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(54) REUSABLE CRUCIBLE FOR SILICON INGOT GROWTH

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(57) **ABSTRACT**

A silicon nitride crucible is coated with a crucible release coating for use in directional solidification of multicrystalline silicon ingots. The crucible preferably includes reaction bonded silicon nitride crucible. After removing the silicon ingot, the release coating is easily removed and the crucible can be repeatedly recoated and reused.

REUSABLE CRUCIBLE FOR SILICON INGOT GROWTH

FIELD OF THE INVENTION

[0001] This invention relates to the use of a reusable crucible for silicon ingot growth.

BACKGROUND OF THE INVENTION

[0002] Silicon ingots are typically produced by one of three methods: (1) pulling an ingot from melt, (e.g., the Czochralski process); (2) solidifying a melt in a crucible by directional solidification techniques; or (3) pouring a melt from a crucible into a mold using casting techniques.

[0003] In a crystal pulling process, such as the Czochralski method, a clear fused silica crucible (commonly called a quartz crucible) is used for melting silicon. The ingot is pulled from the melt such that there is contact between the melt and the crucible, but no contact between the solidified silicon ingot and the crucible.

[0004] In a directional solidification process, silicon is typically melted in the crucible and directionally solidified in the same crucible. In this case, there is contact between the silicon melt and the crucible, as well as contact between the solidified silicon ingot and the crucible.

[0005] In a casting process, the silicon is melted in a crucible and the melt is then poured from the crucible into a mold, where the silicon solidifies. In this case, there is contact between the melt and the crucible, the melt and the mold (although minimal), and the mold and the solidified ingot.

[0006] Casting useful and acceptable silicon ingots can be difficult due to the characteristics of silicon in its solid and molten forms. One problem that arises is that impurities from the container can contaminate the silicon melt because of the high reactivity of the silicon melt. Furthermore, the solidifying melt can adhere to the container walls, causing an ingot and/or a container to crack during the cooling process because of differences in respective thermal expansion coefficients. Protective layers of compacted Si_3N_4, SiO_2, Si, and graphite powder, or of a low-melting encapsulant, are used to reduce such adherence.

[0007] Various methods of silicon ingot casting have been proposed in the past to attempt to overcome these obstacles. For example, molds have been lined/coated with Si_3N_4 powder. When the silicon melt has been poured into an adequately heated mold, a reaction between the mold wall and the molten silicon is minimized.

[0008] Historically, clear fused silica crucibles have been favored for crystal pulling processes. Clear fused silica can be used because there is no contact between the ingot and the crucible. In addition, the reaction between the melt (Si) and the crucible (SiO_2)

$$Si+SiO_2 \rightarrow 2SiO$$

[0009] is minimized by keeping the pressure in the chamber above approximately 20 torr so formation of the reaction product, SiO, is minimized.

[0010] Silica remains the material of choice for crucible and mold applications because it is readily available in high purity form, and because the reaction product of Si and SiO_2 is a gaseous phase and removable from the heat zone, thereby minimizing the contamination that can occur during the production of silicon ingots.

[0011] However, when clear fused silica crucibles was initially used for directional solidification or as molds for casting techniques, the SiO_x ($0 \leqq x \leqq 2$) phase was formed between the ingot and the crucible/mold, resulting in a tenacious bond between the ingot and the crucible/mold. During the cooling process, this tenacious bond caused the ingot to crack. Thus, while clear fused silica crucibles can be used for melting silicon, they are not appropriate for use in directional solidification processes or as molds for casting (without a coating) if the desired result is crack-free silicon ingots.

[0012] Schmid et al. U.S. Pat. No. 4,218,418, describes a silica crucible with a graded structure that can be utilized as a crucible for producing crack-free silicon ingots because the crucible delaminates during the cooling process. Other approaches, such as using protective coatings of Si_3N_4 powder on the inner walls of quartz or sintered silica crucibles, have also been described for production of crack-free silicon ingots. In all such cases, the crucible/mold is sacrificed to produce a crack-free silicon ingot. Therefore, although these crucibles can be used to produce crack-free silicon ingots, they can only be used in production once, thereby adding significantly to the cost of silicon ingot production. During production of a silicon ingot, high temperatures cause the initial amorphous or glass phase silica to transform, at least partially, to the crystalline phase. This transformation reduces the reliability of the silica crucible to contain molten silicon during reuse.

[0013] A typical processing cycle for producing multicrystalline silicon ingots using a graded silica crucible involves the following procedure. The square cross-section crucible is supported with graphite plates at the bottom and sides of the crucible. Polycrystalline silicon meltstock, with an appropriate amount of dopant to achieve the desired resistivity in the ingot, is loaded into the crucible and the crucible is placed on the heat extraction system in the heat zone of a Crystal Systems, Inc. Heat Exchanger Method (HEM) furnace designed for directional solidification of silicon ingots. The furnace chamber is evacuated and heat is applied with a graphite resistance heater. The temperature in the heat zone is increased to approximately 1500° C. and maintained at this temperature until the entire silicon is in a molten stage. The chamber is maintained at approximately 0.1 torr pressure.

[0014] The furnace temperature is slowly decreased until the heat zone is less than approximately **100** above the melting point of silicon. During this decrease of furnace temperature, heat is extracted with a heat extraction system so that directional solidification of molten silicon is achieved from the bottom of the crucible towards the top surface of the melt with a slightly convex solid-liquid interface. The movement of the solid-liquid interface from the bottom of the crucible to the top surface of the melt is approximately 1-3 cm per hour. After complete solidification of silicon has been achieved in the crucible, the furnace temperature is decreased and the silicon ingot is cooled in the furnace within the crucible. The crucible delaminates, thereby preventing the ingot from cracking. The delamination causes the ingot to be rough and an allowance of nearly an inch is required to fully clean up the surface.

[0015] The requirements for the use of silica as a mold are less stringent than those for its use as a crucible. Molten silicon is poured from a crucible into a mold which is maintained at a temperature just below the melting point of silicon (1412° C.) so that a chilled solid layer is formed on the inner walls of the mold. Solidification of the ingot is achieved in a controlled manner; therefore, in the case of a mold, (i) the highest temperature used is 1412° C.; (ii) there is essentially no contact between the silicon melt and the mold; and (iii) the solidification is rapid so that the time the mold has to contain the molten silicon is short. Mold materials that have been used to produce crack-free silicon ingots include mullite, Si_3N_4 and graphite. Applying a protective coating to these molds makes it easier to remove the ingot and increases the reusability of the molds.

[0016] The requirements for the use of silica as a crucible, by contrast, are quite stringent. A crucible for use in silicon ingot production (i) must withstand significantly higher temperatures than 1412° C. so that the entire silicon meltstock can be melted; (ii) is initially in contact with the solid meltstock and with the molten silicon after it has melted; (iii) has to withstand longer solidification times; and (iv) is in contact with the solid silicon. In other words, the crucible must withstand much higher temperatures and for a significantly longer period of time. Any protective coating put on the inner walls of the crucible has to withstand similar conditions and retain its integrity through any movement of the melt during meltdown and solidification.

[0017] In an effort to reduce the costs of producing crack-free silicon ingots, two reusable crucibles have been developed. Graphite with liners, such as Si_3N_4, and/or encapsulant has been used as a reusable crucible. The liner and/or encapsulant is used to prevent the contact of the silicon ingot with the crucible which minimizes the cracking problem. However, use of the encapsulant adversely affects dimensional control of the ingot and removal from the crucible. The dimensional control problem occurs because the thickness of the encapsulant layer is non-uniform. This non-uniformity leads to variation in the ingot size and therefore, poor utilization of usable standard size bars. In order to remove the ingot from the encapsulated ingot, the crucible is placed upside down after solidification and re-heated to a temperature at which the encapsulant will melt. After the encapsulant has melted, the ingot can be removed from the crucible.

SUMMARY OF THE INVENTION

[0018] The present invention is directed to a reliable and reusable crucible for use in directional solidification of multicrystalline silicon ingots and in casting of silicon ingots.

[0019] Embodiments of the invention include use of a silicon nitride crucible coated with a crucible release coating for use in directional solidification/ingot casting of multicrystalline silicon ingots. The crucible is preferably made of reaction bonded silicon nitride, but can also be isopressed silicon nitride. The coating prevents the crucible from direct contact with the silicon melt when used for solidification of multicrystalline silicon ingots. After removing the silicon ingot, the release coating is easily removed and the crucible can be repeatedly recoated and reused.

[0020] Other features and advantages will become apparent from the following detailed description and claims.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The invention is directed to use of silicon nitride, preferably reaction bonded silicon nitride (RBSN) or isopressed silicon nitride, in reusable crucibles for silicon ingot growth formation with directional solidification. The crucible is coated with a release coating that adheres to the crucible and acts as a buffer between the crucible and the ingot so that the ingot can be removed from the crucible and the crucible can be reused after it is coated again.

[0022] The RBSN crucible can also be used as a reusable mold. In addition, one of skill will understand that it is possible to use the crucible as a mold for creating one or more crack-free silicon ingots, to then use the crucible as a reusable crucible before switching back to using the crucible as a mold. Other variations are also contemplated.

[0023] In one embodiment, the crucible release coating is Si_3N_4. The Si_3N_4 coating also acts as a barrier to the incorporation of impurities in the silicon melt from the crucible during processing. Other materials that can be used for a release coating include, but are not limited to, SiO_2, mixture of SiO_2 and Si_3N_4, SiC, graphite wool/cloth, and silica wool/cloth.

[0024] The ingots that are produced have flat sides with good uniformity, so the material utilization is high, and less is wasted around the sides than in some other processes.

[0025] The crucible is preferably designed to have an expansion coefficient that is low and is similar to that of the silicon. Silica, by contrast, has a much lower coefficient than silicon nitride. In the case of RBSN, additives (such as a grog) can be provided to provide a lower density in the silicon nitride and thereby RBSN will be more resilient to expansion changes.

[0026] The crucible is preferably designed with an approximate 2°-5° vertical taper for the side walls which range from about 10 mm to about 25 mm thick for ease of removal of the ingot after directional solidification.

[0027] For the times and temperatures required for use of crucibles, Si_3N_4 has a high vapor pressure, so it is desirable to develop a processing cycle that is compatible with the crucible. The temperature and pressure parameters should be designed to substantially prevent silicon from wicking up the inner surface of the crucible, and to prevent decomposition of the coating. The modified processing cycles described in the following examples were developed for use in HEM graphite resistance heated furnace. If another type of furnace, such as an induction heated furnace, were used, optimal temperature and pressure parameters could be somewhat different. One of skill in the art could determine an efficient temperature and pressure to use in their particular furnace.

EXAMPLE 1

Directional Solidification using RBSN Crucible

[0028] Dimensions of a nominal 20 cm×20 cm RBSN crucible were chosen so that a resulting ingot could be sectioned into four 10 cm×10 cm bars of usable material. A RBSN crucible with exterior dimensions of 22 cm×22 cm×16 cm height, about 10 mm wall thickness and 3° taper of the sidewalls was used. The dimensions of the RBSN crucible can be determined based on exact dimensions of the silicon bar (100 mm square or 104 mm square), limiting the waste to the kerf resulting from sectioning the bars, accuracy of cuts and from the tapered section of the crucible.

[0029] A Si_3N_4 coating was applied on the inner surfaces of the RBSN crucible to prevent the direct contact of the silicon with the crucible. The coating was sprayed with a thickness of about 0.015-0.05 inches (about 0.375 to 1.25 mm) and the RBSN crucible was fired at approximately 1100° C. to drive off the organic carrier components in the spraying solution and to adhere the coating to the crucible. Since Si_3N_4 does not soften at the melting point of silicon, it was unnecessary to support the RBSN crucible with graphite plates.

[0030] The RBSN crucible was loaded with approximately 11 kg polycrystalline silicon meltstock and placed on the heat exchange system in an HEM furnace. To maintain the integrity of the RBSN crucible, heat was applied with a graphite resistance heater after evacuation of the chamber and the heat-up cycle was tailored so that there were no sharp temperature gradients on the RBSN crucible. At approximately 1200° C., the furnace chamber was backfilled with an inert gas (argon). The gas inlet and evacuation were adjusted so that the furnace chamber pressure was maintained at approximately 300 to 600 torr. Above 1412° C., the silicon meltstock started melting and the heat zone temperature was limited to approximately 1450° C. After meltdown of the silicon, the directional solidification and the cooling processes were conducted in a manner consistent with standard practice.

[0031] The silicon ingot was removed from the RBSN crucible after chipping the top edge of the ingot in contact with the coating. The ingot surface in contact with the coating was flat and there was coating left between the ingot and the crucible. After removing the ingot, the Si_3N_4 coating was in a powdery state and was easily removed from the surface of the RBSN crucible. The RBSN crucible showed no visible signs of deterioration after the removal of the ingot. However, characterization of the silicon material produced in this experiment showed that the resistivity was lower than expected from the dopant additions, indicating that the silicon was contaminated with impurities from the RBSN crucible or the Si_3N_4 coating.

EXAMPLE 2

Removal of Impurities

[0032] An RBSN crucible was heated to approximately 1460° C. in reduced pressure so that volatile impurities were removed prior to use of the crucible. After the bake-out, the RBSN crucible was sprayed with a Si_3N_4 coating, and then heated in a flowing nitrogen gas atmosphere to approximately 1200° C. so that the impurities in the RBSN crucible were nitrided and tied up in the RBSN crucible. The RBSN was then used in a standard directional solidification process. The resistivity of the silicon produced in this experiment was nearly the same as expected from the doping additions. This demonstrates that the Si_3N_4 coating and the RBSN crucible can be treated so that the impurities are tied up in the crucible and do not travel through the coating and contaminate the silicon.

EXAMPLE 3

Temperature/Pressure Optimization

[0033] Directional solidification experiments were carried out at various pressures ranging from 300 to 600 torr in the furnace. It was observed that at lower pressures (typically less than 300 torr) in the chamber, the molten silicon wet the crucible sidewalls, ran up to the top of the crucible and started going down on the outside of the crucible; at intermediate pressures (typically about 300-400 torr) the molten silicon wicked up the inside wall of the crucible but did not go over to the outside wall; and at high pressures (typically at least 500 torr) there was no wicking. This data showed that the furnace chamber should be backfilled prior to melting of the silicon and that the wetting tendency of molten silicon to the crucible changes as a function of chamber pressure. This caused the silicon to flow up the inside walls of the RBSN crucible and overflows to the outside surface of the RBSN crucible at low chamber pressures. As the pressure was increased, the wetting tendency was decreased and the molten silicon flow was minimized.

EXAMPLE 4

Reusing the Crucible

[0034] A 30 cm×30 cm cross section of RBSN crucible with 25 mm wall thickness was prepared the same way as Example 2 and used for directional solidification of multicrystalline silicon ingot using an HEM furnace. A crack-free silicon ingot was produced and the RBSN crucible was cleaned, coated with Si_3N_4, baked and reused for directional solidification of silicon ingots. This procedure was repeated and sixteen (16) ingots were produced from the same crucible.

EXAMPLE 5

Sidewall Taper

[0035] A 40 cm×40 cm cross section RBSN crucible with a wall thickness of about 20 mm was also prepared as in Example 2 and used for directional solidification of a silicon ingot. A crack-free silicon ingot was produced. The crucible and ingot were cut and it was observed that there was no attachment of the ingot and crucible; however, the sidewalls of the crucible did not have enough taper to allow the ingot to be removed easily.

EXAMPLE 6

Isopressed Crucible

[0036] A 19 cm outside diameter, 17 cm high, 20 mm wall thickness isopressed Si_3N_4 crucible was prepared as described in Example 2. The crucible was loaded with 5.4 kg silicon meltstock and processed for directional solidification of a silicon ingot by an HEM furnace. After removal of the ingot from the crucible, a light coating could be seen on the outside surface of the ingot and on the interior of the crucible.

[0037] Having described preferred embodiments and examples, it should be understood that modifications can be made without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. A reusable crucible for use in directional solidification of multicrystalline silicon ingots wherein the crucible comprises reaction bonded silicon nitride.

2. The reusable crucible of claim 1, wherein the crucible is coated with a release coating selected from the group consisting of Si_3N_4, SiO_2, a mixture of SiO_2 and Si_3N_4, SiC, graphite wool/cloth and silica wool/cloth.

3. The reusable crucible of claim 2, wherein the release coating is Si_3N_4.

4. The reusable crucible of claim 1, wherein the crucible walls have a thickness between 10 mm and 25 mm.

5. The reusable crucible of claim 1, wherein the silicon nitride crucible has a coefficient of expansion that is similar to that of silicon.

6. A method for production of multicrystalline silicon ingots in a furnace wherein the method comprises:

a. coating a silicon nitride crucible with a release coating;

b. baking the coated crucible to remove impurities;

c. directionally solidifying a multicrystalline silicon ingot in the reusable crucible;

d. removing the silicon ingot and the release coating;

e. recoating the crucible; and

f. using the recoated crucible for producing at least one additional silicon ingot.

7. The method of claim 6, wherein the release coating is selected from the group consisting of Si_3N_4, SiO_2, a mixture of SiO_2 and Si_3N_4, SiC, graphite wool/cloth and silica wool/cloth.

8. The method of claim 7, wherein the release coating is Si_3N_4.

9. The method of claim 6, wherein the furnace is a graphite resistance heated furnace.

10. The method of claim 6 wherein the furnace is an induction heated furnace.

11. The method of claim 6, wherein the furnace is backfilled at between 1200 and 1450° C. and with a pressure of at least 300 torr.

12. The method of claim 9 wherein the furnace is backfilled at between 1200 and 1450° C. and with a pressure of at least 300 torr.

13. The method of claim 6, wherein the crucible is made of RBSN.

14. The method of claim 6, wherein the furnace temperature and pressure are sufficient to prevent silicon in molten form from wicking up inner walls of the crucible.

15. The method of claim 6, wherein the crucible is made of isopressed silicon nitride.

16. The method of claim 11, wherein the pressure is at least 500 torr.

17. The method of claim 9 wherein the pressure is at least 300 torr.

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