

Method for purification and compaction of
feedstock for photovoltaic applications

SUMMARY

In one aspect, there is provided a process for the re-use of silicon powder recovered from band saws and other silicon mechanical operations, as feed material to prepare the crucible charges for casting of polycrystalline-multicrystalline silicon ingots usable for photovoltaic applications, which process is characterised by the following steps:

- a) silicon powder recovery from band saws, wire saws, grinding operations by filtration or centrifugal agglomeration and treatment of the exhausted slurries;
- b) conditioning in non-oxidizing environment;
- c) treatment with hydrofluoric acid;
- d) treatment with hydrochloric acid and/or hydrofluoric acid and hydrogen peroxide;
- e) second treatment with hydrofluoric acid;
- f) preparation for the compaction step by drying under vacuum and inert gas, or by washing with an organic solvent;
- g) compaction of the silicon powder.

DETAILED DESCRIPTION

The present invention relates to a method to re-use the waste silicon powder recovered from band saws and other silicon mechanical operations for both photovoltaic and microelectronic industry, as feed material to prepare the crucible charges for casting of polycrystalline-multicrystalline silicon ingots usable for photovoltaic applications.

Photovoltaic technology (PV) is a well established reliable, renewable and environmentally benign source of clean electrical energy and the photovoltaic industry is expected to add tens of GW/year of additional power.

So far the photovoltaic industry has been using, and in a certain extent it is still using, as feedstock materials for solar cells the excess capacity in the high purity electronic grade polysilicon and the recycled waste from electronic grade silicon single-crystal industry (ingot tops/tails and broken wafers), with the built-in disadvantages of a limited and unreliable availability of silicon poly-crystalline at non competitive cost.

As photovoltaic industry is growing faster than microelectronic industry, the silicon raw material has become rarer and more expensive. To overcome the shortage of silicon for photovoltaic applications the following technologies capable to provide solar grade silicon have been developed and are at least in part already used:

- Changes to the set-up of the chemical production processes for electronic grade silicon via trichlorosilane, aimed to reduce the production costs by providing a polycrystalline with quality characteristics less stringent than those required by the micro-electronic industry, but at the same time

well in line with the requirements of photovoltaic industry

- Direct purification of metallurgical silicon
- Carbon thermal reduction of quartz

5 However these additional technologies are not enough to satisfy the growing demand of solar grade silicon that has grown and will grow at the estimated rate of 25 % to 30 % per year. In conclusion there is not enough poly-silicon capacity to supply both microelectronic and photovoltaic
10 markets.

In spite of the fact that the market is adjusting to these new requirements by installing additional polysilicon capacity, there will continue to be a silicon feedstock shortage over the next few years until the new capacity can
15 match the growing demand.

It has been estimated that availability of solar grade polysilicon will not match the photovoltaic growth trend until 2010. As consequence of this situation there is the urgent need to find out new or alternative source of solar
20 grade silicon.

This serious shortage of solar grade silicon at competitive price for the photovoltaic industry has pressed toward the development of techniques for the recovery and re-use of the silicon waste powder that is generated as kerf (micron-size silicon powder) at mechanical operations in
25 photovoltaic and electronic industries.

In fact it has been estimated that the silicon kerf, that could be recovered as fine silicon powder is about up to 35 % of the total silicon that is fed as raw material in the
30 processes for the production of solar cells.

The recycling of silicon rejects from PV and micro-electronic productions has been and still is the object of several research projects involving both european and governmental offices for the solar energy development and
5 also some sawing equipment producers.

The key issues that any silicon powder recovery process has to solve are the following:

- a) effective separation of silicon kerf from the waste water of band saws and grinders or from cakes or sludges
10 coming from exhausted slurries from wire saws operations
- b) avoiding the oxidation and hydrogen development of the kerf during operations
- c) efficient removal of metal impurities at the level required by photovoltaic industry
- 15 d) serious difficulties when melting the recovered kerf because of the small size of the particles and their low density as well as their surface oxidation conditions.

No fully satisfactory solutions have been found so far relates to an economical and environmental benign method to
20 recover cristalline silicon metal kerf from mechanical operations and melting of said recovered crystalline silicon kerf.

Regarding point a) of the issues that faces the industry nowadays it is interesting to mention the patent US
25 2003/0041895 which describes a method to re-use of the silicon from wire-saw operations in order to manufacturer thin layer PV cell.

The method to recovery silicon kerf and obtain material from PV applications consists of the following steps:

- a) by means of a commercially available slurry recovery system, concentrate the silicon slurry into silicon sludge
- b) recover the silicon kerf from the said sludge by means of froth flotation (or other separation-concentration techniques) and surfactants
- c) the silicon kerf obtained by flotation or other concentration methods is mixed with an organic binder in order to produce a silicon kerf molding compound
- d) the silicon kerf molding compound is shaped into thin-layer PV cell configuration
- e) to remove the binder and sinter the binder free structure to its final dense configuration.

US 2003/0041895 relates to the recovery of silicon kerf from wire saw slurries by mean of commercially available systems and of silicon flotation, with the final target to obtain by sintering a silicon thin layer structure to be directly used to build photovoltaic cells. Worth to mention that this invention does not address the issue of the high likelihood of silicon oxidation and that the purity of final product is not addressed either. The low flexibility of the method in terms of feedstock and products produced is a severe drawback either. Important to underline that the recovery of the silicon kerf coming from mechanical operations of silicon, such as band saws and grinders, where not considered in this application.

Regarding the points b), meaning avoiding the oxidation of silicon and point c) that is about contaminants level in the recovered silicon, the literature does not provide sound solutions.

At this very point the authors wanted to list the methods commonly used in the industry of semiconductors to clean silicon.

- 5 a) Piranha etching: H_2SO_4 , H_2O_2 , 4:1 at 90 °C, used mainly to remove organic contaminants
- 10 b) Hydrofluoric acid: silicon surface oxide is removed by HF dilute solutions or by buffered HF solutions; however when rinsing silicon with deionised water or exposing the cleaned surface to the air, a layer of native oxide is immediately grown (with a thickness of about 15 Anstrong)
- 15 c) Standard Clean 2 (SC-2): it is based on HCl , H_2O_2 , H_2O mixed with different ratios; its main task is the removal of metallic contaminations (to this purpose the recommended ratios are $\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1:1:5$)
- 20 d) Standard Clean 1 (SC-1): it is based on NH_4OH , H_2O_2 , H_2O mixed with different ratios, while the classic formulation is 1:1:5, at 70 °C; its main task is the removal of multivalent metallic ions.
- 25 e) RCA wet cleaning process: it involves both SC-1 and SC-2 at 70 °C, where SC-1, due to ammonia, complexes many multivalent metal ions, while SC-2 due to its HCl content removes alkali and transitions metals.
- 25 All these methods do not solve the two listed issues because:
- 30 a) it is applied to standard wafers and silicon chunks or silicon rods and not to fine powder and this is crucial because the fine silicon powders typically shows a higher metals contamination level than silicon wafers or chunks, just because it has a much

higher specific surface and typically it has been in contact with metallic tools and piping.

b) All the listed processes do cause the oxidation of treated silicon, including that with HF.

5 Herewith the authors wanted to discuss the literature that tries to address the purification (metal contamination) and the oxides removal topics.

US 2006/0042539 provides a pure water cleaning method that is applied after a preliminary etch of polycrystalline
10 silicon chunks by means of a mixture of nitric and hydrofluoric acids.

The removal effects of the proposed method, with respect to certain types of metal ions, are extremely improved by using pure water that has been purified by combining
15 reverse osmosis treatment and ion exchange treatment.

The patent does not guarantee the removal of oxide layer on the final product because the last step is a washing with clean water. Moreover it is used only for chunks of silicon and not for the more challenging powder (micro and sub-
20 micro powder)

The patent CN 1947870 relates to a cleaning method for removing contaminants from the surface of rejected silicon pieces in order to re-use them. The following steps are described: immerse waste silicon pieces in alkali solution,
25 flushing with purified water, drying, dip in a second alkali solution, flush with purified water, drying, immersing in solution containing HCl and H₂O₂, bubble with compressed air, rinse with purified water and bake. The authors of that patent claim the removal of dirt and
30 contaminants from the surface of rejected Silicon scrap material, that typically have discrete sizes. On the other end the type of chemicals used and the baking applied at the end cause the formation of oxides.

CN 1947869 provides a cleaning method for removing the impurities from the surface of rejected silicon material in order to re-use it; it includes steps such as dipping the rejected silicon materials in a mixed solution of
5 hydrofluoric acid and nitric acid, rinsing with purified water several times, dipping in purified water, measuring the electrical conductivity of the rinsing water and baking to dry. This patent does not solve the issues listed because of the high content of oxide on the surfaces. This
10 is not a major concern for the authors because the application field is very different from that discussed in this application.

WO 2006126365 filed by Sumitomo provides a method for cleaning polycrystalline silicon with a high level of
15 surface quality, suitable to be used as raw material for melting in the production of CZ silicon single-crystal for semiconductor applications or used for solar cells applications.

The advantages of the proposed process are: lower cleaning
20 costs, reduction of silicon loss and of environmental issues related to the disposal of waste chemicals and of NOx gas. The drawbacks of this patent are due to the fact that this method is suitable for chunk but not for powder or kerfs because it would lead to a very low yield.

25 Process steps: polycrystalline silicon is cleaned with hydrofluoric acid to remove the contaminated oxide, followed by a light etching with fluor-nitric mixture or, more preferably the polycrystalline silicon is treated in a furnace with a clean gas containing water vapour, in order
30 to grow an oxide film with no significant contamination left on the surface of the polycrystalline silicon.

The WO 2006126365 process target is to growth an oxide layer on the silicon surface, while present invention

process claims to provide a surface oxide and metal contamination free silicon powder.

KR 20020065105 provides a method for recycling the silicon particles collected from the waste water of a saw process,
5 with the target of obtaining high purity silica.

The purpose of the invention, including a cleaning step by mean of acetone, is aimed to obtain as final product, a high purity silica sol.

KR 20020065105 and the present invention relate to the same
10 feedstock, that is silicon powder collected from waste water of silicon sawing process, but they have different targets, that are the production of silica sol for KR 20020065105 and purified silicon powder for melting application in the field of solar cells for the present
15 invention.

TW 279393 B provides a method to purify silicon powder, by means of a treatment in a tank with an acid solution heated at a predetermined temperature and for predetermined period of time, with the support of a stirring system.

20 The powder is then separated from the acid solution and can be submitted to a second or to multiple acid corrosion treatment to obtain silicon powder with higher purity for silicon material to be used as substrate for solar cell.

The stirring system can be a mechanical one as well as an
25 ultrasonic based system.

The cleaning process described by TW 279393 uses multiple steps of "acid corrosion" to etch off silicon not just to remove surface oxide; this means that some hydrofluoric acid is mixed with an oxidizing agent, while the process
30 claimed in the present invention just removes surface oxide and the metals.

The cleaning process described by TW 289393 is performed with the support of a heating system and of a ultrasonic stirring system, while the process claimed by the present invention is run at room temperature.

- 5 TW 279393 claimed process does not have the target of providing a surface oxide free silicon powder, that is instead one of target of the present invention.

With regards to the issue called D), that is about the potential difficulties that one could face in the melting
10 process of a silicon powder it is worth to mention the US 7,175,685 which describes a process for making silicon pellets by compaction of the high purity ultra fine silicon powder coming as by-product of the fluid bed process used to manufacture high purity electronic grade polysilicon or
15 coming as reaction residues from preparation of chlorosilanes using elemental silicon and hydrogen chloride.

The target of the compaction is to make silicon pellets for melting applications.

- 20 To the purpose a controlled amount of silicon powder free from additives and binders is fed into a pellet die and compacted at room temperature and at high pressure to obtain pellets having a density from about 50 % to 75 % of theoretical density of silicon and specified size and
25 weight.

US 7,175,685 relates to the recovery of the ultra fine silicon powder available as by-product from the fluid bed process used to manufacture high purity electronic grade polysilicon and to the re-use of said silicon powder for
30 directly making silicon pellets for high purity silicon ingots production. The authors do not provide a solution to the melting of fine powder coming from the processes that this invention means to address. The present invention

relates instead to the recovery and the re-use of waste silicon powder deriving as kerf from silicon mechanical operations.

5 US 2007014682 describes methods of compaction and densification high purity silicon powder to defined geometric forms and shapes; to the purpose high purity silicon powder is first mixed with a selected binders and pressed into desired shapes in a mechanical equipment.

10 The binder is removed either in separate step or combined with a subsequent sintering operation.

The patent relates to the recovery of the ultra fine silicon powder coming as by-product of the fluid bed process used to manufacture high purity electronic grade polysilicon or coming as reaction residues from the
15 preparation of chlorosilanes using elemental silicon and hydrogen chloride and to the re-use of said silicon powder for directly making pellets to be used as feedstock in the photovoltaic industry. Therefore the feedstock is completely different as well as the problems that are
20 considered from those addressed by the authors of the present invention.

As already said the present invention describes a process for the re-use of silicon powder recovered from band saws and other silicon mechanical operations at both
25 photovoltaic and microelectronic industry, as feed material to prepare the crucible charges for casting of polycrystalline-multi-crystalline silicon ingots usable for photovoltaic applications.

30 In very general terms the process is characterised by the following steps:

- a) silicon powder recovery from band saws / wire saws, grinding operations by filtration and by treatment of the exhausted slurries

- b) conditioning in non-oxidizing environment
- c) treatments with hydrofluoric acid
- d) treatment with hydrochloric acid and/or hydrofluoric acid and hydrogen peroxide
- 5 e) second treatment with hydrofluoric acid
- f) preparation for the compaction step
- g) compaction of the silicon

In this section the authors wanted to go more in depth in the process steps description.

- 10 Most of the times the conditioning is done by addition of DI water and non-oxidant acid. Worth to mention that also the conditioning of silicon with ethanol or acetone or any other organic solvent compatible with strong acids (excluding H_3PO_4) could be used in either way with and
- 15 without conditioning in HCl/water. Non-oxidant acids are, among the others, HCl, H_2SO_4 , mono and dicarboxylic acids.

Re-slurry of cakes and/or sludges is done with DI water and hydrochloric acids, by using the following recipes and process conditions:

- 20 [Silicon content] : [HCl] = [1] : [0,05-0,5] by weight

Next step is the treatment of said slurry with hydrofluoric acid: hydrofluoric acid is added in such a quantity to obtain the following ratios:

- [Silicon content] : [HCl] : [HF] = [1] : [0,05-0,5] :
25 [0.01-1] by weight

After the treatment the slurry is filtrated and the filtration cake is washed with DI water; afterwards the cake is treated with DI water in order to re-slurry.

Treatment of said slurry with hydrochloric acid and hydrogen peroxide, with the following recipes

[Silicon content] : [HCl] : [H2O2] = [1] : [0,05-0,5] : [0,05-0,2] by weight

- 5 After the treatment the slurry is filtrated and the filtration cake is washed with DI water and then re-slurried with D.I. water.

- Alternativey to the treatment with HCl/H2O2 the authors recognize that this very step can be carried out also with
10 HF/H2O2. More in detail: the slurry undergoes the following treatment with hydrofluoric acid and hydrogen peroxide, with the following recipes:

[Silicon content] : [HF] : [H2O2] = [1] : [0,01 - 0,1] : [0,05-0,5] by weight.

- 15 Afterwards comes a re-slurry step with DI and then the treatment of said slurry with hydrofluoric acid with the following recipes

[Silicon content] : [HF] = [1] : [0,05-0,15] by weight.

- After the treatment the slurry is filtrated and afterwards
20 the acid cake is dried under vacuum / nitrogen to prevent the oxidation of the silicon particles. The authors wanted to underline that the acidic cake could be also treated with alcohol in order to obtain a "wet-cake".

- At the end of the process comes the melting / casting
25 charges preparation, herewith the authors propose three methods. The first is based on Vacuum-Nitrogen silicon powder compaction process, applied to the decontaminated and dried silicon kerf directly inside any industrially available casting crucible, ready for transportation and
30 melting.

The second method is a compaction process of the recovered, decontaminated and dried silicon powder by means of an industrially available binders free compaction process that has as output some compacted silicon pellets or discs
5 suitable as silicon casting charges.

The third is about a sol-gel based method that leads to green bodies that can be shaped directly into the crucible.

The techniques described in this invention, can be according to Figure 1 summarized as follows:

10 1.1 Recover the silicon powder from the waste waters of silicon mechanical operations of photovoltaic and microelectronic industries and from cakes or sludges coming from the exhausted wire saw slurries after separation of suspending agents and abrasives.

15 see Figure 1, section A

1.2 Chemical Conditioning of the recovered silicon powder to control the oxidation of the powder for safe transportation and storing of the silicon powder.

see Figure 1, section A

20 1.3 Decontamination of surface impurities of recovered and conditioned silicon powders.

see Figure 1, section B

1.4 Compaction method number 1: treating the purified silicon powder with a vacuum-nitrogen densification process
25 for the preparation of compacted silicon powder charges directly inside standard size casting crucibles.

In the details the steps characterising the methods are:

a) dry silicon powder is added inside an industrial standard casting crucible that is maintained under nitrogen environment

5 b) the crucible filled with the silicon dry powder is put under vacuum, until the vacuum reaches the values in the range (20-60) kPa

c) by means of a nitrogen flow at room temperature, the vacuum of the environment containing the crucible filled with the silicon powder is released and the pressure is
10 raised to the value of about 1 bar; in its path through the silicon particles, nitrogen creates a drag effect on the silicon particles, yielding a consistent compaction of the silicon powder (reduction to 60%-70% of initial volume).

see Figure 1, section C

15 1.5 Compaction method number 2: treating the purified silicon powder with an industrially available binder free compaction process for the preparation of silicon pellets or discs. In detail the steps are: the dry silicon powder under nitrogen is used as feed for this compaction process
20 for charges preparation. The dry silicon powder, kept under nitrogen to prevent oxidation, can be used as feedstock for one of the industrially available compaction processes, without binding agent, to make silicon pellets or discs

25 see Figure 1, section C

1.6 Compaction method number 3: preparation of green bodies out of the purified silicon powder by means of sol-gel techniques.

The sol-gel based method is the only for which either the
30 dried powder or the wet (with alcohol) powder are suitable. Sol-gel based method is based on the following steps: as

feed can be used both alcohol containing material or dried powder, the feed is then mixed with an alcoholic solution containing a silane and then kept under stirring. The green body so formed is then dried till the organic content level
5 complies with the requirements defined by the silicon smelters.

see Figure 1, section C

The effectiveness of the silicon powder compaction processes described below of this invention, varies widely
10 according to the process used, as hereafter indicated:

- a) sol-gel based compaction: the density of the body is the range 0,9-1,4 gr/cm³
- b) Vacuum-Nitrogen compaction process: the volume of the silicon powder after compaction is reduced to 60%-70% of
15 the initial volume and the density is increased in the range 08-1,0 gr/cm³.
- c) tableting compaction process: the final density of the pellets is about 60-70% of the density of the elemental silicon.

20 The authors wanted to underline that the compaction step by sol-gel can be done directly in a mold. Once that the silicon has been compacted in the mold comes the transfer of the compacted silicon in a crucible or alternatively the authors do not rule out the possibility to carry out the
25 process directly in the crucible.

As already said after the compaction step the silicon is molten in the crucible that most of times is made of pure silica. A problem that the operator could face in performing such melting step is due to the difference in
30 terms of thermal coefficient between silicon and silica and this could lead to a stress into the crucible that causes breakage of silica crucible and leakage. The silicon

thermal expansion coefficient is about $1 \cdot 10^{-6} ^\circ\text{C}$ whereas for silica it is $0.55 \cdot 10^{-6} ^\circ\text{C}$. This is particular likely for those compaction methods that allow to fill the crucible at its maximum capacity.

- 5 A possible solution to this very issue that the author would like to describe is the use of an inner mold for the crucible. More in detail: in order to avoid that the silicon by melting causes the stress on the crucible mold the author suggest to have some cavities created before the
10 compaction step is complete. The cavities would be created by means of the inner mold in a way similar to that described in the patent WO2007 065766, where are listed some inner molds suitable for the making of silica glass by means of sol-gel techniques. The created cavities work as
15 "buffer" in order to give some space to the silicon to swell and not create stress on the crucible.

- Here the authors would like to give some more insights on the inner molds features. The inner molds can be extracted before the melting step and when the compaction step is at
20 completion but special care has to be put at the issue of the adhesion of the compacted silicon to the mold. The mold could be removed by mechanical extraction, especially if the mold is stiff, or by deflating the mold in case have been used inflatable molds or by melting the molds and
25 extracting the melt (by sucking). The inner mold can be made of: plastic, glass, metal, waxes and silica glass among the others.

- The following examples are illustrative and not to be considered as limited of the invention described in the
30 claims.

EXAMPLES 1

Step 1: (A1 in scheme attached)

The filtration cake is washed with a diluted solution of hydrochloric acid and maintained at pH of (3,5-4,5) to prevent the reaction of the silicon powder with water that generates hydrogen.

- 5 The water content of the filtration cakes is typically in the range 20 % - 60 %.

Step 2 (B,1 in the attached scheme):

- 10 The recovered silicon powder is sent to the re-slurry, either as cake from filtration or sludges from centrifugal treatment or as dry powder; the re-slurry operation is made by addition of DI water and Hydrochloric acid; the ratios among the chemicals used in the re-slurry are shown hereafter : [Silicon content] : [HCl] = [1] : [0,2] by weight.

- 15 DI water is added in such a quantity to adjust the density of the slurry in the range 200-400 gr/l.

Step 3 (B,2 in the attached scheme):

- 20 The slurry coming from step 2, is sent to Reactor R2 (see scheme) and then mixed with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HCl] : [HF] = [1] : [0,2] : [0,5]

DI water is adjusted to control the density in the range 200-400 gr/l.

Treatment Conditions for step 3:

- 25 a) Stirring: continuous
b) Temperature: 20 - 40 °C
c) treatment time: 1 hour

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After the treatment the slurry is sent to filtration and the resulting silicon cake is washed with D.I.

Step 4 (B,3 in the scheme):

- 5 The slurry coming from step 3, is mixed with hydrochloric acid and with hydrogen peroxide in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HCl] : [H₂O₂] = [1] : [0,2] : [0,1] by weight.

- 10 DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

Treatment Conditions for step 4:

- a) Stirring: continuous
 - b) Temperature: 20 - 40 °C
 - c) treatment time: 1 hour
- 15 After the treatment the slurry is filtrated and the filtration cake is washed with DI water; liquids from filtration and washing containing HCl and H₂O₂, are sent to a neutralization tank, which contains Ca(OH)₂ in a water solution.
- 20 The process step ends with the Re-Slurry of the silicon cake with D.I. water.

Step 5 (B,4 in the scheme):

- 25 Slurry coming from reactor R3 is again mixed with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HF] = [1] : [0,1] by weight

Treatment Conditions:

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- a) Stirring: continuous
- b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

DI water is adjusted to control the density of the slurry
5 in the range 200-400 gr/l.

After treatment the slurry is filtrated and the filtration
cake, wet by hydrofluoric acid, is sent directly to the
cake drying step, while the liquid from filtration and
washing, containing hydrofluoric acid is sent to the
10 neutralization tank.

Step 6 (B,5 in the scheme):

The silicon cake from process step (B,4 see scheme) kept
acidic by HF to prevent the oxidation of the silicon
particles by water and air and is dried under vacuum:

- 15 a) Vacuum values: 20 mBar, in nitrogen atmosphere
- b) Temperature: 70 °C by RF heating
- c) at the end of the drying cycle vacuum is released
in nitrogen atmosphere.

Step 7 (sol-gel method)

- 20 0.7 g of tetramethoxysilane are mixed with 5 g ethanol and
1 g water and the solution so obtained is kept under
stirring until complete hydrolysis of tetramethoxysilane
occurs (solution becomes completely transparent). Then 14 g
of silicon powder are added to the silane-based premix
25 (weight ratio 1:0,49) and kept under stirring. The sludge
so obtained is then poured in the mold. The whole process
is conducted under nitrogen. Before the start of the drying
phase the sample is kept in a sealed container at room
temperature for the consolidation of the green body.

Silicon body is then dried under ventilated hood for 3 days. The product has been characterized by means of XRD spectroscopy that has shown that the content of SiO₂ in the silicon product raised only of 0.5 wt% because of the
5 described treatment.

The advantage of the process described in this example is that the green body is obtained already inside the casting crucibles; as the green body withstand mechanical stresses due to handling, meaning that it can be easily packed,
10 shipped and used directly in final casting facilities for melting without any further treatment.

EXAMPLES 2

Step 1: (A1 in scheme attached)

The filtration cake is washed with a diluted solution of
15 hydrochloric acid and maintained at pH of (3,5-4,5) to prevent the reaction of the silicon powder with water that generates hydrogen.

The water content of the filtration cakes is typically in the range 20 % - 60 %.

20 Step 2 (B,1 in the attached scheme):

The recovered silicon powder is sent to the re-slurry, either as cake from filtration or sludges from centrifugal treatment or as dry powder; the re-slurry operation is made by addition of DI water and Hydrochloric acid; the ratios
25 among the chemicals used in the re-slurry are shown hereafter : [Silicon content] : [HCl] = [1] : [0,2] by weight.

DI water is added in such a quantity to adjust the density of the slurry in the range 200-400 gr/l.

30 Step 3 (B,2 in the attached scheme):

The slurry coming from step 2, that is already acid because of the hydrochloric already added at step B,1, is sent to Reactor R1 and then added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

- 5 [Silicon content] : [HCl] : [HF] = [1] : [0,2] : [0,5]

DI water is adjusted to control the density in the range 200-400 gr/l.

Treatment Conditions for step 3:

- a) Stirring: continuous
- 10 b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

- After the treatment the slurry is sent to filtration and the resulting silicon cake is washed with D.I, re-slurried with DI adjusting the density to the range 200-400 gr/l and
- 15 sent to reactor R3.

Step 4 (B,3 in the scheme):

The slurry (2) coming from reactor R2, is added with hydrofluoric acid and with hydrogen peroxide in such a quantity to obtain the following ratios by weight:

- 20 [Silicon content] : [HF] : [H2O2] = [1] : [0,4] : [0,15]
by weight.

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

Treatment Conditions:

- 25 a) Stirring: continuous
- b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

After the treatment the slurry is filtrated and the filtration cake is washed with Deionised water; liquids from filtration and washing containing HF and H₂O₂, are sent to a neutralization tank.

- 5 The process step (B3) ends with the Re-Slurry of the Silicon cake with D.I. water, adjusting the density of the slurry in the range 200-400 gr/l (slurry 3).

Step 5 (B,4 in the scheme):

- Slurry coming from reactor R3 is again added with
10 hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HF] = [1] : [0,1] by weight

Treatment Conditions:

- a) Stirring: continuous
15 b) Temperature: 20 - 40 °C
c) treatment time: 1 hour

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

- 20 After treatment the slurry is filtrated and the filtration cake, wet by hydrofluoric acid, is sent directly to the cake drying step, while the liquid from filtration and washing, containing hydrofluoric acid is sent to the neutralization tank.

Step 6 (B,5 in the scheme):

- 25 The silicon cake from process step (B,4) kept acidic by HF to prevent the oxidation of the silicon particles by water and air is dried under vacuum:

- a) Vacuum values: 20 mBar, in nitrogen atmosphere

b) Temperature: 70 °C by RF heating

c) at the end of the drying cycle the vacuum is released in nitrogen atmosphere.

Step 7 (sol-gel method)

- 5 0.7 g of tetramethoxysilane are mixed with 5 g ethanol and 1 g water and the solution so obtained is kept under stirring until complete hydrolysis of tetramethoxysilane occurs (solution becomes completely transparent). Then 14 g of silicon powder are added to the silane-based premix
- 10 (weight ratio 1:0,49) and kept under stirring. The sludge so obtained is then poured in the mold. The whole process is conducted under nitrogen. Before the start of the drying phase the sample is kept in a sealed container at room temperature for the consolidation of the green body.
- 15 Silicon body is then dried under ventilated hood for 3 days. The product has been characterized by means of XRD spectroscopy that has shown that the content of SiO₂ in the silicon product raised only of 0.5 wt% because of the described treatment.
- 20 The advantage of the process described in this example is that the green body is obtained already inside the casting crucibles; as the green body is very stable and can withstand mechanical stresses, it can be easily packed, shipped and used directly in final casting facilities for
- 25 melting without any further treatment.

EXAMPLES 3

Step 1: (A1 in scheme attached)

- The filtration cake is washed with a diluted solution of hydrochloric acid and maintained at pH of (3,5-4,5) to
- 30 prevent the reaction of the silicon powder with water that generates hydrogen.

The water content of the filtration cakes is typically in the range 20 % - 60 %.

Step 2 (B,1 in the attached scheme):

The recovered silicon powder is sent to the re-slurry,
5 either as cake from filtration or sludges from centrifugal treatment or as dry powder; the re-slurry operation is made by addition of DI water and hydrochloric acid; the ratios among the chemicals used in the re-slurry are shown hereafter : [Silicon content] : [HCl] = [1] : [0,2] by
10 weight.

DI water is added in such a quantity to adjust the density of the slurry in the range 200-400 gr/l.

Step 3 (B,2 in the attached scheme):

The slurry coming from step 2, that is already acid because
15 of the hydrochloric already added at step B,1, is sent to Reactor R1 and then added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HCl] : [HF] = [1] : [0,2] : [0,5]

DI water is adjusted to control the density in the range
20 200-400 gr/l.

Treatment Conditions for step 3:

- a) Stirring: continuous
- b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

25 After the treatment the slurry is sent to filtration and the resulting silicon cake is washed with D.I, re-slurried with DI adjusting the density to the range 200-400 gr/l and sent to reactor R3.

Step 4 (B,3 in the scheme):

The slurry (2) coming from reactor R2, is added with hydrofluoric acid and with hydrogen peroxide in such a quantity to obtain the following ratios by weight:

- 5 [Silicon content] : [HF] : [H2O2] = [1] : [0,4] : [0,15]
by weight.

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

Treatment Conditions:

- 10 a) Stirring: continuous
b) Temperature: 20 - 40 °C
c) treatment time: 1 hour

- After the treatment the slurry is filtrated and the filtration cake is washed with Deionised water; liquids
15 from filtration and washing containing HF and H₂O₂, are sent to a neutralization tank.

The process step (B3) ends with the Re-Slurry of the Silicon cake with D.I. water, adjusting the density of the slurry in the range 200-400 gr/l (slurry 3).

20 **Step 5 (B,4 in the scheme):**

Slurry coming from reactor R3 is again added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HF] = [1] : [0,1] by weight

25 Treatment Conditions:

- a) Stirring: continuous
b) Temperature: 20 - 40 °C

c) treatment time: 1 hour

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

- 5 After treatment the slurry is filtrated and the filtration cake, wet by hydrofluoric acid, is sent directly to the cake drying step, while the liquid from filtration and washing, containing hydrofluoric acid is sent to the neutralization tank.

Step 6 (B,6 in the scheme):

- 10 The silicon cake from process step (B,4) kept acidic by HF to prevent the oxidation of the silicon particles by water and air is washed with a alcoholic solution made of ethanol and water in ratio by weight 95:5

Step 7 (sol-gel method)

- 15 0.7 g of tetramethoxysilane are mixed with 5 g ethanol and 1 g water and the solution so obtained is kept under stirring until complete hydrolysis of tetramethoxysilane occurs (solution becomes completely transparent). Then 17 g of wet silicon coming from step 6 are added to the silane-based premix (weight ratio 1:0,49) and kept under stirring.
- 20 The sludge so obtained is then poured in the mold. The whole process is conducted under nitrogen. Before the start of the drying phase the sample is kept in a sealed container at room temperature for the consolidation of the green body. Silicon body is then dried under ventilated
- 25 hood for 3 days. The product has been characterized by means of XRD spectroscopy that has shown that the content of SiO₂ in the silicon product raised only of 0.5 wt% because of the described treatment.
- 30 The advantage of the process described in this example is that the green body is obtained already inside the casting crucibles; as the green body is very stable and can

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withstand mechanical stresses, it can be easily packed, shipped and used directly in final casting facilities for melting without any further treatment.

5 **EXAMPLES 4**

Step 1: A1 in scheme attached)

The filtration cake is washed with a diluted solution of hydrochloric acid and maintained at pH of (3,5-4,5) to prevent the reaction of the silicon powder with water that
10 generates hydrogen.

The water content of the filtration cakes is typically in the range 20 % - 60 %.

Step 2 (B,1 in the attached scheme):

The recovered silicon powder is sent to the re-slurry,
15 either as cake from filtration or sludges from centrifugal treatment or as dry powder; the re-slurry operation is made by addition of DI water and Hydrochloric acid; the ratios among the chemicals used in the re-slurry are shown hereafter : [Silicon content] : [HCl] = [1] : [0,2] by
20 weight.

DI water is added in such a quantity to adjust the density of the slurry in the range 200-400 gr/l.

Step 3 (B,2 in the attached scheme):

25 The slurry coming from step 2, that is already acid because of the hydrochloric already added at step B,1, is sent to Reactor R1 and then added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HCl] : [HF] = [1] : [0,2] : [0,5]

DI water is adjusted to control the density in the range 200-400 gr/l.

Treatment Conditions for step 3:

- a) Stirring: continuous
- 5 b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

After the treatment the slurry is sent to filtration and the resulting silicon cake is washed with D.I, re-slurried with DI adjusting the density to the range 200-400 gr/l and
10 sent to reactor R3.

Step 4 (B,3 in the scheme) / case B:

The slurry (2) coming from reactor R2, is added with hydrofluoric acid and with hydrogen peroxide in such a quantity to obtain the following ratios by weight:

- 15 [Silicon content] : [HF] : [H2O2] = [1] : [0,4] : [0,15]
by weight.

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

Treatment Conditions:

- 20 a) Stirring: continuous
- b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

After the treatment the slurry is filtrated and the filtration cake is washed with Deionised water; liquids
25 from filtration and washing containing HCl and H₂O₂, are sent to a neutralization tank (containing Ca(OH)₂).

The process step (B3) ends with the Re-Slurry of the Silicon cake with D.I. water, adjusting the density of the slurry in the range 200-400 gr/l (slurry 3).

Step 5 (B,4 in the scheme):

- 5 Slurry coming from reactor R3 is again added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HF] = [1] : [0,1] by weight

Treatment Conditions:

- 10 a) Stirring: continuous
b) Temperature: 20 - 40 °C
c) treatment time: 1 hour

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

- 15 After treatment the slurry is filtrated and the filtration cake, wet by hydrofluoric acid, is sent directly to the cake drying step, while the liquid from filtration and washing, containing hydrofluoric acid is sent to the neutralization tank.

20 **Step 6 (B,5 in the scheme):**

The silicon cake from process step (B,4) kept acidic by HF to prevent the oxidation of the silicon particles by water and air and is dried under vacuum:

- a) Vacuum values: 20 mBar, in nitrogen atmosphere
25 b) Temperature: 70 °C by RF heating
c) at the end of the drying cycle the vacuum is released in nitrogen atmosphere.

Step 7 (vacuum-nitrogen method)

The process describes the method for the compaction of the dry, oxide free silicon powders coming from process step (B,5); it is based on the densification capacity of a gas, in this case nitrogen, when it makes its path through the mass of dry silicon particles, kept in a vacuum environment.

The choice of nitrogen is due to the need of avoiding any oxidation of the silicon particles.

10 Compaction process, steps description:

- a) the dry silicon powder is poured inside an industrial standard casting crucible that is maintained under nitrogen environment
- b) the crucible filled with the silicon dry powder is put under vacuum, until the vacuum reaches the values in the range 30 kPa
- c) by mean of a nitrogen flow at room temperature, the vacuum of the environment containing the crucible filled with the silicon powder is released until the pressure is raised to the value of 1 bar.

In its path through the silicon particles, nitrogen creates a drag effect on the silicon particles, yielding a consistent compaction of the silicon powder (reduction to 60%-70% of initial volume).

25 EXAMPLES 5**Step 1 (A1 in scheme attached)**

The filtration cake is washed with a diluted solution of hydrochloric acid and maintained at pH of (3,5-4,5) to prevent the reaction of the silicon powder with water that generates hydrogen.

The water content of the filtration cakes is typically in the range 20 % - 60 %.

Step 2 (B,1 in the attached scheme):

The recovered silicon powder is sent to the re-slurry,
5 either as cake from filtration or sludges from centrifugal treatment or as dry powder; the re-slurry operation is made by addition of DI water and Hydrochloric acid; the ratios among the chemicals used in the re-slurry are shown
10 hereafter : [Silicon content] : [HCl] = [1] : [0,2] by weight.

DI water is added in such a quantity to adjust the density of the slurry in the range 200-400 gr/l.

Step 3 (B,2 in the attached scheme):

The slurry coming from step 2, that is already acid because
15 of the hydrochloric already added at step B,1, is sent to Reactor R1 and then added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HCl] : [HF] = [1] : [0,2] : [0,5]

DI water is adjusted to control the density in the range
20 200-400 gr/l.

Treatment Conditions for step 3:

- a) Stirring: continuous
- b) Temperature: 20 - 40 °C
- c) treatment time: 1 hour

25 After the treatment the slurry is sent to filtration and the resulting silicon cake is washed with D.I, re-slurried with DI adjusting the density to the range 200-400 gr/l and sent to reactor R3.

Step 4 (B,3 in the scheme) / case B:

The slurry (2) coming from reactor R2, is added with hydrofluoric acid and with hydrogen peroxide in such a quantity to obtain the following ratios by weight:

- 5 [Silicon content] : [HF] : [H₂O₂] = [1] : [0,4] : [0,15]
by weight.

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

Treatment Conditions:

- 10 a) Stirring: continuous
b) Temperature: 20 - 40 °C
c) treatment time: 1 hour

- After the treatment the slurry is filtrated and the filtration cake is washed with Deionised water; liquids
15 from filtration and washing containing HCl and H₂O₂, are sent to a neutralization tank.

The process step (B3) ends with the Re-Slurry of the Silicon cake with D.I. water, adjusting the density of the slurry in the range 200-400 gr/l (slurry 3).

20 **Step 5 (B,4 in the scheme):**

Slurry coming from reactor R3 is again added with hydrofluoric acid in such a quantity to obtain the following ratios by weight:

[Silicon content] : [HF] = [1] : [0,1] by weight

25 Treatment Conditions:

- a) Stirring: continuous
b) Temperature: 20 - 40 °C

c) treatment time: 1 hour

DI water is adjusted to control the density of the slurry in the range 200-400 gr/l.

- After treatment the slurry is filtrated and the filtration
- 5 cake, wet by hydrofluoric acid, is sent directly to the cake drying step, while the liquid from filtration and washing, containing hydrofluoric acid is sent to the neutralization tank.

Step 6 (B,5 in the scheme):

- 10 The silicon cake from process step (B,4) kept acidic by HF to prevent the oxidation of the silicon particles by water and air and is dried under vacuum:

a) Vacuum values: 20 mBar, in nitrogen atmosphere

b) Temperature: 70 °C by RF heating

- 15 c) at the end of the drying cycle the vacuum is released in nitrogen atmosphere.

Step 7 (pelletisation/tabletting method)

- The dry silicon powder, kept under nitrogen to prevent oxidation, can be used as feedstock for one of the
- 20 industrially available compaction processes, without binding agent.

- The chemical cleaning with hydrofluoric acid applied to the silicon powders according to section (4.2) of this invention, provides an oxide-free silicon particles that
- 25 are suitable for the fabrication of compacted silicon pellets or discs by mean of high pressure at room temperature.

The density of the pellets obtained with this process is about 60-70% of the density of the elemental silicon; they

can be used stand alone or mixed with silicon nuggets for the charges preparation for casting applications.

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Claims

1. A process for the re-use of silicon powder recovered from band saws and other silicon mechanical operations, as feed material to prepare the crucible charges for casting of polycrystalline-multicrystalline silicon ingots usable for photovoltaic applications, which process is characterised by the following steps:
- a) silicon powder recovery from band saws, wire saws, grinding operations by filtration or centrifugal agglomeration and treatment of the exhausted slurries;
 - b) conditioning in non-oxidizing environment;
 - c) treatment with hydrofluoric acid;
 - d) treatment with hydrochloric acid and/or hydrofluoric acid and hydrogen peroxide;
 - e) second treatment with hydrofluoric acid;
 - f) preparation for the compaction step by drying under vacuum and inert gas, or by washing with an organic solvent;
 - g) compaction of the silicon powder.
2. A process according to claim 1 characterized in that the chemical conditioning, step b), to prevent the oxidation of the cakes and/or sludges recovered from step a), is performed at pH between -0,5 and 5,5 and more preferably between 3 and 5, by means of a non-oxidising acid such as a mineral acid, mono carboxylic and dicarboxylic organic acids.
3. A process according to claim 1 characterized in that the chemical conditioning, step b), to prevent the oxidation of the cakes and/or sludges recovered from step a), is

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performed with an organic solvent not acid sensitive, such as, acetone, ether, ethanol, propanol, iso-propanol, methanol, butanol.

4. A process according to claim 1 characterized in that the chemical conditioning, step b), to prevent the oxidation of the cakes and/or sludges recovered from step a), is performed in two steps: first a conditioning in an organic solvent not acid sensitive, such as, acetone, ether, ethanol, propanol, iso-propanol, methanol, butanol followed by a conditioning in a non-oxidising acid such as a mineral acid, organic acid, such organic acid can be monocarboxylic or dicarboxylic.
5. A process according to claim 1 characterized in that the treatment with hydrofluoric acid, step c), is performed in a way where the ratio Si and HF is [1]: [between 0.01 and 1] by weight.
6. A process according to claim 1 characterized in that the treatment d) with hydrofluoric acid and hydrogen peroxide is performed in a way where the ratios Si:HCl:H₂O₂ are [1]:[from 0,05 to 0,5]: [from 0,05 to 0,2] by weight.
7. A process according to claim 1 characterized in that the treatment d) with hydrofluoric acid and hydrogen peroxide is performed in a way where the ratios Si:HF:H₂O₂ are [1]:[from 0,01 to 0,1]: [from 0,05 to 0,5] by weight.
8. A process according to claim 1 characterized in that the second treatment with hydrofluoric acid, step e), is performed in a way where the ratio Si: HF is [1] : [from 0,05 to 0,15].
9. A process according claim 1 characterized in that the treatment f) of preparation for the compaction step is performed under inert gases or vacuum and the temperature is raised up to 100°C.

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10. A process according to claim 1 characterized in that the treatment f) of preparation for the compaction step is performed by washing the silicon cake with ethanol, isopropanol, butanol, methanol, ether or a mixture thereof.
- 5 11. A process according to claim 1 characterized in that the compaction step, g), is performed in a mold.
12. A process according to claim 11 characterized in that the mold is a crucible made of silica.
13. A process according claim 11 characterized in that the
10 mold has inner mold that can be removed.
14. A process according to claim 13 characterized in that the mold is inflatable.
15. A process according to claim 13 characterized in that the mold is water soluble and/or ethanol soluble and/or
15 acetone soluble.
16. A process according to claim 13 characterized in that the mold is characterized by a melting point lower than 150°C.
17. A process according to claim 1 characterized in that
20 the compaction step g) is performed following the steps hereafter listed:
- a) dried silicon powder is added inside an industrial standard casting crucible that is maintained under nitrogen environment;
- 25 b) the crucible filled with the silicon dry powder is put under vacuum, until the vacuum reaches the values in the range (20-60) kPa;
- c) by means of a nitrogen flow at room temperature, the vacuum of the environment
30 containing the crucible filled with the silicon

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powder is released and the pressure is raised to the value of about 1 bar; in its path through the silicon particles, nitrogen creates a drag effect on the silicon particles, yielding a consistent compaction of the silicon powder.

18. A process according to claim 1 characterized in that the compaction step g) is performed by tableting or pelletizing the dried silicon powder.

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