SPECIFICATION

TITLE OF INVENTION: QUARTZ GLASS CRUCIBLE, MANUFACTURING METHOD THEREOF, AND MANUFACTURING METHOD OF SILICON SINGLE CRYSTAL

TECHNICAL FIELD

[0001]

The present invention relates to a quartz glass crucible and a manufacturing method thereof, and particularly to a quartz glass crucible used for pulling up a silicon single crystal by the Czochralski method (CZ method). In addition, the present invention relates to a manufacturing method of a silicon single crystal using such a quartz glass crucible.

BACKGROUND ART

[0002]

Most of silicon single crystals are manufactured by the CZ method. In the CZ method, a polycrystalline silicon raw material is melted in a quartz glass crucible to generate a silicon melt, a seed crystal is immersed in the silicon melt, and the seed crystal is gradually pulled up while rotating the quartz glass crucible and the seed crystal. Thus, a large single crystal is grown at the lower end of the seed crystal. According to the CZ method, it is possible to increase a yield of large-diameter silicon single crystals.

[0003]

A quartz glass crucible is a silica glass container for holding a silicon melt during the pulling up step of the silicon single crystal. Therefore, the quartz glass crucible is required to have high durability to withstand a long duration use without being deformed at high temperature not less than the melting point of silicon. In addition, the quartz glass crucible is required to have high purity for preventing impurity

contamination of the silicon single crystal.

[0004]

It is known that a brown ring-shaped crystal of cristobalite, which is called brown ring, grows on the inner surface of the quartz glass crucible that comes into contact with the silicon melt when the silicon single crystal is pulled up. When the brown ring is peeled from the surface of the crucible and mixed into the silicon melt, it may be transported to the solid-liquid interface by melt convection and incorporated into the single crystal. Peeling of cristobalite causes dislocation in the silicon single crystal. Therefore, the inner surface of the crucible is actively crystallized by a crystallization accelerator to prevent the peeling of the crystal pieces.

[0005]

Regarding a method for strengthening the inner surface of the crucible by crystallization, for example, Patent Literature 1 describes a devitrification agent for a crucible with improved efficiency than a conventional one. The devitrification agent, which includes barium, and tantalum, tungsten, germanium, tin, or a combination of two or more thereof, is melted into a crucible during construction, applied to the surface of a finished crucible, and/or added to the silicon melt used for crystal pulling up.

[0006]

Patent Literature 2 describes a surface-treated crucible with improved dislocation-free performance. The crucible includes first and second devitrification accelerators distributed on the inner and outer surfaces, respectively, of the sidewall formation of the main body of vitreous silica. The first devitrification accelerator is distributed such that a first layer of substantially devitrified silica is formed on the inner surface of the crucible, which comes into contact with the molten semiconductor material when the semiconductor material melts in the crucible during crystal growth. In

addition, the second devitrification accelerator is distributed such that a second layer of substantially devitrified silica is formed on the outer surface of the crucible when the semiconductor material melts in the crucible during crystal growth.

[0007]

Patent Literature 3 describes a quartz glass crucible that can withstand a very long duration single crystal pulling up step such as multi-pulling up. This quartz glass crucible includes a crucible main body consisting of quartz glass, and first and second crystallization accelerator-containing coating films formed on the inner and outer surfaces of the crucible main body, respectively. The first and second crystallization accelerator-containing coating films contain a polymer, and the crystallization accelerator is a water-insoluble barium compound. By the action of the crystallization accelerator, a crystal layer composed of an aggregate of dome-shaped or columnar crystal grains is formed on the surface layer portions of the inner and outer surfaces of the crucible main body.

BACKGROUND ART LITERATURE

PATENT LITERATURE

[0008]

Patent Literature 1: Japanese Unexamined Patent Application No. 2019-509969

Patent Literature 2: Japanese Patent Laid-open Publication No. H09-110590

Patent Literature 3: Japanese Patent Laid-open Publication No. 2020-200236

SUMMARY OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009]

As described above, the method of applying a crystallization accelerator is effective in uniformly crystallizing the inner surface of the crucible. However, not only

is the crucible filled with a large amount of polycrystalline silicon lumps such that a considerably large load is applied to the bottom surface of the crucible, but also individual silicon lumps are finely crushed during the manufacturing process and have sharp corners, and thus damage to the coating film of the crystallization accelerator becomes an issue. In a case where a portion of the coating film of the crystallization accelerator is peeled from the time when the crucible is filled with the polycrystalline silicon raw material until the melting is completed, it is difficult to uniformly crystallize the inner surface of the crucible, and thus the formation of a coating film that is difficult to peel is strongly required.

[0010]

Accordingly, an object of the present invention is to provide a quartz glass crucible capable of preventing the peeling of the coating film of the crystallization accelerator and maintaining the in-plane distribution of the concentration of the crystallization accelerator as uniform as possible, and a manufacturing method of the quartz glass crucible. Another object of the present invention is to provide a manufacturing method of a silicon single crystal using such a quartz glass crucible.

MEANS FOR SOLVING THE PROBLEMS

[0011]

In order to solve the issue described above, a quartz glass crucible according to the present invention includes a crucible base body consisting of silica glass and a coating film containing a crystallization accelerator formed on an inner surface of the crucible base body, in which the coating film has a peel strength of 0.3 kN/m or more.

[0012]

According to the present invention, peeling of the coating film of the crystallization accelerator can be prevented.

Therefore, the inner surface of the crucible base body can be uniformly crystallized during the single crystal pulling up step, and the dislocation and pinhole formation in the silicon single crystal can be prevented to increase the yield.

[0013]

In the present invention, it is preferable that a concentration of the crystallization accelerator is 2.5×10^{15} atoms/cm^2 or less, and a peel strength of the coating film is 0.6 kN/m or more. In a case where the peel strength of the coating film is 0.6 kN/m or more, the inner surface of the crucible base body can be uniformly crystallized even in a case where the concentration of the crystallization accelerator is 2.5×10^{15} atoms/cm^2 or less.

[0014]

In the present invention, the concentration of the crystallization accelerator is preferably higher than 2.5×10^{15} atoms/cm^2. In a case where the concentration of the crystallization accelerator is higher than 2.5×10^{15} atoms/cm^2, even in a case where a portion of the coating film is peeled due to the low peel strength of the coating film, due to the action of the strong crystallization accelerator, crystallization also progresses in the lateral direction, making it possible to crystallize the peeled portion. Therefore, the inner surface of the crucible base body can be uniformly crystallized.

[0015]

In the present invention, a range of the coating film on the bottom of the crucible base body is preferably a range of 0.25 times or more and 1 time or less a crucible outer diameter. Thus, by setting the peel strength of the coating film to 0.3 kN/m or more in the range of at least 0.25 times the crucible outer diameter, dislocations in the silicon single crystal due to peeling of cristobalite and the rate of pinhole formation in silicon single crystal can be reduced.

[0016]

In the present invention, the coating film formed within a range of 0.5 times or less an outer diameter of the crucible base body from a center of the bottom preferably has a peel strength of 0.9 kN/m or more. Thereby, it is possible to reduce the dislocation and the rate of pinhole formation in the silicon single crystal.

[0017]

In the present invention, the crystallization accelerator is preferably a water-soluble compound of an element (Mg, Ca, Sr, or Ba) in the group 2a, which has no carbon atoms in a molecule.

Thereby, the carbon concentration in the coating film can be reduced, and the carbon contamination in the silicon single crystal can be reduced. In addition, the solubility in water is high and the aqueous solution can be easily handled, and thus uniform application of the crystallization accelerator to the crucible surface can be easily achieved.

[0018]

The thickness of the coating film is preferably 0.1 μm or more and 50 μm or less.

Thereby, a uniform coating film can be formed on the inner surface of the crucible base body.

[0019]

The surface roughness (Ra) of the coating film is preferably 0.1 μm or more and 0.25 μm or less. As a result, peeling of the coating film can be prevented, and the inner surface of the crucible base body can be uniformly crystallized.

[0020]

The average carbon concentration in the coating film and the crucible base body

within the range of 0 μm or more and 300 μm or less in depth from the inner surface thereof is preferably 1.0×10^{12} atoms/cc or more and 3.0×10^{19} atoms/cc or less. In the quartz glass crucible according to the present invention, the carbon concentration not only in the vicinity of the inner surface of the crucible base body but also in the coating film containing the crystallization accelerator is reduced, and thus the amount of carbon incorporated into the silicon single crystal can be reduced.

[0021]

The average carbon concentration in the coating film is preferably 3.0×10^{18} atoms/cc or less. Thereby, the amount of carbon incorporated into the silicon single crystal can be further reduced. The average carbon concentration in the coating film can be measured by Secondary Ion Mass Spectrometry (SIMS).

[0022]

In addition, a manufacturing method of a quartz glass crucible according to the present invention includes a step of producing a crucible base body consisting of silica glass, and a step of spraying a coating liquid containing a crystallization accelerator on an inner surface of the crucible base body to form a coating film of the crystallization accelerator, in which the step of spraying the coating liquid includes spraying the coating liquid with an average droplet diameter of 5 μm or more and 1,000 μm or less using a two-fluid nozzle that mixes gas and liquid at a spray tip and sprays the mixture.

[0023]

According to the present invention, liquid dripping of the coating liquid on the surface of the crucible can be prevented to uniformly apply the crystallization accelerator. Therefore, a uniform coating film can be formed on the inner surface of the crucible base body, and the peel strength of the coating film can be increased.

[0024]

In the step of forming the coating film in the present invention, it is preferable that the maximum thickness of the coating film formed by one applying is set to 0.5 μm or less, and the coating film is formed into multiple layers by alternately repeating drying of the coating film and reapplying. Thereby, a dense and uniform coating film can be formed, and the peel strength of the coating film can be increased.

[0025]

In the present invention, the spray amount of the coating liquid is preferably 300 mL/min or less. Thus, by suppressing the spray amount of the coating liquid to 300 mL/min or less, a dense coating film can be uniformly formed.

[0026]

The crystallization accelerator is preferably a water-soluble compound of an element (Mg, Ca, Sr, or Ba) in the group 2a, which has no carbon atoms in a molecule. Thereby, the carbon concentration in the coating film can be reduced, and the carbon contamination in the silicon single crystal can be reduced. In addition, the solubility in water is high and the aqueous solution can be easily handled, and thus uniform application of the crystallization accelerator to the crucible surface can be easily achieved.

[0027]

In the step of forming the coating film, the spraying of the coating liquid is preferably performed while heating the crucible base body at a temperature of 60°C or more and 500°C or less, and more preferably heating at a temperature of 100°C or more and 180°C or less. In this case, the spraying of the coating liquid is preferably performed while heating the crucible base body such that a difference between a boiling point of a solvent in the coating liquid and a temperature of the crucible base body is −40.0°C or more and 100°C or less, and it is more preferable to set the heating

temperature of the crucible base body to the boiling point of the solvent or more and 80°C or less. Thereby, it is possible to suppress the generation of a carbonate and to reduce the carbon concentration in the coating film.

[0028]

The step of spraying the coating liquid is preferably performed under a low vacuum of 1×10^2 Pa or more and 1×10^5 Pa or less. By spraying the coating liquid to the heated crucible base body under a low vacuum in this way, it is possible to instantly evaporate the solvent and to uniformly fix the crystallization accelerator, and unevenness in the coating film due to liquid dripping of the coating liquid on the crucible surface, or the like can be prevented. In addition, since the solvent can be evaporated in a short time to shorten the heating time, the generation of a carbonate can be suppressed.

[0029]

Furthermore, in the manufacturing method of a silicon single crystal according to the present invention, a silicon single crystal is pulled up by the CZ method using the quartz glass crucible according to the present invention. According to the present invention, it is possible to prevent a decrease in yield due to dislocations in a silicon single crystal.

EFFECTS OF THE INVENTION

[0030]

According to the present invention, it is possible to provide a quartz glass crucible in which a coating film of a crystallization accelerator is not easily peeled, and a manufacturing method of the quartz glass crucible. In addition, according to the present invention, it is possible to provide a manufacturing method of a silicon single crystal using such a quartz glass crucible.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031]

[FIG. 1] is a schematic perspective view illustrating a configuration of a quartz glass crucible according to an embodiment of the present invention.

[FIG. 2] is a schematic side sectional view and a partially enlarged view of the quartz glass crucible illustrated in FIG. 1.

[FIG. 3] is a schematic diagram illustrating a method of measuring the peel strength of a coating film.

[FIG. 4] is a schematic plan view showing the measurement positions of the carbon concentration at the bottom of the crucible.

[FIG. 5] is a schematic diagram illustrating a manufacturing method of a quartz glass crucible according to a rotational molding method.

[FIG. 6] is a schematic diagram illustrating a method of applying a crystallization accelerator to the inner surface of a crucible base body.

[FIG. 7] is a diagram for explaining a single crystal pulling up step using the quartz glass crucible according to the present embodiment, and is a schematic sectional view illustrating a configuration of a single crystal pulling apparatus.

MODE FOR CARRYING OUT THE INVENTION

[0032]

Hereinafter, preferred embodiments of the present invention are described in detail with reference to the accompanying drawings.

[0033]

FIG. 1 is a schematic perspective view illustrating the configuration of a quartz glass crucible according to an embodiment of the present invention. In addition, FIG. 2 is a schematic side sectional view and a partially enlarged view of the quartz glass crucible illustrated in FIG. 1.

[0034]

As shown in FIG. 1 and FIG. 2, a quartz glass crucible 1 is a silica glass container for holding a silicon melt and has a cylindrical sidewall 10a, a bottom 10b provided below the sidewall 10a, and a corner 10c provided between the sidewall 10a and the bottom 10b. The bottom 10b is preferably a so-called round bottom that is gently curved, but may also be a so-called flat bottom. The corner 10c is a portion having a larger curvature than the bottom 10b.

[0035]

The aperture (diameter) of the quartz glass crucible 1 also varies depending on the diameter of the silicon single crystal ingot that is pulled up from the silicon melt, but is 18 inches (approximately 450 mm) or more, preferably 22 inches (approximately 560 mm), and particularly preferably 32 inches (approximately 800 mm) or more. This is because such a large crucible is used for pulling up a large silicon single crystal ingot having a diameter of 300 mm or more, and is required not to affect the quality of the single crystal even with the long duration use.

[0036]

The wall thickness of the crucible varies slightly depending on its part, but it is preferable that the wall thickness of the sidewall 10a of the crucible of 18 inches or more is 6 mm or more, and the wall thickness of the sidewall 10a of the crucible of 22 inches or more is 7 mm or more, and the wall thickness of the sidewall 10a of the crucible of 32 inches or more is 10 mm or more. As a result, a large amount of silicon melt can be stably held at high temperature.

[0037]

As shown in FIG. 2, a quartz glass crucible 1 includes a crucible base body 10 consisting of silica glass and a coating film 13 of a crystallization accelerator and formed

on the inner surface 10i of the crucible base body 10. The crucible base body 10 mainly has a two-layer structure, and has a transparent layer 11 containing no bubbles (non-bubble layer) and a bubble layer 12 containing a large number of minute bubbles (opaque layer), and the coating film 13 is provided inside the transparent layer 11.

[0038]

The transparent layer 11 is a layer that configures the inner surface 10i of the crucible base body 10, which comes into contact with the silicon melt, and is provided to prevent a yield of the silicon single crystals from decreasing due to bubbles in the silica glass. Since the inner surface 10i of the crucible reacts with the silicon melt to melt away, the bubbles in the vicinity of the inner surface of the crucible cannot be trapped in the silica glass and the bubbles burst due to thermal expansion, and thus the crucible fragments (silica fragments) may be peeled. In a case where the crucible fragments released into the silicon melt are transported by melt convection to a growth interface of the silicon single crystal and are incorporated into the silicon single crystal, they cause dislocation in the single crystal. In addition, in a case where the bubbles released into the silicon melt float up and reach a solid-liquid interface and are incorporated into the single crystal, they cause pinhole formation in the silicon single crystal.

[0039]

Containing no bubbles in the transparent layer 11 means having a bubble content and a bubble size to the extent that the single crystallization rate does not decrease due to bubbles. Such a bubble content is, for example, 0.1 vol% or less, and the bubble diameter is, for example, 100 μm or less.

[0040]

The thickness of the transparent layer 11 is preferably 0.5 to 10 mm, and is set to an appropriate thickness for each portion of the crucible such that the bubble layer 12 is

not exposed by completely vanishing the transparent layer 11 due to melting away during a crystal pulling up step. The transparent layer 11 is preferably provided over the entire crucible from the sidewall 10a to the bottom 10b of the crucible, but the transparent layer 11 can be omitted at the upper end portion of the crucible that does not come into contact with the silicon melt.

[0041]

The bubble layer 12 is a principal layer of the crucible base body 10 located on the outer side than the transparent layer 11 and is provided to improve the heat retention property of the silicon melt in the crucible, and to heat the silicon melt in the crucible as uniformly as possible by dispersing radiant heat from a heater in a single crystal pulling apparatus. Therefore, the bubble layer 12 is provided over the entire crucible from the sidewall 10a to the bottom 10b.

[0042]

The bubble content of the bubble layer 12 is higher than the transparent layer 11 and is preferably more than 0.1 vol% and 5 vol% or less. This is because in a case where the bubble content of the bubble layer 12 is 0.1 vol% or less, the bubble layer 12 cannot exhibit the required heat retention function. In addition, this is because when the bubble content of the bubble layer 12 exceeds 5 vol%, the crucible may be deformed due to the thermal expansion of the bubbles and decrease the yield of the single crystals, and further heat transfer property is insufficient. From the viewpoint of the balance between the heat retention property and the heat transfer property, the bubble content of the bubble layer 12 is particularly preferably 1 to 4 vol%. The above-mentioned bubble content is a value obtained by measuring the crucible before use under a room temperature environment.

[0043]

In order to prevent contamination of the silicon melt, the silica glass configuring the transparent layer 11 is preferably of high purity. Therefore, the crucible base body 10 preferably has a two-layer structure of a synthetic silica glass layer (synthetic layer) formed from synthetic quartz powder and a natural silica glass layer (natural layer) formed from natural quartz powder. The synthetic quartz powder can be manufactured by vapor-phase oxidation of silicon tetrachloride ($SiCl_4$) (dry synthesis method) or by hydrolysis of silicon alkoxide (sol-gel method). In addition, the natural quartz powder is manufactured by pulverizing natural minerals containing α-quartz as a main component into granules.

[0044]

The two-layer structure of a synthetic silica glass layer and a natural silica glass layer can be manufactured by depositing the natural quartz powder along the inner surface of the mold for manufacturing the crucible, depositing the synthetic quartz powder thereon, and melting these raw material quartz powder with Joule heat generated by arc discharge. The arc melting step includes strongly evacuating from outside of the deposited layer of raw material quartz powder to remove bubbles and form the transparent layer 11, stopping or weakening the evacuation to form the bubble layer 12. Therefore, the interface between the synthetic silica glass layer and the natural silica glass layer does not necessarily coincide with the interface between the transparent layer 11 and the bubble layer 12, but the synthetic silica glass layer preferably has, as similar to the transparent layer 11, a thickness to the extent that does not completely vanish due to melting away of the inner surface of the crucible during the single crystal pulling up step.

[0045]

The quartz glass crucible 1 according to the present embodiment has a

configuration in which the inner surface 10i of the crucible base body 10 is covered with a coating film 13 of a crystallization accelerator. The crystallization accelerator is a compound of an element (Mg, Ca, Sr, or Ba) in the group 2a and plays a role in accelerating crystallization of the inner surface 10i of the crucible base body 10 during the single crystal pulling up step. In the present embodiment, the crystallization accelerator is preferably a hydroxide or oxide having no carbon atoms in the molecule, and particularly preferably a hydroxide that is highly soluble in water and easy to handle. Barium (Ba) is particularly preferred as the element in the group 2a as the crystallization accelerator. This is because barium has a smaller segregation coefficient than silicon, is stable at room temperature, and is easy to handle. In addition, barium has an advantage that the crystallization rate of the crucible is not attenuated with crystallization and orientation growth is induced more strongly than other elements.

[0046]

The coating film 13 of the crystallization accelerator is formed in a range of 0.25 times or more and 1 time or less a crucible outer diameter. In the present embodiment, the coating film 13 of the crystallization accelerator is preferably formed on the entire inner surface 10i of the crucible base body 10 excluding the vicinity of the upper end of the rim. The reason for excluding the vicinity of the upper end of the rim is that the vicinity of the upper end of the rim does not come into contact with the silicon melt and does not necessarily need to be crystallized. This is also because peeling of crystals is occurred in the vicinity of the upper end of the rim during crystallization and thus the crystal pieces mixed in the silicon melt cause dislocations in the silicon single crystal.

[0047]

The thickness of the coating film 13 is not particularly limited, but is preferably 0.1 to 50 μm and particularly preferably 1 to 20 μm. This is because in a case where the

thickness of the coating film 13 is too thin, the peel strength of the coating film is weak, and the peeling of the coating film 13 causes nonuniform crystallization. Also in a case where the coating film 13 is too thick, the peel strength is lowered and the crystallization is nonuniform.

[0048]

It is preferable that the coating film 13 does not peel, and for this purpose a peel strength of 0.3 kN/m or more is required. The coating film 13 needs to satisfy such peel strength at least in the bottom central region of the crucible base body 10, and preferably satisfies such peel strength over the entire region where the coating film 13 is formed. In this example, the bottom central region of the crucible base body 10 means a region within a range of 0.5r (r is the outer diameter (radius) of the crucible) from the center of the bottom of the crucible base body 10.

[0049]

FIG. 3 is a schematic diagram illustrating a method of measuring the peel strength of a coating film 13.

[0050]

As shown in FIG. 3, the peel strength of the coating film 13 can be measured using a SAICAS (Surface And Interfacial Cutting Analysis System) 30. The SAICAS 30 can obtain the apparent shear strength from the vertical load F_Z (vertical force) and the horizontal load F_Y (horizontal force) when the diamond blade 31 obliquely cuts the coating, and can obtain the peel strength from the horizontal load F_Y (horizontal force) when the diamond blade 31 parallelly cuts the interface between the coating and base body. The peel strength of the coating film 13 can be obtained from the horizontal load F_Y when a crucible piece sample 1s having the coating film 13 formed thereon is placed on a stage and diamond blade 31 cuts the interface (the inner surface 10i of the crucible

base body 10) between the coating film 13 and the crucible base body 10.

[0051]

The concentration of the crystallization accelerator contained in the coating film 13 is preferably 2.5×10^{15} atoms/cm^2 or more. In this way, in a case where the concentration of the crystallization accelerator is relatively high, even in a case where a portion of the crystallization accelerator is peeled, it is possible to accelerate crystallization in the surface direction and to achieve the uniform crystallization of the inner surface 10i of the crucible base body 10.

[0052]

On the other hand, in a case where the concentration of the crystallization accelerator on the crucible surface is high, the crystallization rate on the crucible surface is high, and crystallization also proceeds in the lateral direction (surface direction), and thus the requirement of the peel strength is alleviated than the case where the concentration is low. Therefore, in a case where the concentration of the crystallization accelerator on the surface of the crucible is higher than 2.6×10^{15} atoms/cm^2, the peel strength of the crystallization accelerator may be 0.3 kN/m or more.

[0053]

The concentration of the crystallization accelerator may also be 2.5×10^{15} atoms/cm^2 or less, and the peel strength of the coating film 13 in that case is preferably 0.6 kN/m or more. In a case where the peel strength of the coating film is high, the inner surface 10i of the crucible base body 10 can be crystallized reliably without using a high-concentrated crystallization accelerator.

[0054]

In a case where the concentration of the crystallization accelerator on the surface of the crucible is as low as 2.6×10^{15} atoms/cm^2 or less, the crystal nuclei of brown rings

cannot be uniformly formed when the crystallization accelerator is peeled, and thus the peel strength of the crystallization accelerator is required to be 0.6 kN/m or more.

[0055]

In the bottom central region of the crucible base body 10, the peel strength of the coating film 13 is particularly preferably 0.9 kN/m or more. As described above, since the quartz glass crucible 1 is filled with a large amount of polycrystalline silicon raw material and a very large load is applied to the bottom of the crucible, the coating film 13 is likely to be peeled. However, in a case where the coating film 13 on the bottom of the crucible base body 10 has a peel strength of 0.9 kN/m or more, peeling can be prevented even when such a large load is applied.

[0056]

The surface roughness (Ra) of the coating film 13 is preferably 0.1 μm or more and 0.25 μm or less. This is because in a case where the surface roughness (Ra) of the coating film is greater than 0.25 μm, the coating film is likely to be peeled, and it is difficult to reduce the surface roughness (Ra) of the coating film to less than 0.1 μm in terms of manufacturing.

[0057]

It is preferable that the carbon concentration in the silicon single crystal grown by the CZ method is as low as possible, and for this purpose the amount of carbon supplied from the quartz glass crucible 1 needs to be as small as possible, particularly the carbon concentration not only in the crucible base body 10 but also in the coating film 13 needs to be paid attention. Therefore, in the quartz glass crucible 1 according to the present embodiment, the average carbon concentration in the coating film 13, and the crucible base body 10 within the range of 0 μm to 300 μm in depth from the inner surface 10i of the crucible base body 10 (that is, the surface layer portion of the crucible base

body 10) is 1.0×10^{12} atoms/cc or more and 3.0×10^{19} atoms/cc or less. Thereby, the amount of carbon dissolved in the silicon melt from the quartz glass crucible 1 can be reduced, making it possible to manufacture a silicon single crystal having a low carbon concentration.

[0058]

The average carbon concentration in the coating film 13 is preferably 3.0×10^{18} atoms/cc or less. In a case where the average oxygen concentration in the coating film is 3.0×10^{18} atoms/cc or less, the amount of carbon supplied from the coating film to the silicon melt can be reduced.

[0059]

Both the average carbon concentration in the coating film 13 and the average carbon concentration in the crucible base body 10 within the range of 0 μm to 300 μm in depth from the inner surface of the crucible base body 10 are preferably 1.3×10^{16} atoms/cc or less. Furthermore, the average carbon concentration in the crucible base body 10 within the range of 300 μm or more and 2,000 μm or less in depth from the inner surface of the crucible base body 10 is preferably 1.1×10^{19} atoms/cc or less. Thereby, a silicon single crystal with a sufficiently low carbon concentration can be manufactured.

[0060]

The average carbon concentration in the crucible base body 10 within the range of 300 μm to 2,000 μm in depth from the inner surface of the crucible base body 10 may be higher than the average carbon concentration of the surface layer portion within the range of 0 μm to 300 μm, but is preferably 1.1×10^{19} atoms/cc or less.

[0061]

Variation in the in-plane distribution of carbon concentration on the inner surface of the crucible causes in-plane variation in the thickness of the cristobalite layer

formed on the inner surface of the crucible, which causes the peeling of the cristobalite crystals. In particular, in a case where the crystal layer is uneven at the bottom of the crucible, it causes pinhole formation in the silicon single crystal. Therefore, it is desirable that the variation in the in-plane distribution of the carbon concentration is small at the bottom of the crucible.

[0062]

Specifically, the variation coefficient of is preferably 1.1 or less when measuring the carbon concentration at five points P1 to P5 of the bottom of the crucible. Here, as shown in FIG. 4, the five points of the bottom of the crucible are the center P1 of the bottom and four points P2 to P5 that are the same distance away from the center P1 in four directions. The other four points P2 to P5 other than the center P1 of the bottom are preferably set to be located 0.08r to 0.7r (r is the radius of the outer diameter of the crucible base body 10) away from the center P1 (first measurement point) of the bottom of the crucible base body 10 in the radial direction. The third to fifth measurement points P3 to P5 are positions rotated 90° clockwise in the circumferential direction from the second to fourth measurement points P2 to P4, respectively.

[0063]

The quartz glass crucible 1 according to the present embodiment can be manufactured by applying a crystallization accelerator to the inner surface of the crucible base body 10 after manufacturing the crucible base body 10 by a so-called rotational molding method.

[0064]

FIG. 5 is a schematic diagram illustrating a manufacturing method of the quartz glass crucible according to a rotational molding method.

[0065]

As shown in FIG. 5, In the rotational molding method, a mold 14 having a cavity matching the outer shape of the crucible is prepared, and the natural quartz powder 16a and the synthetic quartz powder 16b are sequentially filled along the inner surface 14i of the rotating mold 14 to form a deposited layer 16 of raw material quartz powder. The raw material quartz powder stay in a fixed position while sticking to the inner surface 14i of the mold 14 by centrifugal force, and are maintained in a crucible shape.

[0066]

In manufacturing the quartz glass crucible 1, crystalline or amorphous silica powder having a carbon content of less than 6 ppm is prepared, and the quartz glass crucible 1 is manufactured using this silica powder as a raw material in the vicinity of the inner surface. By using silica powder having a very low carbon content as the raw material in the vicinity of the inner surface of the quartz glass crucible, the carbon concentration in the vicinity of the inner surface of the crucible can be reduced.

[0067]

Next, an arc electrode 15 is installed in the mold 14, and the deposited layer 16 of the raw material quartz powder is arc-melted from the inside of the mold 14. Specific conditions such as heating time and heating temperature are appropriately determined in consideration of the properties of the raw material quartz powder, the size of the crucible, and the like.

[0068]

In order to reduce the carbon concentration on the inner surface 10i of the crucible base body 10, it is preferable to use a carbon electrode having a bulk specific gravity of 1.50 g/cc to 1.75 g/cc and a specific resistivity of 330 μΩ·cm to 600 μΩ·cm as the arc electrode 15. During arc melting, CO_2 gas is generated by oxidative wear of the carbon electrode from the surface. In this example, in a case where the specific gravity

or specific resistivity of the electrode is lower than the above range, the electrode will be rapidly consumed, thereby generating a large amount of CO_2 gas and adversely affecting the shape of the crucible. On the other hand, in a case where the specific gravity or specific resistivity of the carbon electrode exceeds the above range, carbon powder may scatter from the electrode surface and be incorporated into the crucible before they are burned out by the arc heat. However, in the present embodiment, a carbon electrode having a specific gravity and a specific resistivity within the above ranges is used, and thus an increase in CO_2 gas and scattering of carbon powder can be suppressed. Therefore, the carbon concentration in the vicinity of the inner surface of the crucible base body 10 can be reduced.

[0069]

During arc melting, the amount of bubbles in the molten silica glass is controlled by evacuating the deposited layer 16 of raw material quartz powder from a large number of vent holes 14a provided on the inner surface 14i of the mold 14. Specifically, the transparent layer 11 is formed by evacuating the raw material quartz powder at the start of arc melting, and the bubble layer 12 is formed by stopping the evacuation to the raw material quartz powder after the transparent layer 11 is formed.

[0070]

Since the arc heat is gradually transferred from the inside to the outside of the deposited layer 16 of the raw material quartz powder to melt the raw material quartz powder, by changing decompression conditions at the timing at which the raw material quartz powder start to melt, the transparent layer 11 and the bubble layer 12 can be made separately. That is, in a case where decompression melting for strengthening the decompression is performed at the timing at which raw material quartz powder melt, arc atmosphere gas is not trapped in the glass, and thus the molten silica becomes silica glass

containing no bubbles. In addition, in a case where normal melting (atmospheric pressure melting) for weakening the decompression is performed at the timing at which raw material quartz powder melt, arc atmosphere gas is trapped in the glass, and thus the molten silica becomes silica glass containing a large number of bubbles.

[0071]

Subsequently, the arc melting is terminated and the crucible is cooled. As described above, the crucible base body 10 is completed, in which the transparent layer 11 and the bubble layer 12 are provided in that order from the inside toward the outside of the crucible wall.

[0072]

Next, the crucible base body 10 is formed in a predetermined shape by cutting the rim portion, or the like, then cleaned with a cleaning liquid, and further rinsed with pure water. The cleaning liquid is preferably prepared by diluting hydrofluoric acid of semiconductor grade or higher with pure water of TOC ≤ 2 ppb to adjust to 10 to 40 w%.

[0073]

Next, the crystallization accelerator is applied to the inner surface 10i of the crucible base body 10. In order to uniformly disperse the crystallization accelerator on the inner surface 10i, a coating liquid is prepared, in which the crystallization accelerator is dissolved in pure water (15°C to 25°C, 17.2 MΩ or more, and TOC ≤ 2 ppb) or a high-purity organic solvent. At that time, the solution is stirred with a stirrer in order to increase the solubility of the powder of the crystallization accelerator and make the concentration of the solution uniform.

[0074]

Next, the crucible base body 10 is heated at a temperature of 60°C to 500°C with a halogen heater or clean oven installed in a clean room, and then spraying of the coating

liquid with a spray nozzle is performed. When the coating liquid comes into contact with the high-temperature crucible, the solvent instantly evaporates, and the crystallization accelerator component is fixed to the crucible. As described above, the crystallization accelerator is a compound of an element (Mg, Ca, Sr, or Ba) in the group 2a, and in particular, a highly hydrophilic hydroxide thereof is most suitable for enhancing fixability to the crucible.

[0075]

The hydroxide of an element of the group 2a reacts with carbon dioxide gas in the atmosphere to form carbonate (for example, in a case of barium hydroxide, 2.5% of barium hydroxide becomes barium carbonate). Carbon on the inner surface of the quartz glass crucible is directly incorporated into the silicon melt when a polysilicon is melted. Furthermore, since the carbon element incorporated into the silicon single crystal accelerates oxygen precipitation and affects device performance such as current leakage to reduce the formation of carbonate, it is important that the surface temperature of the crucible is set to 500°C or less, and preferably 200°C or less. Furthermore, in order to accelerate evaporation of the solvent, it is preferable to heat the crucible base body 10 such that the difference between the boiling point of the solvent and the temperature of the crucible is -40.0°C to 100°C.

[0076]

In order to evaporate the solvent in a short time and reduce the formation of carbonate, the heating temperature of the crucible base body 10 is set more preferably to the boiling point of the solvent or more and 80°C or less. This is because in a case where the temperature of the crucible base body 10 is lower than the boiling point of the solvent, the evaporation time of the solvent becomes long, and the thickness of the coating film and the concentration distribution of the crystallization accelerator become

nonuniform, thereby reducing the peel strength of the coating film. In addition, in a case where the evaporation time of the solvent becomes long, condensation of the coating liquid may occur on the surface of the crucible, which may cause the carbon concentration to become high and nonuniform. In a case where the temperature of the crucible base body 10 is 80°C or less, the carbon concentration in the coating film can be reduced by sufficiently suppressing the generation of carbonate.

[0077]

In spraying of the coating liquid, a two-fluid nozzle that mixes gas and liquid at a spray tip and sprays the mixture is preferably used and the average droplet diameter is preferably adjusted to 5 μm to 1,000 μm. This is because in a case where the droplet diameter is too large, the fixing of the coating liquid becomes nonuniform, and the uniformity of the coating film deteriorates, resulting in a decrease in peel strength, and in a case where the droplet diameter is too small, the spraying of the coating liquid is difficult. The average droplet diameter is particularly preferably 200 μm or less.

[0078]

The spray amount of the coating liquid is preferably 300 mL/min or less. This is because in a case where the spray amount of the coating liquid is more than 300 mL/min, the liquid dripping of the coating liquid is likely to occur on the coating surface, making it difficult to uniformly fix the crystallization accelerator.

[0079]

The spraying of the coating liquid is preferably performed under a low vacuum of 1×10^2 Pa to 1×10^5 Pa. The evaporation of the solvent is accelerated under low pressure (vacuum), and the crystallization accelerator can be fixed uniformly, thereby the coating film having high peel strength can be formed. In addition, in a case where the solvent is evaporated in a short time, the heating time is shortened, and thus the

generation of carbonate can be suppressed.

[0080]

In the formation of the coating film, it is preferable that the thickness of the crystallization accelerator formed by one application is set to about 0.5 μm at the maximum, and the application is performed in several steps until the desired concentration is achieved. Thereby, the strength of the coating film can be improved.

[0081]

In a case where the crucible is only simply heated when spraying the coating liquid, the coating film tends to become patchy, and it is difficult to form a dense and uniform coating film. However, by controlling the coating conditions as described above, a dense and uniform coating film can be formed, and the peel strength of the coating film can be improved.

[0082]

FIG. 6 is a schematic diagram illustrating a method of applying the crystallization accelerator to the inner surface 10i of the crucible base body 10.

[0083]

As shown in FIG. 6, in the application of the crystallization accelerator, the crucible base body 10 is placed on the rotary support 17A with the opening of the crucible base body 10 facing upward, and the coating liquid 6 is sprayed from the spray nozzle 19 attached to a distal end of the robot arm 18 installed inside the crucible base body 10. At this time, in order to prevent the liquid dripping of the coating liquid 6, it is preferable to install a heater 17B outside the crucible base body 10 and apply while heating the crucible base body 10 to 60°C to 500°C, and particularly preferably 100°C to 180°C. In a case where the surface temperature of the crucible base body 10 is 60°C or more, the solvent instantly evaporates on the surface of the crucible base body 10, and

thus the crystallization accelerator can be uniformly fixed on the inner surface 10i of the crucible base body 10.

[0084]

In a case where the crystallization accelerator is a hydroxide of metal, it reacts with carbon dioxide gas in the atmosphere to form a carbonate. For example, 2.5% of barium hydroxide becomes barium carbonate in the atmosphere and normal pressure. The carbonate in the coating film 13 causes an increase in the carbon concentration of the silicon single crystal. In order to suppress the formation of such carbonates, the surface temperature of the crucible when applying the crystallization accelerator is set preferably to 500°C or less and particularly preferably to the boiling point of the solvent or more and 80°C or less. Thereby, the weight ratio of the carbonate in the total weight of the coating film can be suppressed to 20.0 w% or less.

[0085]

FIG. 7 is a diagram for explaining a single crystal pulling up step using the quartz glass crucible 1 according to the present embodiment, and is a schematic sectional view illustrating the configuration of a single crystal pulling apparatus.

[0086]

As shown in FIG. 7, a single crystal pulling apparatus 20 is used for the pulling up step of a silicon single crystal by the CZ method. The single crystal pulling apparatus 20 includes a water-cooled chamber 21, a quartz glass crucible 1 holding a silicon melt in the chamber 21, a carbon susceptor 22 holding the quartz glass crucible 1, a rotating shaft 23 supporting the carbon susceptor 22 to be capable of rotation and elevation, a shaft driving mechanism 24 that rotates and elevation-drives the rotating shaft 23, a heater 25 that is arranged around the carbon susceptor 22, a single crystal pulling-up wire 28 that is arranged above the quartz glass crucible 1 and on the same axis

with the rotating shaft 23, and a wire winding mechanism 29 arranged above the chamber 21.

[0087]

The chamber 21 is configured by a main chamber 21a and a slender cylindrical pull chamber 21b which is connected to an upper opening of the main chamber 21a. The quartz glass crucible 1, the carbon susceptor 22, and the heater 25 are provided in the main chamber 21a. A gas entry 21c for introducing inert gas (purge gas) such as argon gas or a dopant gas into the main chamber 21a is provided in the upper portion of the pull chamber 21b, and a gas outlet 21d for discharging atmospheric gas inside the main chamber 21a is provided in the lower portion of the main chamber 21a.

[0088]

The carbon susceptor 22 is used to maintain the shape of the quartz glass crucible 1 which is softened at high temperature, and holds the quartz glass crucible 1 to wrap around it. The quartz glass crucible 1 and the carbon susceptor 22 configure a double-structured crucible that supports the silicon melt in the chamber 21.

[0089]

The carbon susceptor 22 is fixed to the upper end of the rotating shaft 23, and the lower end of the rotating shaft 23 passes through the bottom of the chamber 21 and is connected to a shaft driving mechanism 24 provided outside of the chamber 21.

[0090]

The heater 25 is used to melt the polycrystalline silicon raw material filled in the quartz glass crucible 1 to generate the silicon melt 3, as well as to keep a molten state of the silicon melt 3. The heater 25 is a resistance heating type carbon heater, and is provided surrounding the quartz glass crucible 1 in the carbon susceptor 22.

[0091]

Although the amount of the silicon melt in the quartz glass crucible 1 decreases as a silicon single crystal 2 grows, the quartz glass crucible 1 is raised such that the height of the melt surface is constant.

[0092]

The wire winding mechanism 29 is arranged above the pull chamber 21b, the wire 28 extends downward from the wire winding mechanism 29 passing through the interior of the pull chamber 21b, and a distal end of the wire 28 reaches the inner space of the main chamber 21a. This figure shows a state in which the silicon single crystal 2 in the middle of growth is suspended on the wire 28. When the silicon single crystal 2 is pulled up, the wire 28 is gradually pulled up while rotating the quartz glass crucible 1 and the silicon single crystal 2 individually to grow the silicon single crystal 2.

[0093]

During the single crystal pulling up step, the inner surface of the crucible crystallizes, and the crystallization of the inner surface of the crucible advances uniformly by the action of the crystallization accelerator, and thus dislocations in the silicon single crystal due to peeling of brown rings can be prevented. In addition, the quartz glass crucible 1 is softened, but the crystallization of the inner surface of the crucible advances uniformly, and thus the strength of the crucible can be secured and deformation can be suppressed. Therefore, contacting with members in a furnace due to deformation of the crucible or changing of a position of the melt surface of the silicon melt 3 due to the change of the volume in the crucible can be prevented.

[0094]

As described above, the quartz glass crucible 1 according to the present embodiment includes the crucible base body 10 consisting of silica glass and the coating film 13 of the crystallization accelerator formed on the inner surface 10i of the crucible

base body 10, and the peel strength of the coating film 13 is 0.3 kN/m or more, and thus it is possible to reduce surface roughening of the inner surface of the crucible due to peeling of the coating film 13, pinhole formation, and dislocation in the single crystal.

[0095]

In addition, in the manufacturing method of a quartz glass crucible according to the present embodiment, when spraying the coating liquid of the crystallization accelerator on the inner surface 10i of the crucible base body 10, the coating liquid with an average droplet diameter of 5 μm or more and 1,000 μm or less is sprayed using a two-fluid nozzle that mixes gas and liquid at a spray tip and sprays the mixture, and thus it is possible to form a dense coating film with a small droplet diameter, thereby increasing the peel strength of the coating film.

[0096]

In addition, in the manufacturing method of a quartz glass crucible according to the present embodiment, when the coating liquid containing the crystallization accelerator is sprayed onto the inner surface of the crucible base body 10 to form the coating film of the crystallization accelerator, the maximum thickness of the coating film formed by one application is 0.5 μm or less, and the coating film is formed into multiple layers by alternately repeating drying of the coating film and reapplying until the desired carbon concentration is achieved, thereby the coating film 13 having a high peel strength can be formed.

[0097]

Although preferred embodiments of the present invention were described above, the present invention is not limited to the above-described embodiments, and various modifications are possible without departing from the scope of the present invention, and such modifications are, needless to say, covered by the scope of the present invention.

[0098]

For example, in the above-described embodiment, the inner surface 10i of the crucible base body 10 is covered with the coating film 13 of the crystallization accelerator, and the outer surface 10o is not covered with the coating film, but both of the inner surface 10i and the outer surface 10o may be covered with the coating film of the crystallization accelerator. That is, the coating film of the crystallization accelerator may cover at least the inner surface 10i of the crucible base body 10. Furthermore, the coating film 13 does not necessarily need to be formed on the entire inner surface of the crucible base body excluding the vicinity of the upper end of the rim, and the coating film on the inner surface of the sidewall 10a may be omitted. That is, the coating film 13 may be provided at least on the inner surface of the bottom central region (within a range of 0.5r from the center of the bottom) of the crucible base body 10.

[0099]

In the above-described embodiment, the crucible base body 10 is facing upward when the coating liquid is sprayed onto the inner surface of the crucible base body 10, but for example, the coating liquid can be applied in a state where the crucible base body 10 is turned upside down to face downward. Furthermore, the heating of the crucible base body 10 may be performed while applying the crystallization accelerator, the application may be performed after preheating the crucible base body 10, or when applying the crystallization accelerator after preheating the crucible base body 10, in order to prevent the temperature of the crucible base body 10 from abruptly dropping during the coating step, the application of the crystallization accelerator can be performed while continuously heating the crucible using a heater different from that for preheating.

[Examples]

[0100]

<Evaluation of peel strength of coating film of crystallization accelerator (1)>

A crucible base body configuring a 32-inch quartz glass crucible was produced by a rotational molding method. The crucible base bodies according to Examples A1 to A4 and Comparative Examples A1 to A4 were produced under the same conditions using the same kind of polycrystalline silicon raw material.

[0101]

A carbon electrode having a bulk specific gravity of 1.50 g/cc to 1.75 g/cc and a specific resistivity of 330 μΩ·cm to 600 μΩ·cm was used during arc melting of quartz powder. In the crucible base body, a transparent layer was formed by evacuating the raw material powder from outside of the rotating mold supporting the raw material powder during melting on the inner surface side, and then a bubble layer was formed by stopping the evacuation or weakening the suction force.

[0102]

Next, the rim portion of the crucible base body was cut, the crucible base body was cleaned with a cleaning liquid and rinsed with pure water, and then a crystallization accelerator was applied to the inner surface of the crucible. The cleaning liquid was prepared by diluting hydrofluoric acid of semiconductor grade with pure water of TOC ≤ 2 ppb (17.2 MΩ or more, 15 to 25°C) to adjust to 10 to 40 w%. An aqueous solution of barium hydroxide was used as the crystallization accelerator, and was uniformly applied by a spray method. The crucible base body was heated with a halogen heater when applying the crystallization accelerator, and the application was performed while measuring the surface temperature of the crucible.

[0103]

A two-fluid nozzle was used to spray the crystallization accelerator, and the spraying conditions were adjusted such that the average droplet diameter was about 200

μm. A laser diffraction particle size distribution measuring apparatus (AEROTRAC II manufactured by MicrotracBEL Corp.) was used to confirm the droplet diameter. The thickness of the coating film of the crystallization accelerator formed by one application was set to about 0.5 μm, and the application was repeated in several steps until the desired concentration was achieved. In this way, as shown in Table 1, a quartz glass crucible having a coating film of a crystallization accelerator formed on the inner surface of the crucible base body was completed.

[0104]

In the formation of the coating film of the crystallization accelerator, the coating conditions were adjusted such that the concentration of the crystallization accelerator at the bottom of the crucible (range within 0.5 times the crucible outer diameter from the center of the bottom of the crucible) was 2.6×10^{15} atoms/cm^2 or less. In addition, the coating conditions were adjusted such that the concentration of the crystallization accelerator was different between the bottom and other than the bottom. Thus, the quartz glass crucibles according to Comparative Examples A1 to A4 and Examples A1 to A4 were completed.

[0105]

Next, the peel strength of the coating film of the crystallization accelerator was measured by SAICAS in each quartz glass crucible. As for the peel strength, each of the peel strength at the bottom of the crucible and the peel strength at the other than the bottom was measured. The measurement position of the peel strength at the bottom of the crucible was one point at the center of the bottom of the crucible. The measurement position of the peel strength at the other than the bottom of the crucible was any one point in the range of 0.55 to 0.6 times the crucible outer diameter from the center of the bottom.

[0106]

Next, the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as the quartz glass crucibles of Comparative Examples A1 to A4 and Examples A1 to A4, and the degree of peeling and surface roughening of the inner surface of the used crucible were evaluated. In addition, the yield of the silicon single crystals (dislocation-free rate) was evaluated. The yield of the single crystals is the weight ratio of the single crystal to the polycrystalline raw material. Table 1 shows the results. In Table 1, the degree of peeling "Low" indicates that the area of the peeled portion is less than 0.1% with respect to the applied area, "Moderate" indicates 0.1% or more and less than 0.5%, and "High" indicates 0.5% or more. The evaluation of the roughened inner surface is an evaluation of the area occupancy of the uneven portion where the brown ring is peeled and the silica glass is exposed. "High" indicates 50% or more, "Moderate" indicates 20% or more and less than 50%, and "Low" indicates less than 20%.

[0107]

[Table 1]

	Crystallization accelerator				Quartz crucible			Yield of single crystal (%)
	Concentration (atoms/cm²)		Peel strength (kN/m)		Degree of peeling		Roughened inner surface	
	Bottom	Other than bottom	Bottom	Other than bottom	Bottom	Other than bottom		
Comparative Example A1	2.6E+14	3.1E+14	0.2	0.3	High	Moderate	High	61.5
Comparative Example A2	2.4E+14	2.1E+15	0.2	0.5	High	Moderate	High	62.2
Comparative Example A3	2.6E+15	2.5E+15	0.5	0.6	Moderate	Low	Moderate	69.1
Comparative Example A4	2.3E+15	2.8E+14	0.4	0.2	Moderate	High	Moderate	65.2
Example A1	2.5E+14	2.4E+14	0.6	0.6	Low	Low	Low	81.2
Example A2	2.6E+14	2.4E+15	0.7	1.2	Low	Low	Low	83.6
Example A3	2.0E+15	2.6E+15	1.0	1.1	Low	Low	Low	85.3
Example A4	2.6E+15	2.2E+14	0.9	0.7	Low	Low	Low	83.1

[0108]

As shown in Table 1, the concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example A1 was 2.6×10^{14} atoms/cm^2 at the bottom and 3.1×10^{14} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.2 kN/m at the bottom and 0.3 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used

crucible was high at the bottom of the crucible and moderate at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was high. The yield of the silicon single crystals pulled up using the quartz glass crucible was 61.5%, which was a result lower than 80%.

[0109]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example A2 was 2.4×10^{14} atoms/cm^2 at the bottom and 2.1×10^{15} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.2 kN/m at the bottom and 0.5 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was high at the bottom of the crucible and moderate at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was high. The yield of the silicon single crystals pulled up using the quartz glass crucible was 62.2%, which was a result lower than 80%.

[0110]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example A3 was 2.6×10^{15} atoms/cm^2 at the bottom and 2.5×10^{15} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.5 kN/m at the bottom and 0.6 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of

cristobalite (brown ring) formed on the inner surface of the used crucible was moderate at the bottom of the crucible and low at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was moderate. The yield of the silicon single crystals pulled up using the quartz glass crucible was 69.1%, which was a result lower than 80%.

[0111]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example A4 was 2.3×10^{15} atoms/cm^2 at the bottom and 2.8×10^{14} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.4 kN/m at the bottom and 0.2 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was moderate at the bottom of the crucible and high at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was moderate. The yield of the silicon single crystals pulled up using the quartz glass crucible was 65.2%, which was a result lower than 80%.

[0112]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example A1 was 2.5×10^{14} atoms/cm^2 at the bottom and 2.4×10^{14} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.6 kN/m at the bottom and 0.6 kN/m also at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and

manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was low both at the bottom of the crucible and at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was low. The yield of the silicon single crystals pulled up using the quartz glass crucible was 81.2%, which was a good result exceeding 80%.

[0113]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example A2 was 2.6×10^{14} atoms/cm^2 at the bottom and 2.4×10^{15} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.7 kN/m at the bottom and 1.2 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was low both at the bottom of the crucible and at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was low. The yield of the silicon single crystals pulled up using the quartz glass crucible was 83.6%, which was a good result exceeding 80%.

[0114]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example A3 was 2.0×10^{15} atoms/cm^2 at the bottom and 2.6×10^{15} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 1.0 kN/m at the bottom and 1.1 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was

performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was low both at the bottom of the crucible and at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was low. The yield of the silicon single crystals pulled up using the quartz glass crucible was 85.3%, which was a good result exceeding 80%.

[0115]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example A4 was 2.6×10^{15} atoms/cm^2 at the bottom and 2.2×10^{14} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.9 kN/m at the bottom and 0.7 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was low both at the bottom of the crucible and at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was low. The yield of the silicon single crystals pulled up using the quartz glass crucible was 83.1%, which was a good result exceeding 80%.

[0116]

<Evaluation of peel strength of coating film of crystallization accelerator (2)>

The quartz glass crucibles according to Comparative Examples B1 to B3 and Examples B1 to B3 were completed in the same manner as in “Evaluation of peel strength (1)” except that the coating conditions were adjusted such that the concentration

of the crystallization accelerator at the bottom of the crucible was higher than 2.6×10^{15} atoms/cm^2. After that, the same evaluations as in "Evaluation of peel strength (1)" were performed. Table 2 shows the results.

[0117]

[Table 2]

	Crystallization accelerator				Quartz crucible			Yield of single crystal (%)
	Concentration (atoms/cm^2)		Peel strength (kN/m)		Degree of peeling		Roughened inner surface	
	Bottom	Other than bottom	Bottom	Other than bottom	Bottom	Other than bottom		
Comparative Example B1	5.2E+15	5.2E+15	0.2	0.2	High	High	High	70.2
Comparative Example B2	5.2E+15	2.8E+16	0.1	0.4	High	Moderate	Moderate	72.3
Comparative Example B3	4.9E+17	2.4E+15	0.2	0.3	High	Moderate	Moderate	71.5
Example B1	5.2E+15	5.2E+15	0.3	0.4	Moderate	Moderate	Low	80.2
Example B2	2.8E+16	5.2E+15	1.0	0.3	Low	Moderate	Low	87.6
Example B3	2.6E+16	4.9E+17	1.3	1.1	Low	Low	Low	87.8

[0118]

As shown in Table 2, the concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example B1 was 5.2 $\times 10^{15}$ atoms/cm^2 both at the bottom and at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.2 kN/m both at the bottom and at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was high both at the bottom of the crucible and at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was high. The yield of the silicon single crystals pulled up using the quartz glass crucible was 70.2%, which was a result

lower than 80%.

[0119]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example B2 was 5.2×10^{15} atoms/cm^2 at the bottom and 2.8×10^{16} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.1 kN/m at the bottom and 0.4 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was high at the bottom of the crucible and moderate at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was moderate. The yield of the silicon single crystals pulled up using the quartz glass crucible was 72.3%, which was a result lower than 80%.

[0120]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Comparative Example B3 was 4.9×10^{17} atoms/cm^2 at the bottom and 2.4×10^{15} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.2 kN/m at the bottom and 0.3 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was high at the bottom of the crucible and moderate at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was moderate. The yield of

the silicon single crystals pulled up using the quartz glass crucible was 71.5%, which was a result lower than 80%.

[0121]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example B1 was 5.2×10^{15} atoms/cm^2 both at the bottom and at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 0.3 kN/m at the bottom and 0.4 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was moderate both at the bottom of the crucible and at the other than the bottom. The surface roughening of the inner surface of the used crucible was low. The yield of the silicon single crystals pulled up using the quartz glass crucible was 80.2%, which was a good result exceeding 80%.

[0122]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example B2 was 2.8×10^{16} atoms/cm^2 at the bottom and 5.2×10^{15} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 1.0 kN/m at the bottom and 0.3 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was low at the bottom of the crucible and moderate at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was low. The yield of the silicon

single crystals pulled up using the quartz glass crucible was 87.6%, which was a good result exceeding 80%.

[0123]

The concentration of the crystallization accelerator on the inner surface of the quartz glass crucible according to Example B3 was 2.6×10^{16} atoms/cm^2 at the bottom and 4.9×10^{17} atoms/cm^2 at the other than the bottom. The peel strength of the coating film of the crystallization accelerator was 1.3 kN/m at the bottom and 1.1 kN/m at the other than the bottom. In a case where the pulling up of the silicon single crystal was performed using another crucible sample having the same properties and manufactured under the same conditions as this crucible sample, the degree of peeling of cristobalite (brown ring) formed on the inner surface of the used crucible was low both at the bottom of the crucible and at the other than the bottom. In addition, the surface roughening of the inner surface of the used crucible was low. The yield of the silicon single crystals pulled up using the quartz glass crucible was 87.8%, which was a good result exceeding 80%.

[0124]

<Evaluation of thickness of coating film of crystallization accelerator>

The correlation between the thickness of the coating film of the crystallization accelerator formed on the inner surface of the quartz glass crucible and the yield of the silicon single crystals was evaluated. Table 3 shows the results.

[0125]

[Table 3]

	Thickness of coating film of crystallization accelerator (μm)	Yield of single crystal (%)
Comparative Example C1	54.3	71.3
Comparative Example C2	55.5	65.5
Comparative Example C3	65.0	66.8
Comparative Example C4	72.5	64.3
Example C1	0.2	80.4
Example C2	1.2	84.2
Example C3	7.0	87.8
Example C4	50.0	84.6

[0126]

As shown in Comparative Examples C1 to C4 in Table 3, in a case where the thickness of the coating film of the crystallization accelerator was 54.3 μm or more, the yield of the silicon single crystals could not be increased to 80% or more. On the other hand, as shown in Examples C1 to C4, in a case where the thickness of the coating film of the crystallization accelerator was 50 μm or less, the yield of the silicon single crystals could be increased to 80% or more.

[0127]

<Evaluation of surface roughness of coating film of crystallization accelerator>

The correlation between the surface roughness (Ra) of the coating film of the crystallization accelerator formed on the inner surface of the quartz glass crucible and the yield of the silicon single crystals was evaluated. Table 4 shows the results.

[0128]

[Table 4]

	Surface roughness of coating film of crystallization accelerator (μm)	Yield of single crystal (%)
Comparative Example D1	0.27	71.5
Comparative Example D2	0.28	60.3
Comparative Example D3	0.29	67.5
Comparative Example D4	0.32	68.3
Example D1	0.10	81.5
Example D2	0.20	84.5
Example D3	0.22	87.3
Example D4	0.25	85.6

[0129]

As shown in Comparative Examples D1 to D4 in Table 4, in a case where the surface roughness (Ra) of the coating film of the crystallization accelerator was 0.27 μm or more, the yield of the silicon single crystals could not be increased to 80% or more. On the other hand, as shown in Examples D1 to D4, in a case where the surface roughness (Ra) of the coating film of the crystallization accelerator was 0.25 μm or less, the yield of the silicon single crystals could be increased to 80% or more.

DESCRIPTION OF REFERENCE NUMERALS

[0130]

1 Quartz glass crucible

1s Crucible sample

2 Silicon single crystal

3 Silicon melt

6 Coating liquid

10 Crucible base body

10a Sidewall

10b Bottom

10c Corner

10i Inner surface of crucible base body

10o Outer surface of crucible base body

11 Transparent layer

12 Bubble layer

13 Coating film of crystallization accelerator

14 Mold

14a Vent hole

14i Inner surface of mold

15 Arc electrode

16 Deposited layer of quartz powder

16a Natural quartz powder

16b Synthetic quartz powder

17A Rotary support

17B Heater

18 Robot arm

19 Spray nozzle

20 Single crystal pulling apparatus

21 Chamber

21a Main chamber

21b Pull chamber

21c Gas entry

21d Gas outlet

22 Carbon susceptor

23 Rotating shaft

24 Shaft driving mechanism

25 Heater

28 Single crystal pulling-up wire

29 Wire winding mechanism

30 SAICAS

31 Diamond blade