

METHOD FOR PRODUCING SILICON INGOTS

The contents of German patent application DE 10 2011 087 759.2 is incorporated by reference.

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The invention relates to a method for producing silicon ingots. The invention also relates to a silicon ingot.

10 Silicon ingots are used as the starting material to produce solar cells. The crystal structure of the silicon ingot has a substantial influence here on the quality of the solar cells that can be produced therefrom. A method for producing silicon ingots is known, for example from EP 0 218 088 B1.

There is continuously a need to improve methods of this type.

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This object is achieved by a method for producing silicon ingots, comprising the following steps:

- providing a container to receive a silicon melt,
- arranging a fine-grain silicon layer in the container,
- 20 - arranging a silicon melt in the container in contact with the fine-grain silicon layer,
- directional solidification of the silicon melt starting from the fine-grain silicon layer.

25 The core of the invention consists in firstly producing a fine-grain silicon layer, starting from which a silicon melt is directionally solidified.

According to the invention, it was recognised that a fine-grain silicon layer can lead to a crystal structure, which is particularly low in defects, of the

silicon ingot. A fine-grain structure of the silicon layer is taken to mean a crystal structure here, in which the majority of the crystallites in particular at least 70%, in particular at least 90%, in particular all the crystallites, have an equivalent diameter in the range from 0.1 mm to 5 mm, in particular
5 in the range from 1 mm to 3 mm. The crystallites have an aspect ratio here of less than 3 to 1. These are, in particular, not so-called dendrites.

The fine-grain silicon melt is preferably produced by rapid solidification of liquid silicon. For this purpose, liquid silicon can preferably be brought
10 into contact with a substrate, the temperature of which is below the melt temperature of silicon. If the thermal capacity of the substrate is adequately large and/or the quantity of liquid silicon, which is brought into contact with the substrate, is adequately small, it is possible to very easily produce a fine-grain silicon layer in this manner. In this regard, it was recognised
15 according to the invention that the temperature of the substrate has a substantial influence on the nucleation frequency and therefore on the grain structure of the silicon layer. In general, a colder substrate leads to a more fine-grain silicon layer. Rapid solidification of the liquid silicon is achieved in that the temperature gradient in the silicon melt, when the latter is ar-
20 ranged in the container in contact with the fine-grain silicon layer, starting from the latter, has an amount of at least 0.1 K/cm, in particular at least 1 K/cm, in particular at least 3 K/cm. This temperature gradient is, in particular, achieved at the interface of the fine-grain silicon layer with the liquid silicon melt.

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The substrate may, for example, be formed by one or more silicon plates, which are arranged on the base of a mould. A layer of fine grain or the base of the mould itself can likewise be used as the substrate.

The substrate is preferably supercooled. On being brought into contact with the liquid silicon, it has, in particular, a temperature of at most 1200°C, in particular at most 1100°C, in particular at most 1000°C.

- 5 The substrate may, for example, be made of silicon or a silicon compound, in particular silicon carbide (SiC) or silicon nitride (Si₃N₄) or of graphite. The substrate consists at least partially of a material selected from this group.
- 10 According to one aspect of the invention, the fine-grain silicon layer is produced in the same mould, in which the silicon melt is solidified. According to another aspect of the invention, the fine-grain silicon layer is produced in a different container than that in which the silicon melt is solidified. In the latter case, the fine-grain silicon melt can be produced in a
- 15 separate process as a seed crystal layer, which can then be placed in a mould. It can pass its grain structure to the silicate ingot growing thereabove, in particular in a Bridgman-like process.

- According to the invention, it is provided that the temperature in the region
- 20 of the fine-grain silicon layer during the solidification of the silicon melt be kept at a temperature below the melt temperature of silicon, in particular below 1400°C, in particular below 1300°C, in particular below 1200°C. This ensures that no nucleation can take place on the fine-grain silicon layer.

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It is furthermore provided that the temperature field in the mould is to be controlled in such a way that the solidification of the silicon melt takes place close to equilibrium. Disregarding the region, which is in direct contact with the fine-grain silicon layer, i.e. disregarding the beginning of the

solidification process, the temperature gradient at the phase boundary between the already solidified silicon and the still liquid silicon melt is a maximum of 15 K/cm. The cooling rate of the silicon melt is preferably at most 3 K/min, in particular at most 1 K/min.

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A further object of the invention consists in improving a silicon ingot. It is in particular an object of the invention to improve a multicrystalline silicon ingot. This object is achieved by a method in which the temperature in the region of the fine-grain silicon layer, during the solidification of the silicon melt, is kept at a temperature below the melt temperature of silicon.. According to the invention, it was determined that the silicon ingot produced according to the invention has a particularly advantageous crystal structure. The silicon ingot produced according to the invention has a particularly advantageous multicrystalline crystal structure.

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It is, in particular, characterised by a grain number, which decreases from the base of the ingot toward the cap thereof. The silicon ingot differs by this from convention silicon ingots. The grain number decreases, in particular from the base to the cap by at least 20%, in particular at least 30%.

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It is particularly advantageous in the silicon ingot produced according to the invention that the defect proportion is substantially constant from a specific height, in particular does not grow further. The defect proportion is constant in particular from a height of 10 cm, measured from the base of the ingot.

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It was recognised according to the invention that silicon ingots with a height of at least 50 cm, in particular at least 75 cm, in particular at least

100 cm, can therefore be produced by the method according to the invention.

Advantages and details of the invention emerge from the description of a plurality of embodiments with the aid of the drawings, in which:

Fig. 1 shows a schematic view of a mould for producing silicon ingots,

10 Fig. 2 shows an exemplary section through an ingot produced according to the invention and

Fig. 3 shows a view of the grain number K and the defect portion D in the silicon ingot produced according to the invention (continuous line) and in conventional silicon ingots (dashed line) depending on the height.

A method according to the invention for producing a silicon ingot 1 will be described below. For this, a mould 2 to receive a silicon melt 3 is firstly provided. The mould 2 is generally a container to receive the silicon melt 3. For details of a mould 2 of this type, reference is made by way of example to DE 10 2005 013 410 A1.

According to the invention, it was recognised that a very fine base structure can be advantageous to produce the silicon ingot 1. Furthermore, it was recognised that a fine base structure of this type can be effected by means of rapid solidification of liquid silicon on solid silicon. One advantage of the method according to the invention is the high process stability.

- According to a first embodiment of the invention it is provided that a silicon plate 4 is to be arranged on the base of the mould 2. The silicon plate 4 in this case preferably covers the entire base of the mould 2. It preferably has a thickness in the range from 1 mm to 10 mm, in particular in the range from 5 mm to 5 cm, in particular in the range from 1 cm to 3 cm. The silicon plate 4 preferably has a smooth surface. The surface of the silicon plate 4 is preferably oriented parallel to the base of the mould 2. In principle, it is also conceivable to structure the surface of the silicon plate 4.
- 10 The silicon plate 4 is kept at a temperature T_1 , which is below the melt temperature of silicon. The temperature T_1 of the silicon plate 4 is, in particular, less than 1400°C, in particular less than 1300°C, in particular less than 1200°C, in particular less than 1100°C, in particular less than 1000°C. While as low a temperature as possible is advantageous for the process of
- 15 rapid solidification, a large temperature difference between the silicon melt 3 and the silicon plate 4 leads more easily to mechanical problems when the silicon melt 3 is brought into contact with the silicon plate 4. The temperature of the silicon plate 4 can therefore be suitably adjusted depending, in particular, on the thickness of the silicon plate 4 and the quantity of the
- 20 silicon melt 3, which are brought into contact with the silicon plate 4 to produce a fine-grain silicon layer 5.

To adjust the temperature of the silicon plate 4, for example, a temperature of the base of the mould 2 can, for example, be adjusted by means of a

25 temperature control device. Reference is made, for example, to DE 10 2005 013 410 A1 for details of a temperature control device of this type. The silicon plate 4 may, in particular, be cooled by the base of the mould 2. Heat is dissipated from the silicon plate 4 by the base of the mould 2, in particular, by heat conduction.

To produce the fine-grain silicon layer 5, which forms a fine-crystalline nucleation layer, liquid silicon 6 is poured into the mould 2 with the silicon plate 4. The silicon plate 4 is an example of a substrate, with which the liquid silicon 6 is brought into contact to produce the fine-grain silicon layer 5. The liquid silicon 6 can, as schematically indicated in Fig. 1, have been melted in a separate crucible 7. Because of the large temperature difference between the liquid silicon 6 and the silicon plate 4, a rapid solidification of the liquid silicon 6 occurs on the silicon plate 4. The fine-grain silicon layer 5 forms here.

The fine-grain silicon layer 5 produced in this manner preferably has a thickness in the range from 1 cm to 5 cm, in particular in the range from 2 cm to 3 cm.

The fine-grain silicon layer 5 has a crystal structure, which consists predominantly of fine-grain crystallites. The crystallites of the fine-grain silicon layer 5 in particular have an equivalent diameter of a maximum of 5 mm, in particular a maximum of 3 mm, in particular a maximum of 2 mm, in particular a maximum of 1 mm. They have an aspect ratio of at most 3 to 1. These are, in particular, not so-called dendrites.

The liquid silicon 6 is firstly present as a silicon melt 3 in a region above the fine-grain silicon layer 5 in the mould 2. The silicon melt 3 is directionally solidified to produce the silicon ingot 1 starting from the fine-grain silicon layer 5. The solidification of the silicon melt 3 takes place close to equilibrium. The silicon melt 3 is, in particular, slowly cooled for this. The cooling rate is, in particular, at most 1 K/min, in particular at most 0.1 K/min. A crystallisation region 8 is formed between the fine-grain silicon

layer 5 and the still liquid silicon melt 3. The crystallisation region 8 forms a grain selection zone. It is provided according to the invention that the temperature field in the mould 2 is to be controlled in such a way that as small a temperature gradient ∇T_2 as possible prevails in the grain selection
5 zone to allow the growth close to equilibrium. The temperature gradient ∇T_2 in the grain selection zone 8 is, in particular, at most 15 K/cm, in particular at most 5 K/cm, in particular at most 1 K/cm.

The silicon melt 3 above the crystallisation region 8 is kept during the so-
10 lidification process at a temperature T_3 , which is just above the melt temperature of silicon. The temperature T_3 is, in particular, at most 1500°C, in particular at most 1450°C.

In the previously known methods for producing silicon ingots, the grain
15 number is substantially constant over the entire height of the ingot.

It was found according to the invention that owing to the solidification, which is close to equilibrium, of the silicon melt 3 on the fine-grain silicon layer 5, silicon ingots 1 with a particularly advantageous crystal structure
20 can be produced. The silicon ingots 1 produced in this manner have a grain number, which decreases from a region adjoining a base 9 of the silicon ingot 1 toward a region adjoining a cap 10 of the silicon ingot 1 (see Fig. 3; curves K). The grain number of the silicon ingot 1 decreases from the base 9 toward the cap 10, in particular by at least 20%, in particular by at least
25 30%, in particular by at least 50%.

It has been found to be particularly advantageous that a defect proportion in the silicon ingot 1 produced according to the invention is substantially

constant from a specific height h_0 . The height h_0 is in the range from 1 cm to 10 cm above the fine-grain silicon layer 5.

While, in the previously known methods for producing silicon ingots, the defect proportion increases substantially monotonically, in particular substantially linearly, with an increasing height (see Fig. 3; curves D), which leads to the fact that the correspondingly produced ingots have too high a defect proportion from a specific height and can therefore only be produced with a limited maximum height, this limitation is no longer necessary in the silicon ingots 1 produced according to the invention. In the ingots 1 according to the invention, the defect proportion is substantially constant from a specific height H_0 . Therefore, it is possible with the aid of the method according to the invention, to produce silicon ingots 1 with any desired height in principle. In particular, it is possible to produce silicon ingots 1 with a height of at least 50 cm, in particular at least 75 cm, in particular at least 100 cm. This is particularly efficient and economical, in particular as the base 9 always developing due to the process, which has to be removed later, only develops once. The overall yield can therefore be improved with silicon ingots 1 with a greater height.

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The silicon ingots 1 produced according to the present invention have in particular a multycrystalline structure with a constant defect proportion from a specific height H_0 .

25 Further details and alternatives of the method according to the invention will be described below.

For example it is possible, instead of a single silicon plate 4, to place a plurality of flat silicon pieces on the base of the mould 2. The base of the

mould 2 may be parquered here, in particular completely covered with flat silicon pieces. Furthermore, it may be provided that solid silicon pieces be arranged on the silicon plate(s) 4 in the mould 2 for rapid solidification of the liquid silicon 6 and be melted from the top to the bottom. The liquid
5 silicon melt 6, which forms during the melting of the solid silicon pieces, drips onto the silicon plate 4, the fine-grain silicon layer 5 in turn being formed by rapid solidification.

Instead of the silicon plate 4, a layer of fine silicon raw material can also be
10 used as the substrate. The layer, in particular, has a height in the range from 1 to 5 cm. As described above, liquid silicon 6, which has been melted in a separate crucible 7, may be poured, or solid silicon pieces arranged, on the layer and melted from the top to the bottom. The fine grain on the base of the mould 2 may also be melted here from the top. At this moment, the
15 crystallisation is initiated. The fine grain silicon layer 5 is produced in turn by rapid solidification of the incompletely melted fine grain on the base of the mould 2.

It is furthermore possible to firstly only produce the fine-grain silicon layer
20 5, as described above. The silicon layer 5 can then be placed in a separate mould 2. It is then used as a seed crystal layer for a silicon melt 3 to be solidified, which is arranged in the mould 2 in contact with the fine-grain silicon layer 5. The silicon melt 3 may in turn be produced here in a separate crucible 7. It can also be produced by melting pieces of silicon in the
25 mould 2.

It is furthermore possible to firstly produce the fine-grain silicon layer 5, as described above, but to leave it in the same mould 2, in which it was produced. The mould 2 can then be filled in a separate, further process step

with pieces of silicon and installed in a different Bridgman-like crystallisation system. The fine-grain silicon layer 5 can therefore be produced in the same mould 2, in which the silicon melt 3 is solidified to produce the silicon ingot 1. The fine-grain silicon layer 5 can also be produced in a different container than that, in which the silicon melt 3 is solidified to produce the silicon ingot 1.

It is also possible for the base of the mould 2 itself to be used as the substrate to rapidly solidify the liquid silicon 6. According to this embodiment, it is provided to only pour a small volume of liquid silicon 6 into the mould 2 to produce the fine-grain silicon layer 5. The volume of liquid silicon is, in particular, measured in such a way that a layer with a height of a maximum of 5 cm, in particular a maximum of 3 cm, is formed in the mould 2. The volume of liquid silicon 6 therefore has a comparatively small thermal capacity. It is therefore possible for the base of the mould 2 itself to be used as a substrate for rapid solidification of the liquid silicon 6. It is cooled accordingly for this. The temperature of the base of the mould 2 has a temperature of less than 1200°C, in particular less than 1100°C, in particular less than 1000°C, in particular, during the pouring in of the liquid silicon 6. The insertion of a separate silicon plate 4 can be omitted in this embodiment.

It is possible in all the embodiments described above to use, instead of the silicon plate 4, one or more plates made of a different material as the substrate. The substrate is in general at least partially made from a material selected from the group of silicon, silicon carbide, silicon nitride and graphite.

Claims:

1. A method for producing silicon ingots (1), comprising the following steps:
 - 5 - providing a container (2) to receive a silicon melt (3),
 - providing a fine-grain silicon layer (5) in the container (2),
 - arranging a silicon melt (3) in the container (2) in contact with the fine-grain silicon layer (5),
 - directional solidification of the silicon melt (3) starting from the fine-grain silicon layer (5),
 - 10 wherein the temperature in the region of the fine-grain silicon layer (5), during the solidification of the silicon melt (3), is kept at a temperature below the melt temperature of silicon.
- 15 2. A method according to claim 1, **characterised by** the following step:
 producing the fine-grain silicon layer (5).
3. A method according to claim 1, **characterised in that** liquid silicon is rapidly solidified to produce the fine-grain silicon layer (5).
- 20 4. A method according to claim 2, **characterised in that** liquid silicon is brought into contact with a substrate having a temperature below the melting temperature of silicon to produce the fine-grain silicon layer (5).
- 25 5. A method according to claim 4, **characterised in that** the substrate is selected from the group of one or more plates (4), a layer of fine grain and a base (9) of the container.

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6. A method according to claim 4, **characterised in that** a layer of a fine-grain raw material with a mean grain size in the range from 0.1 mm to 3 mm is used as the substrate and is placed directly on a base (9) of the container (2).
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7. A method according to claim 6, **characterised in that** the layer of a fine-grain raw material has a thickness in the range from 1 cm to 5 cm.
8. A method according to claim 4, **characterised in that** the substrate, when brought into contact with the liquid silicon, has a temperature of at most 1200°C.
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9. A method according to claim 4, **characterised in that** the substrate, when brought into contact with the liquid silicon, has a temperature of at most 1100°C.
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10. A method according to claim 4, **characterised in that** the substrate, when brought into contact with the liquid silicon, has a temperature of at most 1000°C.
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11. A method according to claim 4, **characterised in that** the substrate consists at least partially of a material selected from the group of silicon, silicon carbide, silicon nitride, graphite.
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12. A method according to claim 1, **characterised in that** the fine-grain silicon layer (5) is produced in the same container (2), in which the silicon melt (3) is solidified.

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13. A method according to claim 1, **characterised in that** the fine-grain silicon layer (5) is produced in a different container (2) to the one in which the silicon melt (3) is solidified.
- 5 14. A method according to claim 1, **characterised in that** the solidification of the silicon melt (3) takes place close to equilibrium.
15. A silicon ingot (1) produced by a method according to claim 1.
- 10 16. A silicon ingot (1) according to claim 15, **characterised by** a grain number, which decreases from a base (9) toward a cap (10) of the ingot.
- 15 17. A silicon ingot (1) according to claim 16, **characterised in that** the grain number decreases from the base (9) to the cap (10) by at least 20%.
- 20 18. A silicon ingot (1) according to claim 16, **characterised in that** the grain number decreases from the base (9) to the cap (10) by at least 30%.
19. A silicon ingot (1) according to claim 15, **characterised in that** a defect proportion is constant from a specific height (h_0).
- 25 20. A silicon ingot (1) according to claim 15, **characterised by** a height of at least 50 cm.
21. A silicon ingot (1) according to claim 15, **characterised by** a height of at least 75 cm.

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22. A silicon ingot (1) according to claim 15, **characterised by** a height of at least 100 cm.