Graphite Crucible and Silicon Single Crystal Manufacturing Apparatus

The present invention relates to a graphite crucible used in the manufacturing of a silicon single crystal according to the Czochralski method. It further relates to a silicon single crystal manufacturing apparatus according to the Czochralski method, comprising said graphite crucible.

As one method for growing silicon single crystals, pulling methods represented by the Czochralski method (CZ method) have been generally used. Normally, an apparatus used therein has a quartz crucible for retaining raw material silicon melt, wherein the crucible is surrounded by a graphite crucible having an inner shape that serves to support the quartz crucible and to achieve uniform heating, and wherein a heater for heating is arranged outside thereof. Usually, the shapes of both the quartz crucible and the graphite crucible consist of a side wall having an approximately cylindrical shape and an appropriately radially chamfered bottom portion.

In the CZ method, a silicon raw material placed in the quartz crucible is heated and melted. Since the melting point of silicon is about 1420°C, heating has to be carried out so as to reach the melting point at first. In such a case, the temperature of the heater has to be increased to about 1700°C. Due to this heating, both the graphite crucible and the quartz crucible are heated to the melting point of silicon or higher. When quartz exceeds about 1200°C, it begins to soften and deform, and, due to the load of the molten silicon in the quartz crucible, the quartz crucible almost entirely comes into close contact

with the inner shape of the graphite crucible supporting the quartz crucible from the outside. Along with a recent increase in the diameter of silicon wafers, an increase in the diameter and capacity of quartz crucibles is required in the CZ method as well, and it is becoming more important to control the temperature range and heating uniformity of the above described heating.

As shown in the equations below, a known problem of the CZ method is that, at the silicon melting temperature, a reaction is generated on the inner surface of the quartz crucible between SiO2, which is a component of the quartz crucible, and the molten silicon Si. As a result, a SiO gas is generated. Furthermore, also outside of the quartz crucible, this SiO gas reacts with the outer surface of the graphite member, thereby forming a SiC solid. Moreover, on the outer surface of the quartz crucible, a SiO gas and a CO gas are generated by a reaction between the outer surface of the quartz crucible and the inner surface of the graphite crucible, and further, a SiC solid is formed by another reaction with the inner surface of the graphite crucible. The formed SiC has a thermal expansion coefficient significantly different from that of graphite. Therefore, SiC becomes a cause of cracks, etc. during the cooling/heating cycle of the graphite crucible, thus limiting its service life in terms of safety, etc. Moreover, as a result, the generated CO gas applies a pressure to the quartz crucible, causing it to deform.

$$SiO2+Si=SiO$$

$$SiO2+C=SiO+CO$$

$$SiO+2C=SiC+CO$$

Several techniques regarding the improvement of the graphite crucible in order to solve the above problems are

known. One of them is a method disclosed in Japanese Patent Application Laid Open No. 61-44791, in which the CO gas generated between the quartz crucible and the graphite crucible is discharged by flowing an inert gas such as argon in a downstream direction between the quartz crucible and the graphite crucible and discharging the gas through the holes which are provided with a downward direction in a lower part of the side surface of the graphite crucible. Moreover, a technique in which horizontal holes are provided in the graphite crucible at positions above the liquid level of the molten silicon in order to prevent deformation of the quartz crucible caused by the generated gas is disclosed in Japanese Patent Application Laid Open No. 10-297992. Furthermore, a method in which the CO gas generated between the quartz crucible and the graphite crucible is discharged by flowing an inert gas such as argon in a downstream direction toward a bottom portion of the crucible along gas guiding grooves which are provided vertically on the inner surface of the graphite crucible and discharging the gas from the bottom portion is disclosed in Japanese Patent Application Laid Open No. 2008-201619.

However, it has begun to be recognized that these conventional methods are no longer adequate for the large-diameter/large-capacity (high weight) quartz crucibles which are, particularly recently, used in the CZ method. More specifically, providing complicated structures, such as gas guiding grooves, on the inner surface of the graphite crucible in order to discharge the generated gas is not preferred in terms of safe retention of the large-capacity (high weight) quartz crucible. Moreover, when a quartz crucible having a large diameter/large capacity (high weight) is used, the quartz crucible softened due to

the high heating temperature deforms so that it almost entirely comes into close contact with the graphite crucible supporting it. Thus, it becomes difficult to provide a sufficient gas flow between said crucibles.

Therefore, novel graphite crucible technologies which prevent accumulation of pressure on the quartz crucible by smoothly discharging the generated CO gas and also prevent formation/accumulation of SiC on the inside of the graphite crucible, both without (i) providing a complicated structure on the inner surface of the graphite crucible and without (ii) providing a sufficient inert gas flow between the graphite crucible and the quartz crucible, are expected.

The present inventors have diligently carried out research in order to develop a graphite crucible that satisfies said expectations. As a result, the inventors succeeded in finding a novel graphite crucible in which at least one approximately horizontal gas venting hole is provided at at least one particular position on the graphite crucible, due to which pressure does not accumulate on the surface of the quartz crucible thanks to a smooth discharge of the generated CO gas, and formation/accumulation of SiC on the inside of the graphite crucible is prevented. Thus, the present invention is accomplished.

Specifically, a first aspect of the present invention relates to a graphite crucible used in the manufacturing of a silicon single crystal according to the Czochralski method and comprising a side portion, a bottom portion and a corner portion connecting the side portion and the bottom

portion, characterized in that at least one gas venting hole is provided in the corner portion of the graphite crucible, wherein the direction of the at least one gas venting hole is upward or horizontal.

The present invention also relates to the graphite crucible characterized in that the direction of the at least one gas venting hole is approximately horizontal.

A second aspect of the present invention relates to a silicon single crystal manufacturing apparatus according to the Czochralski method, comprising the graphite crucible according to the first aspect of the present invention.

Here, the graphite crucible of the present invention includes not only the divided type but also the one-piece type. Furthermore, the present invention also includes a crucible made of CFC composite (carbon fibers reinforced carbon).

In the graphite crucible according to the present invention, the at least one gas venting hole is provided in the corner portion of the crucible. Therefore, said graphite crucible is capable of smoothly releasing the gas generated by the reaction between the quartz crucible and the graphite crucible, thereby preventing formation of SiC on the surface of the graphite crucible and deformation of the quartz crucible caused by the gas pressure. Since the silicon single crystal manufacturing apparatus according to the Czochralski method of the present invention comprises the graphite crucible according to the present invention, during silicon single crystal manufacturing, the gas generated by the reaction between the quartz crucible and the graphite crucible can be smoothly released. Thereby, formation of SiC on the surface of the graphite crucible and deformation of the quartz crucible caused by the gas pressure can be prevented, ensuring safety in manufacturing, and extending the life cycle of the graphite crucible.

FIG. 1 shows a graphite crucible of the present invention.

FIG. 2 is a drawing explaining the effects of gas venting holes of the present invention.

As illustrated by an example of a graphite crucible 1 of the present invention shown in FIG. 1, in the graphite crucible of the present invention, a (inner) side portion 2 usually has an approximately perpendicular cylindrical shape and a bottom portion 3 an appropriately radially chamfered shape. A characteristic of said graphite crucible resides in that gas venting holes 5 are provided in a corner portion 4 thereof. Here, the graphite crucible 1 may be basically the same as conventionally publicly known graphite crucibles used in the manufacturing of silicon single crystals according to the Czochralski method, and there are no particular limitations imposed on whether said graphite crucible is a divided type or an one-piece type, and no particular limitations regarding its size, shape, or material. The crucible regarded as one unit has the above-explained shape during usage, even in the case of the conventionally publicly known divided type, where the crucible is divided into two or three parts. Here, the corner portion of the graphite crucible of the present invention means the part (region) connecting the side portion and the bottom portion. The graphite crucible of the present invention has a function of supporting a major load of a quartz crucible and molten silicon with its corner portion during usage. Since the quartz crucible is heated during usage to about its softening point, the quartz crucible is caused to be in a state in which it almost entirely comes into close contact with the graphite crucible at the bottom portion and the corner portion, and

a desired heating effect is achieved. The gas venting holes 5 are provided as approximately horizontal holes in said corner portion from inside to outside of the graphite crucible.

As schematically shown in FIG. 2, during usage, an inert gas 21 (usually argon gas) is, usually under reduced pressure, flowed outside of the graphite crucible and discharged. Therefore, the pressure of the inside 26 of the gas venting holes 25 and the gap 28 is at a state in which it is somewhat lower than the outside pressure 27 of the graphite crucible. Thus, as explained above, a CO gas is formed during usage due to the reaction between a SiO gas and C of the surface of the graphite crucible during the short period of time until said SiO gas reaches the gas venting holes. However, the gas is quickly discharged from the gas venting holes, and accumulation of pressure applied to the quartz crucible can be prevented. Therefore, the reaction of SiO and the surface of the graphite crucible mainly takes place in the gas venting holes or in their outside peripheries alone.

In the present invention, the positions, shapes, number, and directions of the gas venting holes provided in the corner portion are not particularly limited, as long as the above-explained work-effect is carried out sufficiently. On the other hand, since the graphite crucible has to safely support the load of the quartz crucible and the molten silicon, in comprehensive consideration of the above, the positions, shapes, number, and directions of the gas venting holes can be selected to be in a preferred range. Particularly, regarding the directions of the gas venting holes, it is preferable to provide gas venting holes with a horizontal direction in

order to more smoothly discharge the generated CO gas in a case when the interior of the furnace is filled with an inert gas such as argon.

Specifically, when a plurality of gas venting holes is provided, the positions thereof are preferred to be positions that equally divide the cylindrical corner portion. In the case of equally dividing positions, the decrease of crucible strength caused by the holes can be minimized. The shapes of the gas venting holes are not particularly limited, and circular shapes and polygonal shapes can be employed. The cross sectional areas thereof are also not particularly limited. However, the cross sectional area can be selected in sufficient consideration of how the quartz wall of the quartz crucible heated to about its softening point can be prevented from deforming in the directions of the gas venting holes. Therefore, in comprehensive consideration thereof, the cross sectional area of each gas venting hole is preferred to be 225 mm2 or less. This means that, if the cross section is circular, the radius thereof is preferred to be in the range of 5 mm to 8 mm. When gas venting holes having this cross sectional area are employed, the number of the gas venting holes is preferably in the range of 2 to 3/crucible with division, and 6 to 8/crucible without division.

The directions of the gas venting holes are not particularly limited. However, the gas venting holes are preferred to be provided in directions with which the above-explained process, in other words, the smooth discharging of the CO gas generated between the quartz crucible and the graphite crucible, can be carried out. Specifically, providing said gas venting holes

approximately horizontally or somewhat upwardly is preferred since it brings about a smooth gas flow.

A silicon single crystal manufacturing apparatus according to the Czochralski method of the present invention is characterized in that it comprises the above-explained graphite crucible of the present invention instead of a graphite crucible used in a conventionally publicly known apparatus. Thus, under conventionally publicly known manufacturing conditions, the CO gas generated between the quartz crucible and the graphite crucible is quickly discharged from the gas venting holes of the graphite crucible to the outside. As a result, formation and accumulation of SiC on the inside of the graphite crucible can be suppressed, and deformation of the quartz crucible due to the accumulated pressure of the CO gas can be suppressed.

Example

50 Silicon ingots were pulled up by using the graphite crucible having an outer diameter of 500 mm and an inner diameter of 460 mm having holes of an inner diameter of 5 mm were horizontally provided equally at six locations in the corner portion. Any deposition of SiC on the inside of the crucible could not be confirmed at all. However, in the peripheries of the holes on the outside of the crucible, SiC deposition of about 3 mm was confirmed. Furthermore, deformation of the quartz crucible due to CO gas was not observed at all.

The graphite crucible according to the present invention can be utilized in silicon single crystal manufacturing apparatuses according to the Czochralski method.

Claims:

1. A graphite crucible used in the manufacturing of a silicon single crystal according to the Czochralski method and comprising a side portion, a bottom portion and a corner portion connecting the side portion and the bottom portion, characterized in that

at least one gas venting hole is provided in the corner portion of the graphite crucible, wherein the direction of the at least one gas venting hole is upward or horizontal.

2. A silicon single crystal manufacturing apparatus according to the Czochralski method, comprising the graphite crucible according to claim 1.