temperature atmosphere 15. The quartz glass crucible according to the present invention is formed by introducing natural silica grain from the silica grain supply means 9 into the rotating mold 7, shaping the

grain into the form of the crucible, inserting the arc electrode 13 therein, and covering the aperture part of the body shaped into the crucible with a plate-like lid body 10, and thus, by using the arc electrode 13, a translucent crucible base body 8 is formed by setting the inside cavity of the crucible-like shaped body to a high temperature gaseous atmosphere and thereby melting and vitrifying at least a partially the inside of the crucible-like shaped body. Then, a first silica grain is supplied into the high temperature atmosphere 15 from the silica grain supply means 9 while controlling the supply rate with the flow control valve 11 to thereby form a quartz glass inner layer at the desired position by melting and vitrifying the grain. Subsequently, a second silica grain is supplied to the high temperature atmosphere 15 from the silica grain supply nozzle 14, and, on forming a quartz glass layer at the desired position by melting and vitrifying the thus supplied silica grain, a synthetic quartz glass inner layer 5 is formed up to at least a height of $0.25H$ from the lowest end of the outer surface of the bottom part, wherein H represents the height from the lowest end of the bottom part to the upper end plane of the shell part; a natural quartz glass layer or a mixed layer 6 of natural and synthetic quartz glass is formed in a range of from at least $0.5H$ to $0.8H$; and the rest of the inner layer is formed with one selected from a synthetic quartz glass, a natural quartz glass, and a natural quartz glass mixed with synthetic quartz glass. In the production method above, preferably employed are production methods such as (i) a method comprising forming a synthetic quartz glass inner layer to at least a height of $0.25H$ by supplying

synthetic silica grain in a high temperature atmosphere and by melting and vitrifying the grain, followed by moving upward, downward, or to the right or left, if necessary, the silica grain supply nozzle 14 that has been used for supplying the synthetic silica grain, and forming, over a height range of at least $0.5H$ to $0.8H$, a natural quartz glass inner layer or an inner layer of natural quartz glass mixed with synthetic quartz glass 6, by supplying a grain of natural silica or of natural silica mixed with synthetic silica from the nozzle; (ii) a method comprising forming an inner layer 6 of natural quartz glass or an inner layer of natural quartz glass mixed with synthetic quartz glass over a height range of at least $0.5H$ to $0.8H$ by melting and vitrifying a grain of natural silica or of natural silica mixed with synthetic silica that is supplied from a silica grain supply nozzle 14, followed by moving, if necessary, upward, downward, or to the right or left the silica grain supply nozzle 14, and then forming a synthetic quartz glass inner layer 5 to at least a height of $0.25H$ from the lowest end of the outer surface of the bottom part by melting and vitrifying the synthetic silica grain supplied from the silica grain supplying nozzle 14; and (iii) a method comprising forming a first quartz glass inner layer over the entire inner surface of the crucible base body by melting and vitrifying a first silica grain supplied from the silica grain supply nozzle 14, followed by forming a second quartz glass inner layer on the desired position by supplying a second silica grain. In the production method (iii), preferred are to use synthetic silica grain for the first grain and a natural silica grain or a grain of natural silica mixed with

synthetic silica for the second grain, such that the inner layer 6 of natural quartz glass or of natural quartz glass mixed with synthetic quartz glass is formed over a height range of from 0.5H to 0.8H.

The present invention is described more specifically below by way of examples, but it should be understood that the present invention is not only limited thereto.

EXAMPLES

Example 1

By using the apparatus shown in Fig. 2, high purity natural silica grain subjected to purification treatment was fed into a rotating mold 7, and the grain was formed into a quartz glass crucible-like shape by the centrifugal force. Then, an arc electrode 13 was inserted into the quartz glass crucible base body, the aperture part was covered with a plate-like lid body 10, and a high temperature gaseous atmosphere was provided inside the inner cavity by using the arc electrode 13 to melt and vitrify the base body. Thus, a translucent quartz glass crucible base body 8 was formed by cooling the molten and vitrified body. Then, after setting high temperature atmosphere 15 inside the inner cavity of the translucent quartz glass crucible base body 8 by means of arc electrode 13 while rotating the mold 7, synthetic silica grain was supplied therein at a rate of 100 g/min from the silica grain supply nozzle 14. In this manner, a synthetic quartz glass inner layer 5 about 2 mm in thickness was molten and joined monolithically with the inner surface of the translucent crucible base body 8 to a height of at least 0.4H from the lowest end of the

outer surface of the bottom part, where H represents the height from the lowest end of the bottom part to the upper end plane of the shell part. Then, the silica grain supply nozzle 14 was moved upward, and by supplying a grain of natural silica at a rate of 100 g/min from a silica grain supply means 9, a natural quartz glass inner layer 6 about 2 mm in thickness was molten and joined monolithically with the inner surface of the translucent crucible base body 8 over a height range of $0.4H$ to $1.0H$. The diameter of the thus obtained quartz glass crucible was 24 inches. On pulling up single silicon crystal according to CZ method by filling the quartz glass crucible with polycrystalline silicon and melting, perfect single silicon crystal was obtained after operation of about 90 hours without generating any vibration on the surface of silicon melt.

Example 2

High purity natural silica grain subjected to purification treatment was fed into a rotating mold to form the grain into a quartz glass crucible-like shape by the centrifugal force. Then, an arc electrode was inserted into the quartz glass crucible body, the aperture part was covered with a plate-like lid body, and a high temperature gaseous atmosphere is provided inside inner cavity by using the arc electrode. Thus, a translucent quartz glass crucible base body was formed by cooling the molten and vitrified base body. Then, after setting high temperature atmosphere inside the translucent quartz glass crucible base body by means of arc electrode while rotating the mold, synthetic silica grain was supplied therein at a rate of 100 g/min from the silica grain supply nozzle. In this manner, a

synthetic quartz glass inner layer about 2 mm in thickness was molten and joined monolithically with the inner surface of the translucent crucible base body. Subsequently, about 0.8 mm thick inner layer of natural quartz glass mixed with synthetic quartz glass was formed on the inner layer over a height range of $0.45H$ to $0.9H$ of the crucible base body by supplying synthetic silica grain at a rate of 50 g/min from the silica grain supply means 9 and natural silica grain at a rate of 50 g/min from the predetermined position through the silica grain supply nozzle above. The diameter of the thus obtained quartz glass crucible was 24 inches. On pulling up single silicon crystal according to CZ method by filling the quartz glass crucible with polycrystalline silicon and melting, perfect single silicon crystal was obtained after operation of about 90 hours without generating any vibration on the surface of silicon melt.

Comparative Example 1

By using the apparatus shown in Fig. 2, high purity natural silica grain subjected to purification treatment was fed into a rotating mold 7, and the grain was formed into a quartz glass crucible-like shape by the centrifugal force. Then, an arc electrode 13 was inserted into the quartz glass crucible base body, the aperture part was covered with a plate-like lid body 10, and a high temperature gaseous atmosphere was provided inside the inner cavity by using the arc electrode 13 to melt and vitrify the base body. Thus, a translucent quartz glass crucible base body 8 was formed by cooling the molten and vitrified body. Then, after setting high temperature atmosphere 15 inside the inner cavity of the translucent quartz glass crucible base body 8 by means of

arc electrode 13 while rotating the mold 7, synthetic silica grain was supplied therein at a rate of 100 g/min. In this manner, a synthetic quartz glass inner layer about 2 mm in thickness was molten and joined monolithically with the inner surface of the translucent crucible base body 8. The diameter of the thus obtained quartz glass crucible was 24 inches. On pulling up single silicon crystal according to CZ method by filling the quartz glass crucible with polycrystalline silicon and melting, vigorous vibration was generated on the surface of the silicon melt to find seeding operation and consecutive operations unfeasible.

Comparative Example 2

By using the apparatus shown in Fig. 2, high purity natural silica grain subjected to purification treatment was fed into a rotating mold 7, and the grain was formed into a quartz glass crucible-like shape by the centrifugal force. Then, an arc electrode 13 was inserted into the quartz glass crucible base body, the aperture part was covered with a plate-like lid body 10, and a high temperature gaseous atmosphere was provided inside the inner cavity by using the arc electrode 13 to melt and vitrify the base body. Thus, a translucent quartz glass crucible base body 8 was formed by cooling the molten and vitrified body. Then, after setting high temperature atmosphere 15 inside the inner cavity of the translucent quartz glass crucible base body 8 by means of arc electrode 13 while rotating the mold 7, natural silica grain was supplied therein at a rate of 100 g/min. In this manner, a natural quartz glass inner layer about 2 mm in thickness was molten and joined monolithically with the inner surface of the translucent crucible base

body 8. The diameter of the thus obtained quartz glass crucible was 24 inches. On pulling up single silicon crystal according to CZ method by filling the quartz glass crucible with polycrystalline silicon and melting, perfect crystal was found unfeasible because disordering is generated on the single crystal after passage of about 50 hours, although no vibration is generated on the surface of the silicon melt.

INDUSTRIAL APPLICABILITY

The quartz glass crucible for pulling up single silicon crystals according to the present invention suffers less vibration of silicon melt surface on pulling up single silicon crystals and enables stable pulling up single silicon crystals at high yield without causing surface roughening or generation of cristobalite spots on the inner surface of the crucible. The quartz glass crucible above is of high industrial value, because it can be produced by a simple production method comprising supplying a synthetic silica grain, a natural silica grain, or a mixed grain of natural silica and synthetic silica to each of the portions of the crucible base, and then melting and vitrifying each of the powders for forming the inner layer.

CLAIMS

1. In a quartz glass crucible for pulling up single silicon crystal comprising a crucible base body having a bottom part and a straight shell part with an inner layer provided to the inner surface thereof, the quartz glass crucible is characterized by that said inner layer comprises a synthetic quartz glass layer from the lowest end to at least a height of $0.25H$; a natural quartz glass layer or a mixed layer of natural and synthetic quartz glass extended in a range of from at least $0.5H$ to $0.8H$; and one selected from a synthetic quartz glass layer, a natural quartz glass layer, and a mixed quartz glass layer of natural and synthetic quartz glass for the rest of the inner layer; wherein H represents the height from the lowest end of the bottom part to the upper end plane of the shell part.

2. The quartz glass crucible of claim 1, wherein the mixing ratio for the natural silica grain in the mixed grain of natural silica and synthetic silica for forming the mixed quartz glass of natural quartz glass and synthetic quartz glass accounts for 30 % or higher.

3. In a method for producing a quartz glass for pulling up single silicon crystal comprising setting a high temperature atmosphere inside the inner cavity portion of a quartz glass crucible base body attached to a rotating mold, and supplying a synthetic silica grain together with a natural silica grain or a mixed grain of natural silica and synthetic silica into said high temperature atmosphere to thereby form an inner layer on the inner surface of the crucible base body by melting and vitrifying the grain, the method is characterized by that it comprises forming a synthetic quartz glass inner layer

from the lowest end to at least a height of $0.25H$; a natural quartz glass layer or a mixed layer of natural and synthetic quartz glass extended in a range of from at least $0.5H$ to $0.8H$; and one selected from a synthetic quartz glass layer, a natural quartz glass layer, and a mixed quartz glass layer of natural and synthetic quartz glass for the rest of the inner layer; wherein H represents the height from the lowest end of the bottom part to the upper end plane of the shell part.

4. The method for producing a quartz glass for pulling up single silicon crystal of claim 3, wherein, in the method comprising supplying synthetic silica grain into a high temperature atmosphere from a silica grain supply nozzle to form a synthetic quartz glass inner layer on the bottom part of the crucible base and to the vicinity thereof, and then moving the silica grain supply nozzle to supply natural silica grain or a mixed grain of natural silica and synthetic silica to form an inner layer on the crucible base body, the silica grain is supplied in such a manner that the inner layer comprises a synthetic quartz glass inner layer from the lowest end to at least a height of $0.25H$; a natural quartz glass layer or a mixed layer of natural and synthetic quartz glass extended in a range of from at least $0.5H$ to $0.8H$; and one selected from a synthetic quartz glass layer, a natural quartz glass layer, and a mixed quartz glass layer of natural and synthetic quartz glass for the rest of the inner layer; wherein H represents the height from the lowest end of the bottom part to the upper end plane of the shell part.

5. The method for producing a quartz glass for pulling up single silicon crystal, comprising forming a first

quartz glass inner layer on the entire inner surface of the crucible base body by supplying a first silica grain into the high temperature atmosphere inside the crucible base body and melting and vitrifying the grain, and then forming an inner layer by melting and vitrifying a second silica grain supplied thereto, wherein, the second silica grain is supplied in such a manner that the inner layer comprises a synthetic quartz glass inner layer from the lowest end to at least a height of $0.25H$, and that a natural quartz glass layer or a mixed layer of natural and synthetic quartz glass extended in a range of from at least $0.5H$ to $0.8H$.

6. The method for producing a quartz glass for pulling up single silicon crystal of claim 5, wherein the first silica grain is a synthetic silica grain, and the second silica grain is natural silica grain or a mixed grain of natural silica and synthetic silica.