



(86) **Date de dépôt PCT/PCT Filing Date:** 2014/08/07
(87) **Date publication PCT/PCT Publication Date:** 2015/02/26
(45) **Date de délivrance/Issue Date:** 2018/11/06
(85) **Entrée phase nationale/National Entry:** 2016/02/19
(86) **N° demande PCT/PCT Application No.:** EP 2014/067009
(87) **N° publication PCT/PCT Publication No.:** 2015/024789
(30) **Priorité/Priority:** 2013/08/21 (DE10 2013 216 557.9)

(51) **Cl.Int./Int.Cl.** **C01B 33/02** (2006.01),
C30B 15/00 (2006.01), **C30B 29/06** (2006.01)
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(54) **Titre : FRAGMENTS DE SILICIUM POLYCRISTALLIN ET PROCEDE DE FRAGMENTATION DE BARREAUX DE SILICIUM POLYCRISTALLIN**
(54) **Title: POLYCRYSTALLINE SILICON FRAGMENTS AND PROCESS FOR COMMINUING POLYCRYSTALLINE SILICON RODS**

(57) **Abrégé/Abstract:**

Polycrystalline silicon fragments with tungsten carbide particles on the surface, where the mass-weighted average size of the tungsten carbide particles is less than or equal to 0.5µm, preferably less than or equal to 0.2 µm or is greater than or equal to 0.8 µm, preferably greater than or equal to 1.3 µm. Process for comminuting polycrystalline silicon rods to give fragments by means of at least one comminuting implement with a surface containing tungsten carbide, where the tungsten carbide content of the implement surface is less than or equal to 95% and the mass-weighted average grain size of the tungsten carbide particles is greater than or equal to 0.8 µm or where the tungsten carbide content of the implement surface is greater than or equal to 80% and the grain size of the tungsten carbide particles is less than or equal to 0.5 µm.

Abstract

Polycrystalline silicon fragments with tungsten carbide particles on the surface, where the mass-weighted average size of the tungsten carbide particles is less than or equal to 0.5 μ m, preferably less than or equal to 0.2 μ m or is greater than or equal to 0.8 μ m, preferably greater than or equal to 1.3 μ m. Process for comminuting polycrystalline silicon rods to give fragments by means of at least one comminuting implement with a surface containing tungsten carbide, where the tungsten carbide content of the implement surface is less than or equal to 95% and the mass-weighted average grain size of the tungsten carbide particles is greater than or equal to 0.8 μ m or where the tungsten carbide content of the implement surface is greater than or equal to 80% and the grain size of the tungsten carbide particles is less than or equal to 0.5 μ m.

Polycrystalline silicon fragments and process for comminuting polycrystalline silicon rods

FIELD OF THE INVENTION

5 The invention provides polycrystalline silicon chunks and a process for comminuting polycrystalline silicon rods.

BACKGROUND OF THE INVENTION

10 On the industrial scale, crude silicon is obtained by the reduction of silicon dioxide with carbon in a light arc furnace at temperatures of about 2000°C.

This gives what is called "metallurgical grade" silicon (Si_{mg}) having a purity of about 98-99%.

15 For applications in photovoltaics and in microelectronics, the metallurgical silicon has to be purified.

20 For this purpose, it is reacted, for example, with gaseous hydrogen chloride at 300-350°C in a fluidized bed reactor to give a silicon-containing gas, for example trichlorosilane. This is followed by distillation steps in order to purify the silicon-containing gas.

This high-purity silicon-containing gas then serves as a starting material for the production of high-purity polycrystalline silicon.

25 The polycrystalline silicon, often also called polysilicon for short, is typically produced by means of the Siemens process. This involves heating thin filament rods of silicon by direct passage of current in a bell jar-shaped reactor ("Siemens reactor"), and introducing a reaction gas comprising a silicon-containing component and hydrogen.

30 The silicon-containing component of the reaction gas is generally monosilane or a halosilane of the general composition $\text{SiH}_n\text{X}_{4-n}$ ($n=0, 1, 2, 3$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$). It is preferably a chlorosilane or chlorosilane mixture, more preferably trichlorosilane. Predominantly SiH_4 or SiHCl_3 (trichlorosilane, TCS) is used in a mixture with hydrogen.

35 In the Siemens process, the filament rods are typically inserted vertically into electrodes present at the reactor base, through which they are connected to the power supply. Every two filament rods are coupled via a horizontal bridge (likewise

composed of silicon) and form a support body for the silicon deposition. The bridge coupling produces the typical U shape of the support bodies, which are also called thin rods.

- 5 High-purity polysilicon is deposited on the heated rods and the bridge, as a result of which the rod diameter grows with time (CVD/gas phase deposition).

After the deposition has ended, these polysilicon rods are typically processed further by means of mechanical processing to give chunks of different size classes,
10 classified, optionally subjected to a wet-chemical cleaning operation and finally packed.

The prior art discloses several processes and devices for comminution of polysilicon.

- 15 US 20070235574 A1 discloses a device for comminuting and sorting polycrystalline silicon, comprising a feed for feeding a coarse polysilicon fraction into a crushing system, the crushing system, and a sorting system for classifying the polysilicon fraction, wherein the device is provided with a controller which allows variable adjustment of at least one crushing parameter in the crushing system and/or at least
20 one sorting parameter in the sorting system. The crusher system comprises roll crushers or jaw crushers, preferably spiked roll crushers. By means of the process, it is possible to selectively produce cubic polysilicon chunks of size 45 to 250 mm which are no longer free-flowing, reproducibly and in a high yield.

- 25 US 20100001106 A1 discloses a method for producing highly pure classified polysilicon fragments, comprising comminuting polysilicon from the Siemens method into fragments by means of a device comprising comminution tools and classifying the fragments by a screening device, and cleaning the polysilicon fragments thus obtained in a cleaning bath, wherein the comminution tools and the screening device
30 have surfaces which contact the polysilicon and consist of a material which contaminates the polysilicon fragments only with extraneous particles that are subsequently removed selectively by the cleaning bath. The comminution is effected in a crushing system comprising a roll crusher or a jaw crusher, preferably a spiked roll crusher.

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However, US 7270706 B2 discloses a perforated roll having teeth spaced around the circumference of the roll, a shaft on which the roll is rotatably mounted, a housing having surfaces defining a cavity inside which the roll is mounted, an inlet port on top

of the housing, an exit port on bottom of the housing, a plate inside the housing opposite the roll, where the roll, teeth, plate, and housing surfaces defining the cavity are made from or clad with a material of construction that minimizes contamination of polycrystalline silicon. The material is preferably selected from the group consisting of carbides, cermets, ceramics and combinations thereof. Particular preference is given to the use of a material selected from the group consisting of tungsten carbide, tungsten carbide with a cobalt binder, tungsten carbide with a nickel binder, titanium carbide, Cr_3C_2 , Cr_3C_2 with nickel-chrome alloy binder, tantalum carbide, niobium carbide, silicon nitride, silicon carbide in a matrix such as Fe, Ni, Al, Ti, or Mg, aluminum nitride, tantalum carbide, niobium carbide, titanium carbide with cobalt and titanium carbonitride, nickel, nickel-cobalt alloy, iron, and combinations thereof.

US 20030159647 A1 discloses comminution of polysilicon by means of a jaw crusher containing tungsten carbide in a cobalt matrix (88% WC and 12% CO), where the WC core has a particle size of 0.6 μm .

US 7950600 B2 discloses a roll crusher comprising a roll which rotates with a shaft, characterized in that the roll comprises a carrier roll of steel and a number of hard-metal segments, wherein the hard-metal segments consist of a cobalt matrix in which tungsten carbide is incorporated, and the hard-metal segments are reversibly fastened on the carrier roll with a form fit. The hard-metal segments consist of over 80% by weight, more preferably of more than 90% by weight, especially preferably of more than 91.5% by weight, of tungsten carbide incorporated in the cobalt matrix.

US 7549600 B2 describes a crusher for producing fine silicon fragments suitable for semiconductor or solar applications from silicon fragments suitable for semiconductor or solar applications, the crusher comprising a plurality of crushing tools, the crushing tools having a surface of a hard, wear-resistant material, wherein the crusher has a comminution ratio of from 1.5 to 3, the crushing tools having a surface of hard metal, preferably tungsten carbide in a cobalt matrix, more preferably with a proportion of tungsten carbide greater than 80% by weight.

It is already known that low contamination of the polysilicon with tungsten can be achieved through a suitable process regime; see, for example, US7549600 (B2) and the examples cited therein.

There are also known process steps that follow crushing with tungsten carbide, in order to reduce contamination with tungsten; see, for example, US 20100001106 A1 or US 20120052297 A1.

5 Basically, it has been the assumption in the prior art and in general and specialist knowledge that a higher hardness of the hard metal, for example through a higher W content or through a reduction in their WC grain size, results in a higher wear resistance. In the prior art, proceeding from a grain size of about 0.6 μm , rising W contents of 80% tending toward > 90% W are cited; see, for example,
10 US20030159647 A1 and US 7950600 B2.

However, it has been found that harder tools also become more brittle, and there is a risk of additional unwanted contamination of the product by fractured tool material.

15 This problem gave rise to the objective of the invention.

SUMMARY OF THE INVENTION

The invention relates to a process for comminuting polycrystalline silicon rods into
20 chunks by means of at least one comminuting tool having a surface comprising tungsten carbide, wherein the tool surface has a tungsten carbide content of less than or equal to 95% and the median grain size of the tungsten carbide particles – weighted by mass – is greater than or equal to 0.8 μm , or wherein the tool surface has
25 a tungsten carbide content of greater than or equal to 80% and the median grain size of the tungsten carbide particles is less than or equal to 0.5 μm .

The remainder to 100% in the material of the tool surface is preferably cobalt binders, which may also include up to 2%, but preferably less than 1%, of other metals.

30 Additional carbides are preferably present to an extent of less than 1%, of which Cr_3C_2 and VC are < 0.4%.

The sintering outcome is also affected by addition of carbon. It is further known that a balanced carbon level is important for achieving the optimal properties of the hard
35

metal. Inferences in this respect can be drawn, for example, via the magnetic saturation, which may be in the range of 7 - 14 $\mu\text{Tm}^3/\text{kg}$, or 75-110%.

The carbon content based on WC is about 6%, and has a tendency to be somewhat higher.

5

For comminution of polycrystalline silicon rods, manual hammers, hammer mills and machine impact tools are suitable, in which case preference is given to using the coarser grains having grain size greater than or equal to 0.8 μm .

10

Likewise envisaged is the use of jaw and roll crushers and mills ball, in which cases preference is given to using the finer grains smaller than or equal to 0.5 μm .

The finer grains preferably have a grain size of less than or equal to 0.2 μm , in combination with a tungsten carbide content of greater than 80%, preferably greater than 90%, more preferably greater than 95%.

15

The coarser grains preferably have a grain size of greater than or equal to 1.3 μm , in combination with a tungsten carbide content of less than 95%, preferably less than 90%, more preferably 65-80%.

20

Preferably, the process comprises at least two comminution steps, the final comminution step being effected with a comminuting tool having a higher tungsten carbide content or a lower grain size of the tungsten carbide particles than in the comminuting tool used in one of the preceding comminution steps.

25

Preferably, the process comprises at least two comminution steps: at least one comminution step with a comminuting tool having a grain size of the tungsten carbide particles of greater than or equal to 0.8 μm , preferably greater than or equal to 1.3 μm , or at least one comminution step with a comminuting tool having a grain size of the tungsten carbide particles of less than or equal to 0.5 μm , preferably less than or equal to 0.2 μm .

30

Preferably, the process comprises at least two comminution steps, wherein the at least two comminuting tools used therein have different WC grain sizes, selected from the group consisting of WC grain size less than 0.5 μm , WC grain size 0.5-0.8 μm , WC grain size greater than 0.8 μm .

35

It is especially preferable when the process comprises at least one comminution step with a comminuting tool having a grain size of the tungsten carbide particles of greater than or equal to 0.8 μm , and a comminution step with a comminuting tool having a grain size of the tungsten carbide particles of less than or equal to 0.5 μm .

5 Preferably, the process comprises at least one comminution step by means of WC tools having a low WC content ($< 90\%$, preferably $< 85\%$) and/or larger grains $> 0.8 \mu\text{m}$ and at least one further comminution step by means of WC tools having an increasingly higher WC content (> 90 , preferably $> 95\%$) and/or small grains $< 0.5 \mu\text{m}$.

10 Preferably, the last comminution step, more preferably the last two comminution steps, is/are effected with WC tools having WC content $> 85\%$, preferably $> 90\%$ and/or a grain size $< 0.5 \mu\text{m}$, more preferably $< 0.2 \mu\text{m}$.

15 Preferably, the comminution of the rods, preferably the second comminution step, is followed by a thermal treatment of the chunks at a temperature of $> 500^\circ\text{C}$ with subsequent quenching in a colder medium, followed by further comminution steps.

DETAILED DESCRIPTION

20 It has been found that the process according to the invention for breaking polycrystalline silicon rods results in polycrystalline silicon chunks having WC particles on the surface, the WC particles having a median size of less than 0.5 μm or a median size of greater than 0.8 μm .

25 Preferably, the median size of the WC particles is less than 0.2 μm .

Preferably, the median size of the WC particles is greater than 1.3 μm .

30 It is likewise possible to obtain polycrystalline silicon chunks having WC particles on the surface thereof, the particle sizes of the WC particles on the surface being in bimodal or multimodal distribution, with at least one maximum in the distribution at less than 0.6 μm and/or at least one maximum in the distribution at greater than 0.6 μm .

35 Preferably, at least one maximum in the distribution is at less than 0.5 μm .

More preferably, at least one maximum in the distribution is at less than 0.2 μm .

Preferably, at least one maximum in the distribution is at greater than 0.8 μm .

More preferably, at least one maximum in the distribution is at greater than 1.3 μm .

It has been found that, surprisingly, the tungsten carbide content, or the hardness, has
5 a much smaller influence on the abrasion than the grain size of the WC particles of
the comminuting tools, which has not been considered to date. For the same
hardness, a tool having smaller grains and a smaller tungsten carbide content showed
much lower abrasion than a tool having larger grains and a higher WC content.

10 It was also surprising that tungsten contamination on the polysilicon, given several
comminution steps, is determined predominantly by the last comminution step.

This enables, in a process comprising several comminution steps, the use of less
wear-resistant but tough hard metal tools in the initial comminution steps, for example
15 in the initial breaking. This is advantageous. In the last comminution step, in contrast,
it should be ensured that a tool having a particularly suitable WC type, namely having
a relatively fine WC grain size and/or relatively high tungsten carbide content, is used.

The inventive polycrystalline silicon chunks, which feature WC particles on the surface
20 with defined particle sizes or particle size distributions, likewise have surprising
advantages.

These become visible when the polysilicon is melted and is processed further on the
part of customers, for example by crystal pulling to give single crystals for solar or
25 semiconductor applications.

The influence of the WC grain size in comminuting tools on the melting characteristics
or the pulling performance in the customer's hands was unforeseeable.

30 In principle, WC particles on the surface of polysilicon (like other extraneous
substances/metals too) can lead to dislocations in crystal pulling. For example, it is
conceivable that very large WC particles are not melted because of the very high
melting point of about 2800°C and, as a result, lead to such dislocations. Smaller
particles too, which are easier to melt, given the same total contamination, can lead to
35 dislocations in single-crystal pulling because of the much higher number thereof – up
to a factor of more than 1000.

However, the inventors were able to show that, with the use of WC having relatively large grains or else having relatively small grains, better results are achieved than with the grains according to the prior art, namely fine grains of $\sim 0.6 \mu\text{m}$; cf. US2003159647 A1.

5

A grain size decreasing with each breaking step is especially preferable.

The preference is especially given to initial breaking using a WC type with large grains ($> 0.8 \mu\text{m}$), and a WC type with small grains ($< 0.5 \mu\text{m}$) for the last breaking step(s).

10

More particularly, however, it is possible to achieve better results through the combination of a plurality of comminution steps with tools of various grain sizes, namely lower contamination, higher service lives and better pulling performance. The dimensions of the processing tools can be increased, and hence processes can be run with higher throughput and lower costs.

15

In addition, no complex reprocessing of the chunks is required, for example through a wet-chemical cleaning operation. Overall, the production process becomes much more economically viable.

20

Examples

Comminution into chunks results in chunk sizes (CS), which can be assigned to the following size classes, each of which is defined as the longest distance between two points on the surface of a silicon chunk (= max. length):

25

Chunk size 0 [mm] 1 to 5;

Chunk size 1 [mm] 4 to 15;

Chunk size 2 [mm] 10 to 40;

Chunk size 3 [mm] 20 to 60;

30

Chunk size 4 [mm] 45 to 120;

Chunk size 5 [mm] 90 to 200

Chunk size 6 [mm] 130 to 400

Example 1

35

Manual breaking of polycrystalline silicon rods with a manual hammer (WC in Co matrix)

- a. (prior art) 88% WC, 12% Co and fine grains (0.5-0.8 μm): small, visible WC splinters, i.e. high contamination
- b. 88% WC, 12% Co and coarse grains (2.5-6.0 μm): no visible WC splinters, i.e. low contamination
- c. 80% WC, 20% Co and fine grains (0.5-0.8 μm): no visible WC splinters

Example 2

Initial breaking as in **example 1 b.** and further breaking with a roll crusher to target size CS4, classification and analysis of the surface contamination of sample pieces of a component fraction according to the prior art with ICPMS (ICP = inductively coupled plasma) to DIN 51086-2; hardness figures according to Vickers, test force 10 kp).

- a. (prior art) hardness HV10 1650: 90% WC + 10% Co, very fine grains (0.5 μm to 0.8 μm): CS1 tungsten 2000 pptw
- b. hardness HV10 1630: 94% WC + 6% Co, fine grains (0.8 μm to 1.3 μm): CS1 tungsten 4000 pptw
- c. hardness HV10 1590: 85% WC + 15% Co; ultrafine grains (0.2-0.5 μm): CS1 tungsten 1000 pptw

Example 3

Manual initial breaking according to **example 1 b.**, then further breaking to target size CS2 with large jaw crusher (88% WC & 12% Co and very fine grains (0.5-0.8 μm)), then two breaking steps with a smaller jaw crusher (88% WC & 12% Co very fine grains (0.5 μm to 0.8 μm)) and a last breaking step

- a. with jaw crusher (88% WC & 12% Co very fine grains (0.5 μm to 0.8 μm): CS2 tungsten 500 pptw (prior art), or
- b. with jaw crusher (93.5% WC & 6.5% Co ultrafine grains (0.2 μm to 0.5 μm): CS2 tungsten 200 pptw

(a. and b. each at about the same comminution ratio)

Example 4

As **example 3 b.**, but with thermal 800°/1 h pretreatment and subsequent quenching
5 in water at 20° and vacuum drying after the second breaking step.

Result: CS2 tungsten 50 pptw

Example 5

10 Poly-Si rods are broken in a controlled manner with several breaking steps and different WC types to CS2, such that the end product of the comparison groups each has about the same W contamination of about 500 pptw, but each group differs by the grain size on the product.

15 Subsequently, the material was pulled to a single crystal by the CZ process and the dislocation-free length was measured.

The mean dislocation-free length is determined from the ratio of a possible cylindrical
crystal rod length (calculated from starting weight minus cone and residual melt
20 losses) and actual length of several crystals.

a. (prior art) manual initial breaking (88% WC / 12% Co / very fine grains 0.5-
0.8 µm) to CS4, followed by two breaking steps with a jaw crusher (88% WC / 12% Co
/ grains 0.5-0.8 µm) to CS2:

25 dislocation-free length ~70%

b. manual initial breaking (88% WC / 12% Co / coarse grains 2.5-6.0 µm) to CS4,
three breaking steps with a jaw crusher (88% WC / 12% Co / coarse grains 2.5-
6.0 µm) to CS2:

30 dislocation-free length ~95%

c. manual initial breaking (88% WC / 12% Co / ultrafine grains 0.2-0.5 µm) to
CS4, one breaking step with a jaw crusher (88% WC / 12% Co / ultrafine grains 0.2-
0.5 µm) to CS2:

35 dislocation-free length ~93%

The embodiments of the present invention for which an exclusive property or privilege is claimed are defined as follows:

1. A process for comminuting polycrystalline silicon rods into chunks by means of at least two comminuting tools each having a surface comprising tungsten carbide, wherein a first tool has a surface with a tungsten carbide content of less than or equal to 95% and the median grain size of tungsten carbide particles – weighted by mass – is greater than or equal to 0.8 μm , and wherein a second tool has a surface with a tungsten carbide content of greater than or equal to 80% and the median grain size of the tungsten carbide particles is less than or equal to 0.5 μm , wherein the process comprises at least two comminution steps, at least one comminution step of the at least two comminution steps is effected with the first comminuting tool having a grain size of the tungsten carbide particles of greater than or equal to 0.8 μm and at least one comminution step of the at least two comminution steps is effected with the second comminuting tool having a grain size of the tungsten carbide particles of less than or equal to 0.5 μm .
2. The process as claimed in claim 1, wherein at least one comminuting tool is a manual hammer, a hammer mill or a machine impact tool, wherein the grain size of the tungsten carbide particles is greater than or equal to 0.8 μm .
3. The process as claimed in claim 1, wherein at least one comminuting tool is a jaw crusher, a roll crusher or a ball mill, wherein the grain size of the tungsten carbide particles is less than or equal to 0.5 μm .
4. The process as claimed in any one of claims 1 to 3, wherein the grain size of the tungsten carbide particles of the second comminuting tool is less than or equal to 0.2 μm and the tungsten carbide content is greater than 80%.
5. The process as claimed in any one of claims 1 to 3, wherein the grain size of the tungsten carbide particles of the first comminuting tool is greater than or equal to 1.3 μm and the tungsten carbide content is less than 95%.

6. The process as claimed in any one of claims 1 to 5, wherein a final comminution step is effected with a comminuting tool having a higher tungsten carbide content or a lower grain size of the tungsten carbide particles than in the comminuting tool used in one of a preceding comminution steps.
7. The process as claimed in any one of claims 1 to 6, wherein a thermal treatment of the chunks at a temperature of greater than 500°C with subsequent quenching in a colder medium is effected between the at least two comminution steps.
8. A process for comminuting polycrystalline silicon rods into chunks by means of at least one comminuting tool having a surface comprising tungsten carbide, wherein the tool surface has a tungsten carbide content of greater than or equal to 80% by weight and the median grain size of the tungsten carbide particles is less than or equal to 0.5 μm , characterized in that the process comprises at least two comminution steps, wherein at least one of the comminution steps is effected with the at least one comminuting tool, wherein the at least one comminuting tool is a jaw crusher, a roll crusher or a ball mill, or wherein a final comminution step is effected with a comminuting tool having a higher tungsten carbide content or a lower grain size of the tungsten carbide particles than the comminuting tool used in one of the preceding comminution steps.
9. The process as claimed in claim 8, wherein the grain size of the tungsten carbide particles is less than or equal to 0.2 μm and the tungsten carbide content is greater than 80% by weight.
10. The process as claimed in claim 1 or 2, wherein a thermal treatment of the chunks at a temperature of greater than 500°C with subsequent quenching in a colder medium is effected between two comminution steps.