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SILICON CRYSTALS: PROCESS FOR MANUFACTURING WAFER-LIKE SILICON CRYSTALS WITH A COLUMNAR STRUCTURE

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16. Abstract

Wafer-like Si crystals suitable for making solar cells are formed by pouring molten Si contg. suitable dopants into a mold of the desired shape and allowing it to solidify in a temp. gradient, whereby the large surface of the melt in contact with the mold is kept at ≦ 200° and the free surface is kept at a temp. 200-1000° higher, but below the m.p. of Si. The mold can also be made in the form of a slit, whereby the 2 sides of the mold are kept at different temps. Thus, 1 kg of highly pure polycrst. Si, doped with 2×10^{15} B atoms/cm^3, was melted in a quartz crucible, heated to 1500°, and poured into a mold formed by milling a cavity 100 x 100 x 70 mm in the surface of a cylindrical graphite block 200 mm in diam. The graphite block was induction heated and the bottom of the mold was cooled by means of a water-cooled Cu plate, so that the surface of the mold in contact with 1 of the largest surfaces of the melt was held at ≅800°. The free surface of the melt was subjected to thermal radiation from a graphite plate located 2 mm from the surface and heated to 1500°. The Si crystal formed after slow cooling to room temp. had a columnar structure in the direction of the shortest axis. The crystal was cut with a diamond saw into wafers ≈500 mm thick. Solar cells prepd. from these wafers had efficiencies of 10-11%.

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SILICON CRYSTALS; PROCESS FOR MANUFACTURING WAFER-LIKE SILICON CRYSTALS WITH A COLUMNAR STRUCTURE

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Patent Claims

1. Process for manufacturing wafer-like silicon crystals with a columnar structure by pouring molten silicon into a mold and allowing it to harden in a temperature gradient, distinguished by the fact that the large surface of the melt in contact with the mold is kept at a maximum temperature of 1200°C and the free surface is kept at a temperature of 200-1000°C higher, but below the melting point of silicon, or if in contact with another mold it is exposed to a temperature below a maximum of 1200°C.

2. Process as per claim 1, distinguished by the fact that the molten silicon is at a temperature of 1450-1600°C when poured into the mold.

3. Application as solar cell material of the wafer-like silicon crystals obtained by the process as per claim 1 or 2.

The invention concerns a process for manufacturing wafer-like silicon crystals with a columnar structure by pouring molten silicon into a mold and then allowing it to harden in a temperature gradient.

With the growing shortage and increased costs of fossil fuels the production of energy by directly converting solar energy into electrical energy with solar cells is becoming increasingly important. While this type of energy production is already the predominant form in the fieldoof satellite technology, so far no limits have been set to the terrestrial use of such solar cells because of high prices. Of greatest interest in this regard are silicon cells, in which about one-third of the costs are due solely to the silicon used. On the one hand, a substantial reduction in costs for semiconductor material, but on the other hand also in the costs due to further processing into solar cells are necessary conditions for the efficient marketing of solar energy.

The demands which have so far been placed on the silicon used in solar cells are extremely high. The silicon should be in monocrystalline form and as perfect as possible, i.e., free of point defects, dislocations, twinnings, stacking defects, swirls or chemical impurities. The efficiency of solar cells produced from such material varies between 10 and 12%, with a theoretically possible 22%. Since, as a rule, the silicon disks must be cut with diamond saws from monocrystalline rods of the above specifications, almost half of these rods is lost as waste. To reduce these wastes efforts are now being made to use as a base material monocrystalline silicon bands such as obtained with the EDFG process (edge defined film fed growth). Using this method, an efficiency of about 10% is expected for such solar cells. From the cost standpoint, polycrystalline siliconswould be especially interesting. Up to now, however, it has been possible to make solar cells from polycrystalline silicon with an admittedly economically uninteresting efficiency of 1% (cf. Electronics, April 4, 1974, p. 109).

The invention therefore addressed itself to the problem of manufacturing inexpensive silicon crystals in a wafer-like form suitable as the base material for the production of solar cells.

A probess was now found for manufacturing wafer-like silicon crystals with a columnar structure by pouring molten silicon into a mold and then allowing it to solidify in a temperature gradient, distinguished by the fact that the large surface of the melt in contact with the mold is kept at a maximum temperature of 1200°C and the free surface is kept at a temperature of 200-1000°C higher, but below the melting point of silicon, or if in contact with another mold, it is exposed to a temperature below a maximum of 1200°C.

The silicon used in the process as per the invention is melted, for example, in a quartz crucible under a vacuum or inert gas and poured into a mold suitable for the production of a wafer-like object, whereby the temperature of the molten silicon during pouring should advantageously measurer 1450-1600°C.

Basically, the molds involved are open and closed molds. In the preferred method of carrying out the process the molten silicon is poured into a pan-shaped cast iron mold, open on top, the bottom of which is in contact with one of the two largest boundary surfaces of the poured melt and in an appropriate manner, for example by means of a metal plate containing a circulating coolant, it is kept at a maximum temperature of 1200°C, but preferably between 600 and 1000°C, while a temperature exceeding the cooled bottom of the mold by at least 200-1000°C, preferably 200-800°C, but below the melting point of silicon, is allowed to operateeon the free surface of the melt, for example by means of radiant heat, such as by placing a suitably heated graphite plate close to it. If the radiant heat is produced by a suitably heated graphite plate, it has proved satisfactory to heat the graphite plate, which is advantageously placed very close to the melt surface, to about 1400-1550°C.

To avoid wetting, it is also advisable to keep the temperature of the side surfaces adjacent to the contact surface of the mold with one of the large boundary surfaces of the melt below 1200°C, while on the other hand the temperature, if possible should be above the temperature of the large, cooled contact surface in order to limit as much as possible growths of the solidifying silicon crystal from the side surface inward, even if with larger wafers this may give rise to only narrow marginal regions. Therefore, the preferred temperature of the side surfaces is 1100°to just under 1200°C.

The material selected for the mold can be, for example, silicon nitride, with a silicon nitride or graphite mold body treated with silicon dioxide, or preferably graphite.

Another variant of the process consists of using a mold which is in contact with the two largest opposing boundary surfaces of the melt, advantageously such that these surfaces are arranged vertically and the silicon melt is poured into the slit formed by this arrangement. In this mold version, which is preferably also made of graphite, the temperature of the warmer surface of the mold in contact with the melt should be less than 1200°C in order to avoid wetting of the melt. If, accordingly, the temperature of this contact surface is kept, for example, at just below 1200°C, then it is advisable--since on the other hand the temperature gradient between the two contact surfaces as per the invention should be 200-1000°C--to cool the other contact surface to 200-1000°C, preferably about 400-800°C. With this arrangement, an allowable temperature for the side surfaces is that which corresponds to the setting for largely open molds.

In principle, breeding is also possible with seed crystals, whereby the cooled surface of the mold in contact with the melt, prior to pouring in the molten silicon is filled with a wafer-like silicon crystal of the desired crystallographic specifications which fills up this contact surface. Another variant consists of open molds in which only one of the largest contact surfaces of the melt is in contact with one of the mold surfaces, namely the cooled mold surface; molten silicon is added from above, either by stages or continuously, so that the solidified silicon melt in each case determines the growth conditions for the succeeding melt poured in with respect to a preferable crystallographic orientation and the wafer-like silicon crystals as per the invention grow into bars or rods. In this process the temperature is continuously and advantageously controlled within limits as per the invention by suitable mechanical or electronic program transmitters. If, for example, by means of a suitable source of radiant heat, we expose the continuously added silicon melt to a temperature of about 1400°C, then the original bottom of the mold will have to be cooled more and more intensively during the growth of the silicon bar in order to regulate the temperature on the solidification front, which is in contact with the added silicon melt, between 400 and a maximum of 1200°C as per the invention. The temperature of the sides surfaces of the mold must be controlled accordingly, whereby each of the areas in contact with molten silicon must be kept at a temperature preferably between 1100 to just below 1200°C.

To obtain silicon crystals with a specific doping with the process as per the invention, the silicon melt, prior to pouring into the mold, is enriched with suitable doping materials, for example boron, aluminum, gallium, indium or arsenic, antimony or phosphorous.

The wafer-like silicon crystals produced according to the process as per the invention exhibit a columnar structure along the shortest axis formed from monocrystalline zones with a preferable crystallographic orientation and the crystals have semiconductor properties. If the melt is doped before being poured into the mold, then the doping material is distributed extremely homogeneously in the silicon without radial or axial gradients.

For using such silicon crystals as a base material in the semiconductor,industry, especially for electronic components, then as much doping material is advantageously added to the melt until the silicon crystals are doped with $5x \times 10^{14}$ to 5×10^{18} atoms of doping material per cubic centimeter.

The wafer-like silicon crystals as per the invention are distinguished by high durability of the monority carriers. As a base material for solar cells, they provide the prerequisite for substantially reducing the cost of these cells. With an achievable efficiency of over 10%, they are at least equivalent to most of the monocrystalline materials used up to now and can be produced at considerably lower production costs. The efficiency can be increased even more by special surface etching, since, for example, surface regions of the crystal growing in the 100 direction are stronger than other areas attacked by the etching. Such quite specifically roughened surfaces have at least partially the effect of black cells with considerablyx increased light absorption and thus also increased efficiency.

<u>Example 1</u>

One kilogram of highly pure, polycrystalline silicon, doped with 2×10^5 boron atoms, was melted in a quartz crucible, heated to 1500°C and poured into the mold.

The mold was formed by milling a cavity 100 x 100 x 70 mm in a cylindrical graphite block 200 mm in diameter. Before the silicon melt was poured, the mold was heated, but at the same time the bottom of the mold was cooled with a water-cooled copper plate, so that the bottom, i.e. one of the surfaces of the mold in contact with one of the largest boundary surfaces of the melt, had a temperature of about 800°C. The free surface of the poured silicon melt, on the other hand, was exposed to the radiant heat of a graphite plate placed about 2 cm above the melt surface and heated to 1500°C.

Under these thermal conditions the silicon melt solidified, without wetting the graphite mold, into a wafer which--so as not to induce any thermal stresses--was slowly cooled to room temperature over a period of several hours.

The wafer-like silicon crystal produced in this way had a columnar structure formed from monocrystalline crystal areas perpendicular to the largest surface, i.e. in the direction of the shortest axis.

To make solar cells this plate was cut into wafers of about 500 μm thick with the conventional diamond saws used in semiconductor techniques. The wafers obtained had a columnar structure of monocrystalline areas arranged perpendicular to the wafer surface. The solar cells made from these disks using familiar methods had an efficiency of 10-11%.

Example 2

Ten grams of highly pure, polycrystalline silicon doped with 2 x 10^5 boron atoms were melted in a quartz crucible, heated to 1550°C and poured into the mold.

The mold consisted of a graphite block measuring 150 x 150 mm in cross-section and 200 mm in height. In the middle, along its long axis, the graphite block was cut into two parts, whereby one part contained a slit-shaped milled recess the size of the silicon disk to be poured. Both parts were bolted back together with graphite bolts so that the smooth surface of the second piece of graphite sealed off the slit-shaped milled recess. On the upper end the slit was enlarged to form a funnel-shaped pouring-in opening.

The two parts of the mold were now kept at two different temperatures while the melt was poured in so that a temperature gradient formed between the two largest opposed surfaces of the slit. The temperature of one surface was about 400°C and that of the opposing surface about 1100°C. Under these conditions the melt solidified in a columnar structure with monocrystalline regions lined up essentially parallel to the temperature gradient.

After cooling, the silicon wafer--without having wetted the graphite mold--could be removed from the mold. A thin layer of the side of the silicon wafer, which was the hot side during solidification, was removed by etching. The solar cells produced from this silicon wafer using familiar methods had an efficiency of 8-10%..