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(71) Applicant: CRYSTAL SYSTEMS, INC. [US/US]; 27 Congress Street, Shetland Industrial Park, Salem, MA 01970 (US).

(72) Inventors: SCHMID, Frederick ; Two Gilbert Heights, Marblehead, MA 01946 (US). KHATTAK, Chandra, P. ; 16 Delaware Avenue, Danvers, MA 01923 (US).

(74) Agent: WEISSBURG, Steven, J.; Hale and Dorr, 60 State Street, Boston, MA 02109 (US).

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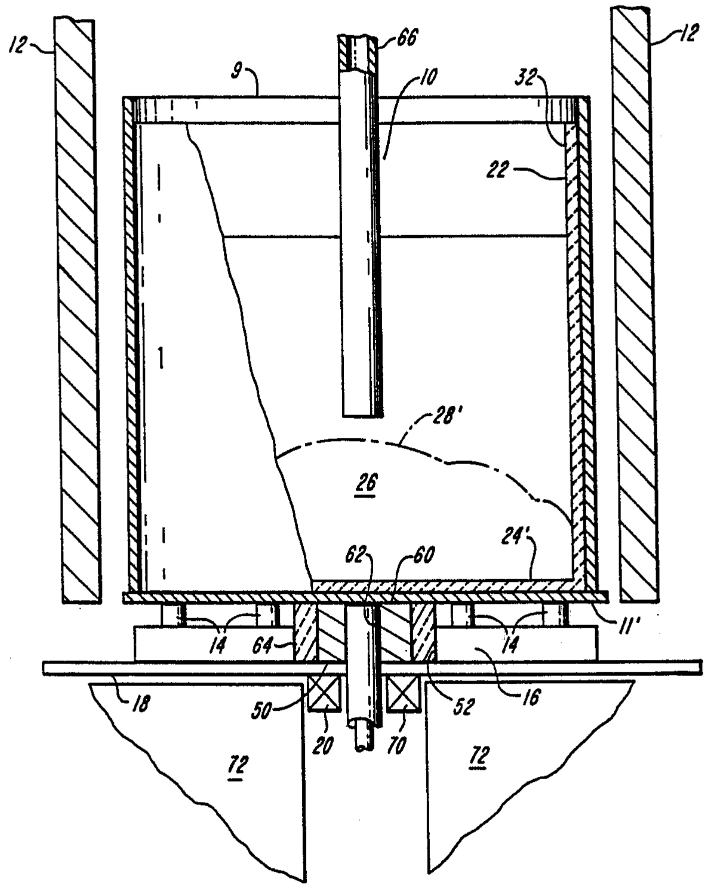
(54) Title: METHOD OF GROWING SILICON INGOTS USING A ROTATING MELT

(57) Abstract

The invention is a method and apparatus for producing silicon ingots of substantially single crystallinity from metallurgical grade silicon by heating it in a crucible to above its melting point to melt it and then extracting heat from the bottom of the crucible with a heat exchanger in heat conducting relationship with the bottom, and by moving the crucible and growing crystal in a first direction and accelerating the motion, thereby detaching from the crystal/liquid interface adhered impurity particles. The crucible may be rotated and the acceleration may be rotational.



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Method of Growing Silicon Ingots Using a Rotating Melt

Field of the Invention

This invention relates to the manufacture of silicon crystals suitable for use in photovoltaic cells from low purity silicon melt stock. This application is a continuation-in-part of co-pending, co-assigned application United States Serial No. 081,560, filed July 31, 1987 in the names of Frederick Schmid and Chandra P. Khattak which is a continuation of U.S.S.N. 825,960, filed February 4, 1986, which is a continuation of U.S.S.N. 598,828, filed May 10, 1984, which is a continuation of U.S.S.N. 423,170, filed September 24, 1982, which is a continuation of U.S.S.N. 191,260, filed September 26, 1980, all co-assigned and all in the names of Frederick Schmid and Chandra Khattak.

Background of the Invention

The best photovoltaic solar cells have been fabricated from high-purity, single-crystal silicon, the making of which by conventional processes involves many steps. The process begins with metallurgical grade silicon, which is only 98-99% pure. This impurity level inhibits single crystal growth and creates conductivity that is too high for solar cells, owing primarily to the presence of boron and phosphorous. Metallurgical grade silicon is typically produced in large quantities in arc furnaces by the carbothermic reduction of silica. The carbothermic process causes the presence of significant amounts of the impurity of carbon, primarily in the form of silicon carbide. Further, since the silicon is poured in air, the surface of the silicon is oxidized to silica. Additional metallic impurities are present, arising from metals present in the naturally occurring silica.

According to a known method, this grade of silicon is then chemically converted by another process to an intermediate compound (e.g., tricholosilane), which is in turn converted by still another process (e.g., Siemens process) to semiconductor grade silicon (having impurities in the ppb range), which in turn is used to grow a single crystal suitable for use in a solar cell. This process is discussed in Pizzini, S., "Solar Grade Silicon as a Potential Candidate Material for Low Cost Terrestrial Cells," Solar Energy Materials 6 North-Holland Publishing Company (1982) p. 257. A method that has proved useful in growing crystals from such resulting high purity silicon (e.g., impurities less than 10 ppb) is the Heat Exchanger Method, which involves heating material in a crucible to above its melting point in vacuum to melt the material therein and thereafter extracting heat from the bottom of the crucible by providing a heat exchanger in heat conducting relationship with the bottom. The Heat Exchanger Method is described in U.S. Patents Nos. 3,653,432 and 3,898,051 and Applications Serial Nos. 4,465 filed January 18, 1979 and 967,114 filed December 7, 1978, all of which are hereby incorporated by reference.

In another process, Dow Corning Corporation used specially selected silica and carbon in an arc furnace, and produced metallurgical silicon that is about 99.8% pure, having low concentrations of boron and phosphorous, impurities which have high segregation coefficients and are therefore difficult to segregate during directional crystal solidification. This silicon was poured in air, resulting in a silica layer, which was then etched away. After etching, an ingot was grown by the Czochralski process (a directional solidification process). Loss of single crystallinity still resulted; but growth of a second crystal, using the best portions from the first growth as starting material, enabled the production of a single crystal material suitable for solar cell production.

In another process, Wacker, GmbH in West Germany conducts a multiple step process to arrive at raw material for use in crystal growth. This process is described in Dietl, J., "Metallurgical Ways of Silicon Meltstock Processing," ch. 6 of Materials Processing Theory and Practices, Khattak, C. and Ravi, K.(ed.) North-Holland (1987) p. 342. Metallurgical grade silicon is pyrometallurgically upgraded by slagging or, alternatively, by solvent extraction (Al based refining). The resultant is ground and acid leached. An additional pyrometallurgical step by liquid gas extraction is applied. Depending on the crystallization technique and type of device processing, final purification by in situ or additional directional solidification may be applied. After this complicated series of steps, the silicon is finally ready for crystallization.

Researchers at Hitachi, Ltd., in Japan, in one project, attempted to grow silicon crystals suitable for solar cells from metallurgical grade silicon using the Czochralski technique. E. Kuroda and T. Saitoh, in "Growth and Characterization of Polycrystalline Silicon Ingots From Metallurgical Grade Source Material," Journal of Crystal Growth 47, p. 251-260 (1979), report that slag floating on the melt surface made growth of single crystals impossible. Further, grown crystals included impurities at greater concentration than would be expected from the segregation coefficient. These impurities caused multi-crystallinity rendering the crystals unsuitable for use in solar cells.

Saitoh, et al., in "Impurity Gettering of Polycrystalline Solar Cells Fabricated from Refined Metallurgical Grade Silicon," IEEE Transactions on Electron Devices, V. ED-27, No. 4, (April 1980) p. 671 et seq., reported a two-stage method of growing crystals for solar cell use. An acid-leached metallurgical grade silicon was solidified in vacuum. This material was pulled according to the Czochralski method to produce polycrystalline ingots. A second pull was required to achieve single crystals.
T. Warabisako, et al., in "Efficient Solar Cells from Metallurgical-Grade Silicon," Proceedings of the 11th Conference (1979 International) on Solid State Devices, Tokyo, 1979; Japanese Journal of Applied Physics, Volume 19 (1980) Supplement 19-1, pp. 539-544, report that, using the Czochralski method, after a single pull, all ingots were polycrystalline, with crystal sizes from 0.1 mm to several cm. A portion of this crystal was pulled a second time and only 66% of the crystal was mono-grain or bi-crystal.

Thus, three distinct impurity problems arise when growing silicon crystals from metallurgical grade silicon. First, boron and phosphorous impurities are incorporated into the crystal. Second, carbon is incorporated into the crystal. Finally, metallic impurities are present in the meltstock. These impurities disrupt growth and contaminate silicon, rendering the end product less uniform and less useful. The impurities increase the conductivity of the crystals beyond that which is useful. Carbon also renders it difficult to cleanly machine the crystals due to SiC inclusions (e.g., by cutting them) because SiC particles are relatively hard as compared to the silicon crystal. Carbon, by itself, is not per se harmful, but in SiC molecules it generates a stress field which in turn generates an electric field (due to the piezoelectric effect), which attracts metal and phosphorous and boron impurities and thus creates unacceptably large regions of unacceptably high impurity.

There are three sources of carbon contamination. It can result from carbon in the furnace. It can result from free carbon in the starting material. Finally, it can result from carbon in the starting material in the form of SiC.

Summary of the Invention

It has been discovered that silicon with impurity levels greater than 10,000 ppm by weight (e.g., metallurgical grade silicon that is less than 99% pure) can be grown into a single crystal ingot using the Heat Exchanger Method (HEM) in a single step. The directional solidification accomplishes removal of a large amount of the metallic impurities. This is because the segregation coefficient of the metals in silicon is quite low.

It has also been discovered that refining processes and reactions can be employed in the Heat Exchanger Method prior to or during crystal growth. In a most preferred embodiment, carbon in the form of SiC is removed from the melt by causing the crucible to rotate and by accelerating and decelerating the rotation periodically. SiC particles that accumulate at the crystal growth interface are broken off and migrate toward the outside of the melt under the influence of their momentum and the temperature gradient. Further, in preferred embodiments, the silica layer covering the starting material metallurgical grade silicon, is left intact rather than being etched away prior to loading. This silica layer promotes silicon carbide removal by slagging of the silicon oxide. Pure powdered silica ((SiO_2) in its amorphous phase, i.e., glass) is also added to the melt prior to crystal growth to encourage reactions that incorporate the carbon into gaseous molecules which leave the melt.

Boron impurities are removed in other embodiments where the melt is also stirred or where moist hydrogen is passed through the melt prior to crystal growth. Chlorine is passed through the melt resulting in volatile reaction products and also causing the removal of impurities. The melt is also heated to high temperatures, prior to crystal growing at a lower temperature, to remove impurities with a high vapor pressure by boiling them off.

In all of the above embodiments, refining is promoted by the expanding area of the solid/liquid interface (as opposed to a constant interface area occurring with directional solidification such as the Czochralski method or a shrinking interface area occurring with casting, when the exterior solidifies before the interior), which increases the impurity concentration on the liquid side of the interface. An impurity increase with known methods can cause deleterious interface breakdown and loss of single crystallinity. The convex to the liquid shape of the solid/liquid interface facilitates removal of SiC particles by the forces from rotation and from rotational deceleration/accelerations. Also, impurities are transported to exterior surfaces where they can be easily cropped off, and the temperature gradient, with the hottest melt at the top, stabilizes temperature gradients. The silica slag layer floats on the surface of the melt and does not interfere with the solid/liquid interface some distance below the interface. In the embodiments featuring gas bubbling and stirring of the melt, the increased turbulence promotes removal of impurities from the interface and their transport to the upper surface.

The vacuum operation of HEM with a high impurity content silicon (such as metallurgical grade silicon) allows further refinement by vaporization of high vapor pressure species. These species are impurities (such as alkali metals, manganese, etc.) that have a tendency to go into vapor phase in preference to staying in the silicon melt. Under vacuum operation (e.g., below 30 torr and preferably near 0.1 torr), the impurity vapor is continuously removed from the site of the reaction in preference to building up near the melt surface, thereby enhancing removal of these impurities from the melt.

The process of the invention removes unwanted impurities from the melt by four processes: 1) vaporization of impurities that is enhanced by vacuum operations eg. alkali metals and group V elements (such as As,P); 2) scavanging and reaction of impurities that is enhanced by slagging with silica and gas blowing, eg. glass forming elements (eg. B, Al, Na), heavy metals (eg. W, Mo, Ti, Zr) and transition metals (eg. Fe, Cr, Mg); 3) segregation of impurities that is enhanced by controlled directional solidification with a convex to the liquid interface and rotational deceleration/acceleration; and 4) centrifuging of insoluable particles such as SiC to the outside enhanced by rotational acceleration of the convex interface. Each of these processes can be practiced individually or in combination to remove unwanted contamination. The process of the invention can achieve over 75% single crystallinity in the grown crystal.

Description of the Preferred Embodiment

Objects, features and advantages of the invention will appear from the following detailed description of the structure and use of a preferred practice thereof, taken together with the attached drawing in which:

Fig. 1 is a schematic view, partially in section, of a crucible, molybdenum retainer, conducting graphite plug, and insulation within the heating chamber of a casting furnace.

Fig. 2a is a schematic elevation view of a growing silicon crystal showing detachment of a SiC partial upon deceleration of rotation of the melt.

Fig. 2b is a schematic plan view of a growing silicon ingot, showing detachment of a SiC particle upon deceleration of rotation of the melt.

Fig. 3 is a schematic view, partially in section, of a crucible suitable for multi-crystalline growth within the heating chamber of a casting furnace.

Referring now to Fig. 1, a silica crucible 10 is shown within the cylindrical heating chamber defined by the resistance heater 12 of a casting furnace of the type disclosed in U.S. Patent No. 3,898,051. The crucible 10 rests on a graphite plate 11 which itself is supported by graphite rods 14 mounted on a graphite support plate 16 on turntable 18 at the bottom of the heating chamber, and is surrounded by a cylindrical graphite retainer 9. A helium cooled molybdenum heat exchanger 20, of the type disclosed in U.S. Patent No. 3,653,432, extends through openings in the center of the plate 16 and turntable 18.

Crucible 10 is about 6 in. (15 cm.) in height and diameter and its cylindrical wall 22 and base 24 are 0.15 in. (3.7 mm.) thick. Graphite plate 11 is about 0.500 in. (1.25 cm.) thick, and graphite retainer 9, is about 0.250 in. (0.625 cm) thick. A silicon ingot

26, partially solidified according to the process described in aforementioned patents, is shown within the crucible, the convex to the liquid solid-liquid interface 28 having advanced from the seed (shown in dashed lines at 30).

A stepped cylindrical graphite plug 50 (upper portion diameter 1.9 in., and lower portion diameter 2.5 in.) extends from turntable 18 upwardly through coaxial holes 52, 54, 56 in, respectively, plate 16, graphite plate 11 and crucible base 24. The top 58 of plug 50 is flush with the inside bottom surface of crucible base 24. The seed 30 is placed over the plug 50 and the adjacent portion of crucible bottom 24 so as to cover opening 56. The exterior of the plug upper portion fits loosely in openings 54, 56 to allow for thermal expansion; and the step 60 between the plug's upper smaller diameter and lower larger diameter portions engages the underside of plate 11. A small quantity of silicon powder is placed in the area of opening 56 where seed 30, crucible 10 and graphite plug 50 are in proximity. Heat exchanger 20 fits within a coaxial recess 62 in the bottom of plug 50, with the top of the heat exchanger about 1/8 in. below the top 58 of the plug. A graphite felt insulation and/or molybdenum heat shield sleeve 64 closely surrounds the larger diameter portion of plug 50, extending axially of the plug the full distance between turntable 18 and plate 11. As shown, the exterior surface of insulation sleeve 64 engages the interior of opening 52.

Bearing 70 in the furnace base rotationally supports the entire crucible structure described above, relative to stationary foundation 72. A suitable coupling (not shown) is provided to permit heat exchange from the rotating heat exchanger shaft 20. Heat exchanger 20 is caused to rotate by suitable means, not shown, such as by applying torque to the end of heat exchanger shaft 20.

In an embodiment described below, movable silica tube 66 is suspended (by means not shown) so that one end extends into crucible 10 and the other end is connected to a gas supply (not shown).

The apparatus described above and the operating conditions and methods disclosed in the above-mentioned patents and patent applications are used in growing single crystals from metallurgical grade silicon. Etched metallurgical grade silicon is upwardly and outwardly solidified in 6 inch crucible 10 using the Heat Exchanger Method (HEM). The melt stock is heated under vacuum condition (0.1 torr pressure). Furnace temperature is increased to 100°C above the melt point until the meltstock is melted and reduced to less than 3°C above melting point. The heat exchanger temperature is kept 113°C below the melting point. The heat exchanger temperature is decreased during growth at a rate of 420°C/hr., the furnace temperature is kept constant, and crystal growth lasts about 7.75 hrs. A single crystal ingot with impurities segregated to the outside of the ingot results. Even impurities present in the crystal in the form of solid particles that do not float or sink but remain suspended do not prevent single crystallinity. This is due to the very stable solid/liquid interface, the low temperature and impurity gradients and to the damping of mechanical vibrations of, and temperature variations in, the heating element by the liquid buffer region between the solid/liquid interface 28 and the crucible wall 22.

An important feature of HEM growth that is useful in removing impurities from metallurgical grade silicon is that the crystal grows outwardly from the bottom center so that the last regions to solidify are at the upper surface and at the crucible walls. As solidification proceeds, impurities are segregated in front of the solid/liquid interface, causing an increase in impurity concentration in the remaining liquid. Although the increase in impurities concentration in front of the interface causes interface breakdown and loss of single crystallinity in other unidirectional solidification processes, because the HEM interface expands, this impurity buildup is distributed over a larger interface area; hence, concentration buildup is not as rapid as for unidirectional solidification. Therefore, by using the HEM process, higher impurities are tolerated without loss of structure. The impurities are transported to exterior surfaces where they can be easily cropped off.

It has also been determined that carbon impurities in the form of SiC can be excluded from the growing crystal by rotating and decelerating or accelerating the rotation of the melt. Silicon carbide particles are present in the liquid due to supersaturation of carbon and the presence of SiC from starting materials. The larger SiC particles settle to the bottom because of their higher density compared to the silicon of the melt; some of the SiC particles are floating on the surface of the melt, supported by surface tension; a number of different size particles are suspended in the melt. During growth the smaller, suspended particles are pushed ahead of the interface till they combine to form larger particles. According to known methods not incorporating the present invention, these particles would be entrapped in the solid growing crystals. Referring to Fig. 2, and in particular Fig. 2b, a top view of a growing crystal is shown schematically, with SiC particles at the surface indicated by the symbol "SiC". The particle may be one that would be entrapped in the solid but for the method of the invention. According to the invention, if the melt is rotated, the silicon carbide can be dislodged from the interface by abruptly changing the rate of rotation, e.g., by decelerating the rotation. Fig. 2b depicts the situation where the melt is rotated counter clockwise, as viewed from above. Consequently, all of the SiC particles adhered to the surface rotate in that direction. If the melt rotation is abruptly decelerated in the clockwise direction, as indicated by the arrow R, the SiC particles continue to move in the counter clockwise direction, due to their momentum in that direction. Meanwhile, the solid crystal has decelerated, including those points at which the SiC particles attach. If the deceleration is abrupt enough, the momentum of the particles break the bond to the crystal interface, and the SiC particles continue to move through the melt in the directions indicated by the arrows for the individual particles. Under the influence of its own momentum, a SiC particle continues to move away from the crystal along a tangent to the surface at the point from which it detached. This is shown schematically in Fig. 2a by the arrows at each illustrated SiC particle. Turbulence caused by the detachment clears out the particle from the interface. The SiC particles come to rest at the outer perimeter of the crucible, and are thereby solidified into the crystal at the outermost surface. They can be easily removed from the surface by cropping or other machining.

It will be understood that this deceleration technique would not provide advantageous results other than with a convex to the liquid interface. With a concave to the liquid interface, any particles which did detach would either be held against the sloping wall, or, fall down the slope to accumulate in the center, which will ultimately become an internal zone of the grown crystal. They will not migrate to the outside of the melt where they can be easily removed.

A suitable rotational velocity depends somewhat on the radius of the crucible. For crucibles on the order of 6 inches (15 cm.) to 36 inches (91 cm), a rotational velocity in the range from 100 revolutions per minute to 5 rpm, respectively, is appropriate. If the melt is decelerated on the order of every one half minute to one minute, the SiC particles will not have a chance to adhere permanently to the interface. Because the detaching force depends on the linear momentum, which depends in part upon the size of the particle, the angular velocity and the radius at which the particle is attached, it is not possible to predetermine an angular deceleration which will detach SiC in every case. However, such deceleration can be easily determined by routine testing.

It is beneficial to provide a modest temperature gradient in the liquid, so that the liquid is less viscous and so that the SiC particles, once detached, can move away from the interface unimpeded by a viscous fluid drag. A temperature difference of 25°C from the interface to the liquid surface (1412°C at the interface and 1437°C at the liquid surface) is adequate at the start of crystallization.

It has been proposed to dislodge the SiC particles from the interface during directional solidification by researchers at Siemens Research Laboratories, of West Germany, by creating turbulence caused by a very high temperature gradient in the crystal. Urbach, H.F., Lerchenberger A., "Important Factors Determining the Removal of SiC From Silicon Employed for the Production of Solar Cells," Presented at the Eighth European Photovoltaic Solar Energy

Conference in Florence, Italy, May 9-13 (1988). This process has met with poor results because it is not possible to generate high temperature gradients in a large crystal. Further, with a large temperature gradient in the crystal, a fine grain structure arises. This result is unacceptable, because the object is to grow crystals with a large grain structure, in order to maximize single crystallinity. Thus, it is necessary to apply to the Si an additional crystallization step, such as a Czochralski pull, as was done by the Siemens researchers.

In addition to enhancing the growth of single crystals, the method is applied advantageously to the growth of ingots having multiple, large-grained crystals. In this embodiment, a seed is not used. Growth proceeds from multiple initiation sites on the crucible floor 24. An apparatus suitable for multiple crystal growth is shown in Fig. 3. This apparatus is identical to that of Fig. 1, but for a modification in graphite plug 50'; graphite plate 11' and crucible base 24. In the embodiment for multiple crystal growth, crucible base 24' and graphite plate 11' are solid, rather than having concentric openings, and graphite plug 50' is not stepped but rather is flush at the top. The reason for the stepped graphite plug 50 in the single crystal embodiment of Fig. 1 relates to the fact that graphite is a much better conductor of heat than is the silica of crucible bottom 24. For a single crystal, it is important to remove heat from the seed so that it remains solid, while allowing solidification of the crystal at a larger radius.

For multiple crystal growth of Fig. 3, it is desired to initiate crystal growth uniformly around crucible floor 24. Therefore it is not desired to cause more efficient heat transfer at the center, and thus it is not beneficial for the graphite plug 50' to extend to the melt.

Concentration of the impurities at the solid/liquid interface 28 is also minimized by stirring the melt.

Unetched silicon with its adherent silica layer is used to reduce even further the silicon carbide content of the end product. Silica reacts with silicon carbide according to the following reactions:

$$\mathrm{SiC + 2\,SiO_2} \qquad \mathrm{3\,SiO + CO}$$

$$\mathrm{SiC + SiO_2} \qquad \mathrm{SiO + CO + Si}$$

$$\mathrm{2\,SiC + SiO_2} \qquad \mathrm{3\,Si + 2\,CO}$$

$$\mathrm{SiC + SiO_2} \qquad \mathrm{2\,Si + CO_2}$$

$$\mathrm{SiC + SiO_2} \qquad \mathrm{C + 2\,SiO}$$

These reactions all have negative free energy at the melting point of silicon and approximately 0.1 torr pressure, and therefore tend to proceed to the right. Because the carbon monoxide, carbon dioxide, and silicon monoxide created by these reactions form bubbles, which rise to the surface, a net removal of the carbon from the melt is caused. The presence of silica also causes the removal of carbide and other impurities (e.g., aluminum) by the slagging phenomenon. The slag layer rises to the melt surface where it does not interfere with the solid/liquid interface, and the impurities are, therefore, not incorporated in the crystal.

High purity silica powder is also added to the melt stock prior to crystal growth by the HEM to further reduce silicon carbide content by virtue of the above reactions. In the 6" crucible 10, 150 grams of silica (99% pure and in powdered form with 100 micrometer particles) is added to 3 kilograms of metallurgical grade silicon.

In both the unetched and the unetched plus added silica embodiments, the slag is removed after crystal growth by cropping.

In the added silica embodiment, the ingot is found to have low enough conductivity to allow use in photovoltaic cells.

Solar cells fabricated from such silicon show up to 12.33% conversion efficiency.

Other Embodiments

It will be understood that in decelerating the rotation of the melt, it may be advantageous to actually reverse the direction of rotation. It may also be advantageous to vibrate the melt at a frequency sufficient to dislodge the adhered SiC particles. In addition to rotating the melt and leaving the metallurgical grade silicon unetched and adding silica to the melt, the use of other refining processes involving reacting a substance with the impurities in the silicon to form either a solid immiscible liquid, or gas is made possible by the stability and expanding nature of the solid/liquid interface.

For example, impurities can be stripped from the melt by passing, via tube 66, gasses that react with the impurities to form reaction products that are volatile or will otherwise remove themselves from the melt. Specifically, moist hydrogen causes the removal of boron by the formation of boron oxide.

Also, chlorine reacts with metallic impurities to form volatile reaction products such as iron chloride.

Finally, the melt stock temperature is increased to 50 to 100°C above the silicon melting point to improve volatization of impurities. After sufficient removal of impurities, the temperature is then lowered to 3°C above melting point to allow crystal growth.

The foregoing description should be taken as illustrative and should not be considered limiting in any way.

What is claimed is:

1. A process for producing a silicon ingot of substantially single crystallinity suitable for use in photovoltaic cells from low purity silicon meltstock, said process comprising the steps of:

a. providing a silicon meltstock having an impurity level greater than 10,000 ppm by weight;

b. heating said silicon meltstock in a crucible to above its melting point;

c. thereafter solidifying said melted silicon meltstock to product said ingot by extracting heat from a central portion of the bottom of said crucible whereby impurity particles are excluded from the solidified meltstock forming the interior of said ingot subsequent to said heating and in the course of said solidifying and adhere loosely to the surface of the growing solid; and

d. periodically,

ii. rotating said solidifying melt in a first direction; and

iii. thereafter decelerating the rotation of the meltstock sufficiently abruptly to dislodge said adhered impurities from the solidified portion of the meltstock.

2. The process of claim 1 wherein said adhered impurities are of silicon carbide.

3. The process of claim 2 where said silicon meltstock is metallurgical grade silicon produced by the carbothermic reduction of silica.

4. The process of claim 1 including the step of providing silica within said crucible prior to said solidifying, and wherein said impurities are removed from said meltstock by the step of reacting said silica with silicon carbide impurities in said silicon meltstock to cause the formation of reaction products that will separate from the melted silicon meltstock.

5. The process of claim 4 wherein before heating said silicon meltstock, said meltstock includes an adherent covering layer of silica.

6. The process of claim 4 wherein said silica is added to said melted silicon meltstock subsequent to said heating and prior to said solidifying.

7. The process of claim 6 wherein said silica is pure powdered silica.

8. The process of claim 1 including the step of reacting non-volatile impurities in said melt stock to form volatile impurities, and removing said volatile impurities from said silicon meltstock by reducing the pressure around said crucible to less than about 30 torr.

9. The process of claim 8 wherein said reduced pressure is about 0.1 torr.

10. The process of claim 8 including the step of heating said silicon to between about 50°C to 100°C. above the melting point of silicon to promote said removal of volatile impurities.

11. The process of claim 8 wherein said volatile impurities are produced by passing moist gas chosen from the group of hydrogen and chlorine through said melted silicon melt.

12. The process of claim 8 wherein said volatile impurities are produced by adding silica to said meltstock.

13. A process for producing a silicon ingot of large grain size multiple crystallinity suitable for use in photovoltaic cells from low purity silicon meltstock, said process comprising the steps of:

a. providing a silicon meltstock having an impurity level greater than 10,000 ppm by weight;

b. heating said silicon meltstock in a crucible to above its melting point;

c. thereafter solidifying said melted silicon meltstock to product said ingot by extracting heat from the bottom of said crucible whereby impurity particles are excluded from the solidified meltstock forming the interior of said ingot subsequent to said heating and in the course of said solidifying and adhere loosely to the surface of the growing solid; and

d. periodically,

ii. rotating said solidifying melt in a first direction; and

iii. thereafter decelerating the rotation of the meltstock sufficiently abruptly to dislodge said adhered impurities from the solidified portion of the meltstock.

14. The process of claim 13 wherein said adhered impurities are of silicon carbide.

15. The process of claim 14 where said silicon meltstock is metallurgical grade silicon produced by the carbothermic reduction of silica.

16. The process of claim 13 including the step of providing silica within said crucible prior to said solidifying, and wherein said impurities are removed from said meltstock by the step of reacting said silica with silicon carbide impurities in said silicon meltstock to cause the formation of reaction products that will separate from the melted silicon meltstock.

17. The process of claim 16 wherein before heating said silicon meltstock, said meltstock includes an adherent covering layer of silica.

18. The process of claim 16 wherein said silica is added to said melted silicon meltstock subsequent to said heating and prior to said solidifying.

19. The process of claim 13 including the step of reacting non-volatile impurities in said melt stock to form volatile impurities, and removing said volatile impurities from said silicon meltstock by reducing the pressure around said crucible to less than about 30 torr.

20. A process for producing a silicon ingot of substantially single crystallinity suitable for use in photovoltaic cells from low purity silicon meltstock, said process comprising the steps of:

a. providing a silicon meltstock having an impurity level greater than 10,000 ppm by weight;

b. heating said silicon meltstock in a crucible to above its melting point;

c. thereafter solidifying said melted silicon meltstock to product said ingot by extracting heat from a central portion of the bottom of said crucible whereby impurity particles are excluded from the solidified meltstock forming the interior of said ingot subsequent to said heating and in the course of said solidifying and adhere loosely to the surface of the growing solid; and

d. periodically,

ii. moving said solidifying melt in a first direction; and

iii. thereafter accelerating the motion of the meltstock sufficiently abruptly to dislodge said adhered impurities from the solidified portion of the meltstock.

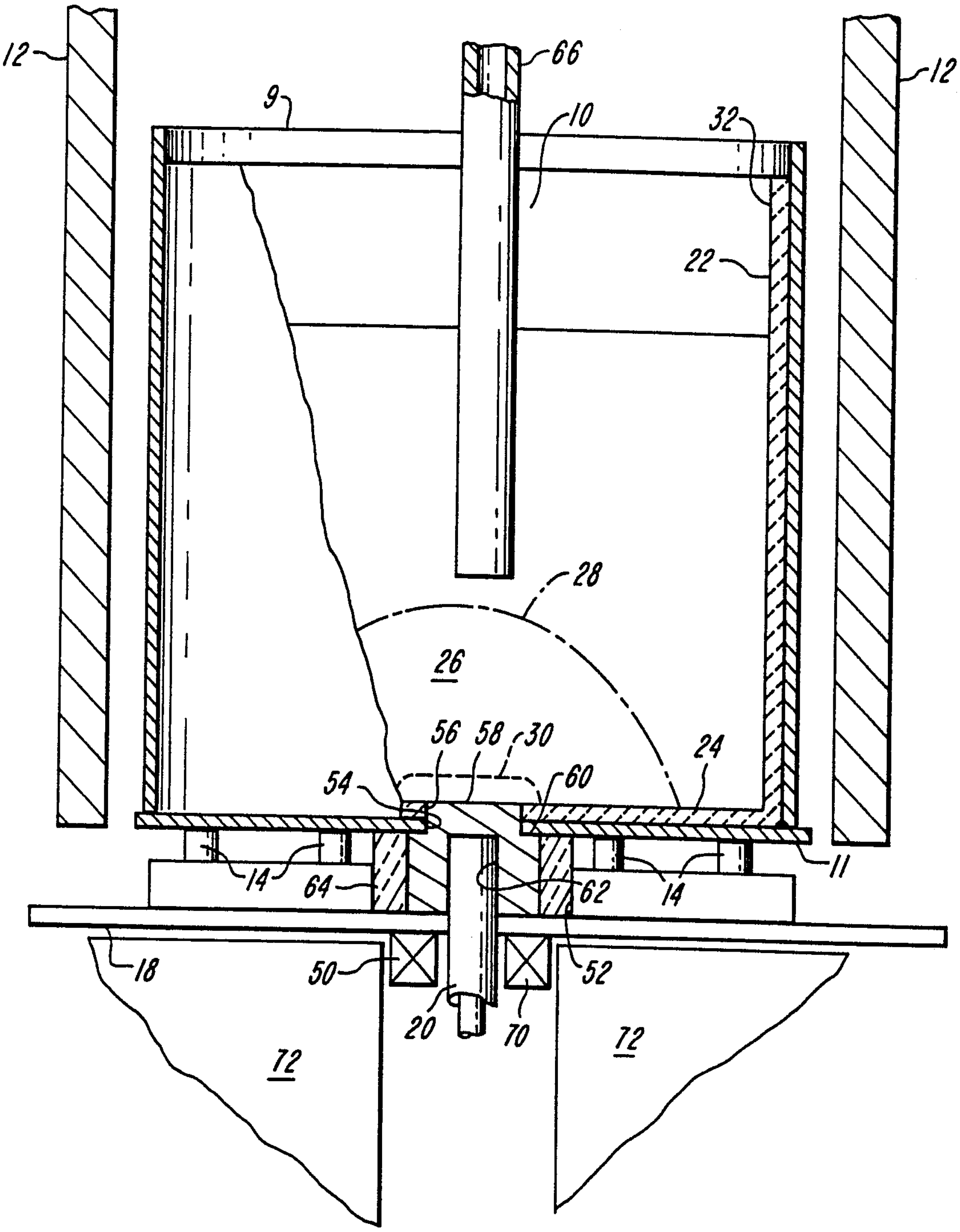
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FIG. 1

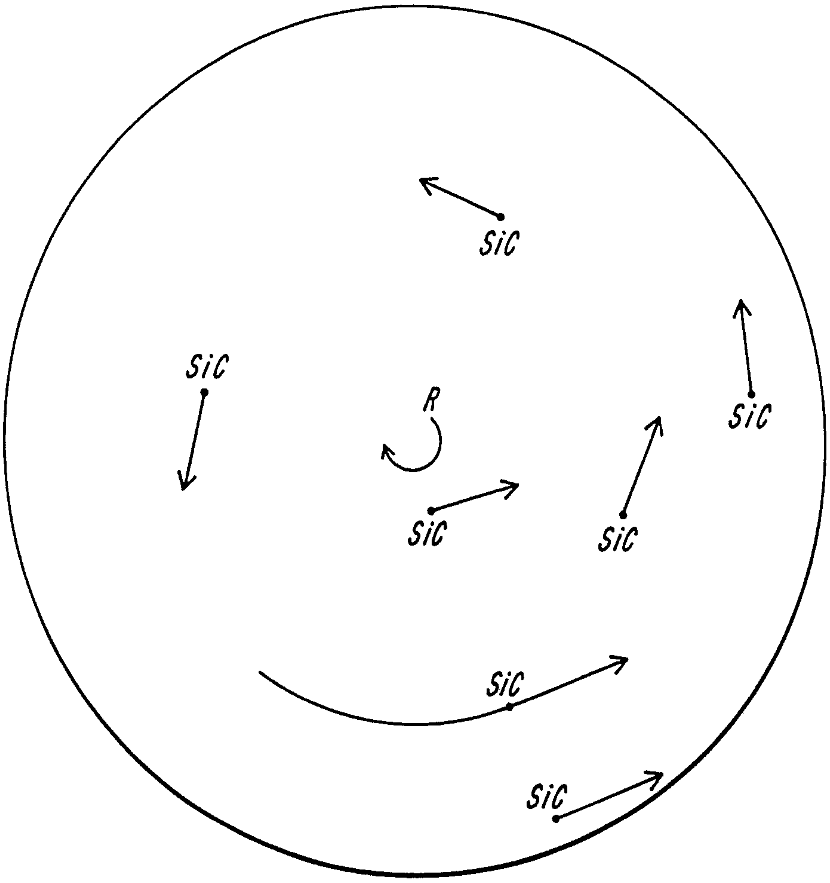

FIG. 2B

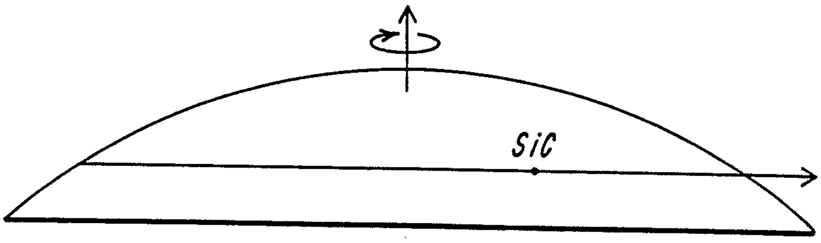

FIG. 2A

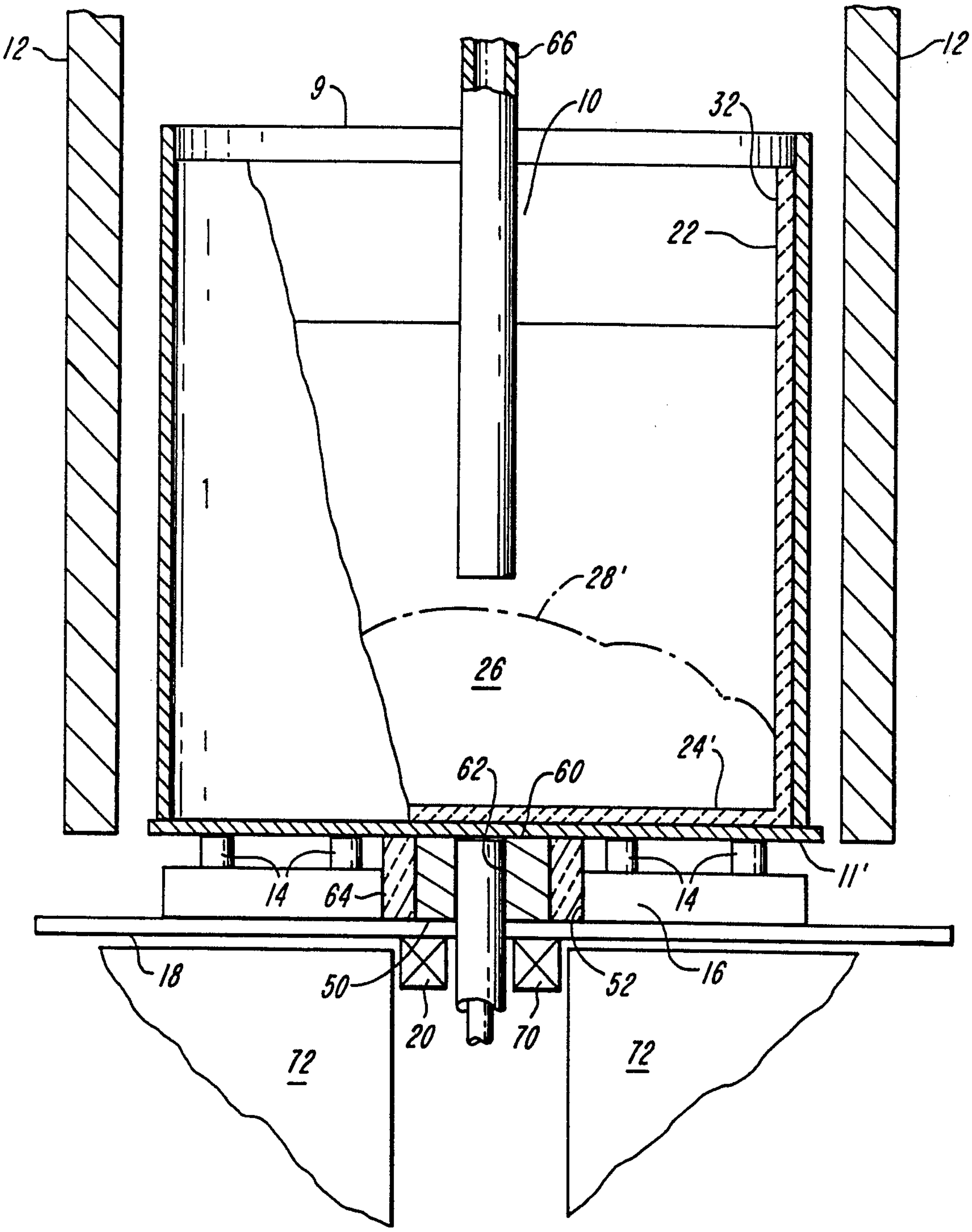

FIG. 3

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/04468

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

INTCL 4: C30B 11/00, 11/02 29/06; C04B 33/02

USCL: 156/616.2, 616.41, Dig 64; 423/348

II. FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
U.S.	156/616.2, 616.4, 616.41, Digest 64, Digest 85; 164/122.2; 165/61; 422/248; 423/348

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

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A	US,A, 4,312,847, (Dawless), 26 January 1982	1-20
A	US,A, 4,094,731, (Keyser et al), 13 June 1978	1-20
A	US,A, 4,643,833, (Aulich et al), 17 February 1987	1-20
A,P	US,A, 4,840,699, (Khattak et al), 20 June 1989	1-20
A	US,A, 4,659,423 (Kim et al) 21 April 1987	1-20

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 06 December 1989	Date of Mailing of this International Search Report 13 FEB 1990
International Searching Authority ISA/US	Signature of Authorized Officer Gary P. Straub Gary P. Straub

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A	Proceedings of the 11th Conference (1979 International) on Solid State Devices, Tokyo, 1979; Japanese Journal Of Applied Physics, Volume 19 (1980) Supplement 19-1, Warabisako et al, Efficient Solar Cells from Metallurgical Silicon, pages 539-544	1-20
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A	Thirteenth IEEE Photovoltaic Specialists Conference - 1978, Washington, DC, 5-8 June 1978, Hanoka et al, Efficient polycrystalline Solar Cells Made from Low-Cost Refined Metallurgical Silicon	1-20
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A	4.	Rustioni et al, Solar Silicon From Directional Solidification Of MG Silicon produced via the Silicon Carbide Route, pages 292-321.	1-20
A	5.	Noda, Toshio, Process and Product Development in Japan, pages 213-231	1-20
A	6.	Hwang, H.L., Process and Product Development in Taiwan, pages 233-249.	1-20

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A	US,A, 4,243,471, (Ciszek et al, 06 January 1981	1-20
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A	US,A, 4,243,471, (Ciszek et al), 06 January 1981	1-20
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