

METHOD FOR PRODUCING FINE SILICON POWDER, AND METHOD FOR PRODUCING FINE SILICON NITRIDE POWDER

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a method for producing high-purity fine silicon powder, and a method for producing high-purity fine silicon nitride powder.

BACKGROUND OF THE INVENTION

[0002] Fine silicon powder has been attracting attention as an electronic material. As fine silicon powder is high-priced, trials have been carried out for recycling cutting waste produced by slicing a high-purity silicon ingot and using the cutting waste as fine silicon powder.

[0003] Under such circumstances, WO 2013/047678 A1 discloses a micronization method for silicon cutting waste using a cutter or a grinder which includes a fixed abrasive grain wire to which abrasive grains have previously been fixed, a support unit for supporting an object to be machined (a silicon ingot to be cut) and pressing against the fixed abrasive grain wire, and a coolant liquid supply unit for supplying a coolant liquid without an abrading agent. According to the micronization method, it is disclosed that cutting waste produced after cutting a silicon ingot by use of the aforementioned cutter or grinder is recovered along with a coolant liquid without an abrading agent as a slurry, and submicron order-fine

silicon powder is extracted from the slurry by a solid-liquid separator, such as a centrifugal separator or a filter pressing machine.

When the fine silicon powder is extracted by such a cutter or a grinder, impurities, such as metals are mixed into the slurry, which makes it difficult to obtain high-purity fine silicon powder. The mixing of metals includes, for example, mixing of nickel from a nickel electro-deposition diamond abrasive grains of a fixed abrasive grain wire, mixing of iron and chromium from a wire rod, mixing from an apparatus path which is in contact with the coolant liquid, and mixing of cutting waste of a fixing plate for fixing the silicon ingot. In addition, when such impurities are removed by pure water only, a vast amount of pure water is needed. As a result, this leads to not only high costs but also difficulty in removing hardly soluble metal compounds.

[0004] JP 2011-051856 A discloses that silicon cutting waste produced from a back grinding process of a semiconductor plant is micronized by a mechanical grinder such as a ball mill and a wet jet mill to extract fine silicon powder having D50 (50% cumulative diameter) of about 0.35 μm to 1.1 μm and obtain fine silicon nitride powder by nitriding the fine silicon powder. A micronization processing by use of a mechanical grinder such as a ball mill and a wet jet mill, however, costs high in production and thus being unsuitable for mass production.

[0005] JP 2013-071864 A discloses that a silicon nitride ingot is produced by nitriding metal silicon as a starting material having an average particle size of 2.9 μm obtained by drying a metal silicon sludge generated by cylindrical grinding of monocrystal metal silicon, heating at 1,450°C for 160 hours at a batch furnace. In addition, JP 2013-071864 A discloses that thus produced silicon nitride ingot is roughly crushed with a Jaw crusher and an Alumina roll double crusher and is crashed with a vibrating mill or a jet mill to adjust silicon nitride powder for a mold releasing agent. In the case where the D50 particle size of this silicon nitride powder is in a range of 1.6 μm to 3.0 μm , the mold releasing agent is peeled off at a low rate, which is preferable. Such a method for mechanically crushing has a disadvantage in high cost as a mass-production line.

[0006] Additionally, non-patent document 1 to be described later discloses an example of cost analysis of silicon nitride powder obtained by the nitridation of metallic silicon powder by a direct nitridation method. As is shown in the table, the ratio between the cost for crushing silicon nitride aggregate and the cost for roughly crushing the silicon nitride aggregate is 29.2% and 28.4%. The total of the ratio reaches 57.6%, which is about 60%. This indicates that a reduction of the crushing process is an important factor of a cost reduction in mass production.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0007] Patent document 1: WO 2013/047678 A1

Patent document 2: JP 2011-051856 A

Patent document 3: JP 2013-071864 A

[0008] Non-patent document 1: "The Economic Aspect of Silicon Nitride Powder Prepared by Direct Nitridation Method" in the magazine "Ceramics" written by Takashi Kawasaki, Japan, Japan Ceramics Association, volume 35, issued on November, 2000, pages 919-922

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0009] It is an object of the present invention to provide high-purity fine silicon powder obtained by improving the aforementioned conventional disadvantages and recovering silicon cutting waste in a state of being effectively and economically advantageous to take a sample without mechanically crushing the silicon cutting waste, and a method for producing the high-purity fine silicon powder.

MEANS FOR SOLVING THE PROBLEMS

[0010] The summary of the present invention is described as below.

In a first preferred embodiment, there is provided a method for producing fine silicon powder according to the present invention which includes the steps of: preparing a

silicon ingot and a fixed abrasive grain wire saw, in which abrasive grains are fixed to an outer periphery of a wire; fixing the silicon ingot to a fixing plate for attaching the silicon ingot; slicing the silicon ingot with the fixed abrasive grain wire saw; recovering a slurry including silicon cutting waste produced in the slicing step; separating solid and liquid to isolate a cake including the silicon cutting waste from the slurry with a solid-liquid separator and extract the cake; washing the cake obtained in the solid-liquid separation step with a washing liquid; and drying a solid content obtained by separating the solid and the liquid with a dryer after the washing step.

[0011] In a second preferred aspect of the method for producing fine silicon powder according to the present invention, the fixing plate contains aluminum hydroxide particles or magnesium hydroxide particles.

[0012] In a third preferred aspect of the method for producing fine silicon powder according to the present invention, the abrasive grains that exist on the outer periphery of the fixed abrasive grain wire saw each have an average particle size of 1 μm to 25 μm and an abrasive grain density of 1,500 pieces/ mm^2 to 3,000 pieces/ mm^2 .

[0013] In a fourth preferred aspect of the method for producing fine silicon powder according to the present invention, the fixed abrasive grain wire saw is a resin bond wire saw.

[0014] In a fifth preferred aspect of the method for producing fine silicon powder according to the present invention, the silicon ingot has an ingot feeding rate of 0.1 mm/minute to 1.0 mm/minute when cutting the silicon ingot and has an ingot feeding rate of 0.05 mm/minute to 0.5 mm/minute when cutting the fixing plate.

[0015] In a sixth preferred aspect of the method for producing fine silicon powder according to the present invention, the washing step further includes the step of washing the cake obtained in the solid-liquid separation step with a first washing liquid and then washing the cake with a second washing liquid.

[0016] In a seventh preferred aspect of the method for producing fine silicon powder according to the present invention, the first washing liquid is a sulfuric acid aqueous solution containing 5 weight % to 40 weight % of sulfuric acid, and the cake obtained by the solid-liquid separation step is washed while immersing and stirring the cake for 20 minutes to 60 minutes with the sulfuric acid aqueous solution that has been heated to 50°C to 90°C.

[0017] In an eighth preferred aspect of the method for producing fine silicon powder according to the present invention, the second washing liquid is a hydrofluoric acid aqueous solution containing 0.5 weight % to 10 weight % of hydrofluoric acid, and the cake that has been extracted after washing with the first washing liquid and has been solid-liquid separated is washed by being immersed into the

hydrofluoric acid aqueous solution for 5 minutes to 30 minutes.

[0018] In a ninth preferred aspect, there is provided a method for producing fine silicon powder according to the present invention which includes the step of: obtaining scale-shaped fine silicon powder.

[0019] In a tenth preferred aspect, there is provided a method for producing fine silicon powder according to the present invention which includes the step of: obtaining scale-shaped fine silicon powder having a specific surface area of $10 \text{ m}^2/\text{g}$ to $50 \text{ m}^2/\text{g}$.

[0020] In an eleventh preferred aspect, there is provided a method for producing fine silicon nitride powder according to the present invention which includes the steps of: obtaining fine silicon powder by the method for producing fine silicon powder; placing the fine silicon powder having a bulk density of 0.3 g/cm^3 to 0.7 g/cm^3 without pressing against a container in a nitride furnace; and nitriding the fine silicon powder by a direct nitridation method.

[0021] In a twelfth preferred aspect, there is provided a method for producing fine silicon nitride powder according to the present invention which includes the step of: obtaining fine silicon nitride powder having a specific surface area of $1 \text{ m}^2/\text{g}$ to $10 \text{ m}^2/\text{g}$.

ADVANTAGES OF THE INVENTION

[0022] According to the present invention, it is possible to extract high-purity fine silicon powder having a scale shape and a size of submicron to micron order by recovering a slurry after slicing a silicon ingot with a fixed abrasive grain wire to perform prescribed treatment without micronization by use of a mechanical grinder. This minimizes production costs of high-purity fine silicon powder, thus enabling mass production.

In addition, high-purity fine silicon nitride powder having a size of submicron to micron order can be produced by nitriding the high-purity fine silicon powder by heating under predetermined conditions without a conventional grinding process. This is because the fine silicon powder can be obtained without the formation of an ingot by aggregating silicon nitride particles like the conventional process. As mentioned above, the mechanically grinding process such as a ball mill and a jet mill which have been used is not needed in production of silicon powder and production of fine silicon nitride powder. This minimizes the production cost of high-purity fine silicon nitride powder, thus enabling mass production. Alternatively, this enables a significant reduction in grinding time even when a mechanical grinder is needed from a viewpoint of productivity. As a result, grinding power can also be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

FIG. 1 is a front vision schematic view of an ingot slicing apparatus used in the present invention;

FIG. 2 is a perspective schematic view of the ingot slicing apparatus used in the present invention;

FIG. 3 is a longitudinal section schematic view of a fixed abrasive grain wire saw used in the present invention;

FIG. 4 is a process flow chart illustrating a recovery process of a slurry obtained by slicing a silicon ingot with two ingot slicing apparatuses, a solid-liquid separation process, and a recycled coolant supply line of a coolant liquid;

FIG. 5 is a process flow chart illustrating that a solid-liquid separated cake obtained by recovering a slurry is subject to a washing process (S03) <implementation of sulfuric acid washing, implementation of hydrofluoric acid washing, and implementation of pure water washing> and a drying process (S04) to obtain high-purity fine silicon powder;

FIG. 6 is an observation image of high-purity fine silicon powder obtained after going through the washing process (S03) and the drying process (S04) illustrated in FIG. 5 by use of a Scanning Electron Microscope (SEM);

FIG. 7 is an observation image of a cross-section of a fixing plate containing aluminum hydroxide particles used

in the present invention by use of a Scanning Electron Microscope (SEM);

FIG. 8 is a process flow chart illustrating that the solid-liquid separated cake obtained by recovering a slurry is subject to a washing process <sulfuric acid washing has not been conducted, hydrofluoric acid washing has not been conducted, and pure water washing has only been conducted> and a drying process to obtain fine silicon powder;

FIG. 9 is a process flow chart illustrating that the solid-liquid separated cake obtained by recovering a slurry is subject to a washing process <implementation of sulfuric acid washing, hydrofluoric acid washing has not been conducted, and implementation of pure water washing> and a drying process to obtain fine silicon powder;

FIG. 10 is a Scanning Electron Microscope (SEM) observation image of high-purity fine silicon nitride powder obtained after going through the washing process (S03) <implementation of sulfuric acid washing, implementation of hydrofluoric acid washing, and implementation of pure water washing> and the drying process (S04) illustrated in FIG. 5 to be nitrated by a direct nitridation method; and

FIG. 11 is a Scanning Electron Microscope (SEM) observation image of fine silicon nitride powder obtained after going through the washing process <sulfuric acid washing has not been implemented, hydrofluoric acid washing has not been implemented, and only pure water washing has

been implemented> and the drying process illustrated in FIG. 8 to be nitrided by the direct nitridation method.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] Next, embodiments of the present invention will be described with reference to the accompanying drawings.

[0025] An ingot slicing apparatus 1 for a silicon ingot 3 will be described with reference to FIG. 1.

[0026] Silicon wafers are obtained by slicing the silicon ingot 3 with a fixed abrasive grain wire saw 2 pressed against the silicon ingot 3. As shown in FIG. 1, the fixed abrasive grain wire saw 2 includes two guide rollers 7 for a wire saw as a front view. The fixed abrasive grain wire saw 2 is being wound around between such guide rollers 7 at a regular pitch so that these guide rollers 7 may be parallel to each other. As a result, wire rows between the guide rollers 7 appear. The fixed abrasive grain wire saw 2 is derived from a bobbin of an unwinding device not shown. After the fixed abrasive grain wire saw 2 is wound around each guide roller 7 via a guide roller 7 located on a supply side, the fixed abrasive grain wire saw 2 is wound on a bobbin of a winding device not shown via a guide roller 7 located on a derivation side. The fixed abrasive grain wire saw 2 is so controlled to be a regular tension.

[0027] The silicon ingot 3 is attached to a fixing plate 4 by an adhesive of an adhesive layer 6 and is movable in a vertical direction by a lifting and lowering device not

shown. The silicon ingot 3 is moved to and approached to a plurality of wire rows of the fixed abrasive grain wire saw 2 wound around the plurality of wire rows between the guide rollers 7 (arrow a direction). The silicon ingot 3 is pressed against the wire rows to be cut-processed. The silicon ingot 3 is cut in a slice state by cutting while supplying a processing section with a coolant liquid from a coolant liquid supply unit 5.

To make sure to cut the silicon ingot 3, a portion of the fixing plate 4 is cut after cutting the adhesive layer 6 as well as the silicon ingot 3. As a result, silicon cutting waste, cutting waste of the fixing plate 4, cutting waste of the adhesive layer 6, and the coolant liquid drop in a coolant tank 8 to be recovered as a slurry. FIG. 2 is a perspective schematic view of the ingot slicing apparatus 1 showing a state in which the fixed abrasive grain wire saw 2 for cutting the silicon ingot 3 is being wound around a plurality of rows between the guide rollers 7.

[0028] The fixed abrasive grain wire saw 2 will be described with reference to FIG. 3. FIG. 3 is a longitudinal section schematic view of the fixed abrasive grain wire saw 2.

[0029] As shown in FIG. 3, the fixed abrasive grain wire saw 2 is a resin bond wire saw obtained by fixing a plurality of abrasive grains 9 such as diamond to an outer periphery of a metal core wire 11 via a resin bond layer (resin adhesive layer) 10 formed by curing of a phenol

resin. Examples of the resin bond may include curable polymer-based resins, such as an epoxy resin, an acrylic urethane resin, a polyurethane resin, a vinyl chloride resin, and a fluorine resin in addition to a phenol resin. Zirconia abrasive grains, cubic system boron nitride (CBN) abrasive grains, alumina abrasive grains, and silicon nitride abrasive grains may be used for the plurality of abrasive grains 9 as well as the diamond abrasive grains. A filler (not shown) composed of inorganic particles may further be added to the resin bond layer 10. In the fixed abrasive grain wire saw 2, the larger the tension becomes, the more improved cutting performance is. This means that the larger the tensile strength of the metal core wire 11 becomes, the more preferable the metal core wire 11 is. The strength relative to fatigue is preferably high. Consequently, a steel wire is preferably used for the metal core wire 11 as the fixed abrasive grain wire saw 2. Examples of the steel wire include a wire rod obtained by thermally treated spring steel such as high-carbon steel and medium carbon low-alloy steel, a wire rod produced by processed spring steel such as hard steel wire, a piano wire, a stainless wire, a cold-rolled steel wire or an oil tempered wire, low alloy steel, medium alloy steel, high alloy steel, a steel wire rod having high-toughness and high fatigue strength such as maraging steel.

[0030] The fixed abrasive grain wire saw 2 may be obtained by fixing the abrasive grains 9 such as diamond on the

outer periphery of the metal core wire 11 via a molten solidified layer (not shown) formed by melting the brazing filler material. Further, the fixed abrasive grain wire saw 2 may precipitate a nickel layer (not shown) on a wire surface by an electro-deposition method. The abrasive grains 9 may be embedded in the nickel layer to be fixed. Examples of the abrasive grains 9 may include zirconia abrasive grains, cubic system boron nitride (CBN) abrasive grains, alumina abrasive grains, and silicon carbide abrasive grains as well as diamond abrasive grains.

While the fixed abrasive grain wire saw 2 is not limited to the aforementioned wire saw, the fixed abrasive grain wire saw 2 is most preferably a resin bond wire saw disclosed in JP 2014-133288 A filed by the applicant of this application.

[0031] In the slicing of the silicon ingot 3 by the fixed abrasive grain wire saw 2, it is preferable to minimize a kerf loss (notch) by minimizing a wire diameter. When the tensile strength is small, a cutting speed is unable to raise. As a result, the wire preferably has a diameter of 0.05 mm to 0.3 mm. The fixed abrasive grain wire saw 2 preferably has a tension of 14 N to 40 N. The fixed abrasive grain wire saw 2 preferably has a running speed of 700 m/minute to 1,200 m/minute. A processing mechanism by use of the fixed abrasive grain wire saw 2 is a cutting mechanism for scraping off the silicon ingot 3 with the abrasive grains 9. As a result, to make fine silicon

particles in the silicon cutting waste submicron to micron order fine particles, the abrasive grains 9 such as diamond each preferably have an average particle size of 1 μm to 25 μm . The abrasive grain density relative to the wire is preferably 1,500 pieces/ mm^2 to 3,000 pieces/ mm^2 . In the case of a resin bond wire saw, the abrasive grain density is higher and the tension at the time of cutting is lower than the fixed abrasive grain wire saw fitted with the abrasive grains 9 by a nickel layer. As a result, the resin bond wire saw softly touches the cutting surface of the silicon ingot, resulting in fine cutting powder and thin scale-shaped fine particles, which is preferable.

[0032] The ingot feeding rate is preferably 0.1 mm/minute to 1.0 mm/minute. The fixed abrasive grain wire saw 2 has small rigidity. As a result, a deflection is produced by cutting resistance generated when cutting the silicon ingot 3. To make sure the cutting of the silicon ingot 3, a portion of the fixing plate 4 for the silicon ingot 3 is cut in view of the deflection of the wire saw. When cutting the portion of the fixing plate 4 fixing the silicon ingot 3, the ingot feeding rate is preferably set at 0.05 mm/minute to 0.5 mm/minute.

[0033] Examples of the material of the silicon ingot 3 may include single-crystal silicon, multi-crystal silicon, and amorphous silicon. The fixing plate 4 where the silicon ingot 3 is attached is preferably obtained by solidifying aluminum hydroxide ($\text{Al}(\text{OH})_3$) powder having excellent heat

absorption with a binder resin so as to prevent an increase in temperature of the silicon ingot 3 and the fixing plate 4 with cutting. When a portion of the fixing plate 4 has been cut, aluminum hydroxide serves a role in preventing the resin inside the fixing plate from being soften or burnt due to its cutting heat. That is, when the fixing plate 4 is heated by cutting heat from 200°C to 350°C, aluminum hydroxide is dehydrated and decomposed. At this time, water is generated by a large endothermic reaction (2.0 KJ/g). This endothermic reaction and vaporization heat of water prevent the resin inside the fixing plate from being soften and burnt. Magnesium hydroxide may be used instead of aluminum hydroxide.

[0034] A water-soluble organic-based (water-soluble cutting fluid) coolant liquid is preferably used as a coolant liquid to be used in the present invention. The coolant liquid whose main component is water obtained by mixing, for example, polyethylene glycol, diethylene glycol, propylene glycol, and polypropylene glycol is used.

[0035] A slurry recovery process (S01) and a solid-liquid separation process (S02) will be described with reference to FIG. 4. FIG. 4 is a flow chart of a slurry recovery process and a solid-liquid separation process in which two ingot slicing apparatuses 1 are disposed.

[0036] In the slurry recovery process (S01), a slurry including silicon cutting waste, cutting waste of the fixing plate 4, cutting waste of the adhesive layer 6, and

a coolant liquid can be stored and extracted. The slurry includes cutting particles produced by slicing aluminum hydroxide ($\text{Al}(\text{OH})_3$) which is a component of the fixing plate 4, a binder resin, and other metal components (Al, Fe, Ca, K, Ni or the like). The other metal components are derived from a channel in contact with the coolant liquid. In addition, the slurry includes components of the adhesive layer 6 to fix the silicon ingot 3 to the fixing plate 4. The slurry in the coolant tank 8 is transferred to a slurry receiving tank 12 along with the coolant liquid by use of a transfer pump (not shown). The slurry is further transferred from the slurry receiving tank 12 to the next solid-liquid separation process (S02). Homogenization of the slurry state by stirring with an agitator 15 prevents silicon cutting powder from aggregating.

[0037] In the solid-liquid separation process (S02), most of the coolant liquid is removed from the slurry by a solid-liquid separator (a) 16, such as a centrifugal separator or a filter pressing machine. As a result, a cake 18 including silicon cutting waste, impurities (the cutting waste of the fixing plate 4, the cutting waste of the adhesive layer 6, and the other metal components), and a very small amount of the coolant liquid is obtained to be placed on a cake receiving container 13. The removed coolant liquid is transferred to a coolant supply tank 14. A new coolant liquid is added to homogenize the mixture state by stirring with the agitator 15 to be recycled. The

recycled coolant is supplied to a plurality of ingot slicing apparatuses 1 through a recycled coolant supply line 17 to be used.

[0038] A plurality of ingot slicing apparatuses 1 and a plurality of coolant tanks 8 may be disposed and recovered by combining slurries. After the coolant liquid is also combined to be recovered and recycled, the coolant liquid can be supplied to the plurality of ingot slicing apparatuses 1. The recovery efficiency of the slurries is improved by incorporating into one production line by disposing the plurality of ingot slicing apparatuses 1.

[0039] Next, a washing process (S03) and a drying process (S04) will be described with reference to FIG. 5. The washing process (S03) is a process for washing a cake including silicon cutting powder to remove impurities and further remove a naturally oxidized coating layer of silicon (SiO_2). The drying process (S04) is a process for drying a solid content 32 extracted by washing and solid-liquid separation with a dryer to obtain high-purity fine silicon powder.

[0040] In sulfuric acid washing of a sulfuric acid washing tank 24, an aluminum component and the other metal components that react the sulfuric acid are removed by a sulfuric acid aqueous solution which is a first washing liquid. More specifically, in the sulfuric acid washing tank 24, the cake 18 containing the silicon cutting waste and impurities and 1 weight % to 40 weight % of a sulfuric

acid aqueous solution are mixed at a weight ratio of 1:10. Washing is performed by immersion and stirring for 20 minutes to 60 minutes for washing time while maintaining the temperature at 50°C to 90°C by use of a constant-temperature unit 23. The temperature in the constant-temperature unit 23 is preferably maintained at 50°C to 80°C. This reduces the aluminum component from about 10,000 ppm to about 40 ppm. The other metal components are also reduced from some tens of ppm to some ppm to a dozen ppm. The metal components that remain even after sulfuric acid washing are metal components that have strongly adsorbed on the naturally oxidized coating layer (SiO_2) formed on a surface of the silicon cutting waste. An aluminum oxide or an iron oxide and a hydroxide substance are chemically stable as compared with SiO_2 and are dehydrated and condensed with a Si-OH group. It is anticipated that such an oxide and a hydroxide substance are incorporated into the naturally oxidized coating layer like Si-O-Al by dehydrating and condensing with Si-OH group to strongly adsorb to the naturally oxidized coating layer on the surface of the silicon cutting powder.

[0041] In hydrofluoric acid washing of a hydrofluoric acid washing tank 25, the metal that has strongly adsorbed to the naturally oxidized coating layer is removed as well as the naturally oxidized coating layer (SiO_2) by use of a hydrofluoric acid aqueous solution which is a second washing liquid. Constantly stirring with the agitator 15

while adjusting an input of a cake 29 prevents mousse-like bubbles from expanding due to generation of a hydrogen fluoride (HF) gas. After washing by the sulfuric acid aqueous solution, the cake 29 extracted by a solid-liquid separator (b) 19, such as a centrifugal separator or a filter pressing machine, and a hydrofluoric acid aqueous solution are mixed at a weight ratio of 1:10 to wash by immersing and stirring at an ordinary temperature and washing time for 5 minutes to 30 minutes. The washing time by use of the hydrofluoric acid aqueous solution is preferably 5 minutes to 20 minutes.

[0042] Pure water washing in a first pure water washing tank 26 is performed by immersing and stirring a cake 30 that has been extracted by a solid-liquid separator (c) 20, such as a centrifugal separator or a filter pressing machine after the hydrofluoric acid washing. A very small amount of hydrofluoric acid aqueous solution adheres to the cake 30. As silicon that has appeared on a surface is dissolved in reaction to moisture in the hydrofluoric acid aqueous solution, pure water washing is preferably performed within five minutes after the hydrofluoric acid washing. Pure water washing is preferably performed within one minute after the hydrofluoric acid washing.

[0043] Pure water washing in a second pure water washing tank 27 is performed by immersing and stirring a cake 31 that has been extracted by a solid-liquid separator (d) 21, such as a centrifugal separator or a filter pressing

machine after the first pure water washing. After the second pure water washing, a solid content 32 is solid-liquid separated by a solid-liquid separator (e) 22 to be extracted. While pure water washing may be performed once, pure water washing is preferably performed twice to raise the degree of washing.

[0044] In a drying process (S04), the solid content 32 that has been extracted after the pure water washing is dried by use of an airborne dryer 28 as a dryer to obtain fine silicon powder. The fine silicon powder can be taken in a powder state free from lumps of the silicon powder by drying with the airborne dryer 28. The aforementioned washing and drying processes make it possible to recover high-purity scale-shaped fine silicon powder having very little impurities. While the dryer is preferably an airborne dryer, the dryer is not limited to a particular dryer.

[0045] An example of the direct nitridation method which is one example of a nitridation process will be described.

[0046] The scale-shaped fine silicon powder obtained by the drying process is used as a raw material and is put into an atmosphere furnace without being pressed to a carbon (graphite)-made, silicon nitride-made, aluminum-made or a boron nitride-made boat or a crucible. After vacuuming inside the atmosphere furnace, nitrogen gas, hydrogen gas or ammonia gas or a mixture of these is introduced into the furnace as nitride gas to increase the temperature. Noble

gas such as argon may be introduced with nitride gas. At least any one kind of gas selected from a gas group consisting of argon, helium, neon, xenon, and krypton is used as noble gas.

With reference to a temperature profile of nitriding treatment, the temperature is increased to a predetermined temperature (maximum temperature) selected in a range of 1,200°C to 1,400°C at a rate of temperature rise of 300°C/hour. The predetermined temperature (maximum temperature) is maintained for 10 hours to 100 hours. After the maintenance, the predetermined temperature drops to an ordinary temperature at a rate of temperature drop of 300°C/hour.

High-purity fine silicon nitride powder with less impurities and an average particle size of submicron to micron order can be obtained by loosening the fine silicon nitride powder obtained by this nitriding treatment.

EXAMPLE 1

[0047] The present invention will be described in more detail in accordance with Examples and Comparative Examples.

[0048] <Examples 1,2 and Comparative Examples 1, 2>

In accordance with a process flow chart in FIG. 4, a cake 18 containing silicon cutting waste and impurities was extracted from a slurry generated at the time of slicing a plurality of silicon ingots 3. In a plurality of ingot slicing apparatuses 1, the plurality of silicon ingots 3

attached to a plurality of fixing plates 4 including aluminum hydroxide were sliced by a plurality of fixed abrasive grain wire saws 2 each having an average particle size of 10 μm of each diamond abrasive grain 9 and an abrasive grain density of 2,300 pieces/ mm^2 under conditions of an ingot feeding rate of 0.5 mm/minute to recover the slurry from a plurality of coolant tanks 8. Resin bond wire saws were used for the plurality of fixed abrasive grain wire saws 2. The recovered slurry was solid-liquid separated by a centrifugal separator to extract the cake 18.

Treatment was performed in accordance with a process flow chart in FIG. 5. As a result, high-purity fine silicon powder was obtained from the cake 18 containing silicon cutting waste and impurities. In sulfuric acid washing in a washing process (S03), the cake 18 containing silicon cutting waste and impurities was mixed with 25 weight % of a sulfuric acid aqueous solution at a weight ratio of 1:10. Washing was performed by immersing and stirring at the temperature of 75°C with a 60-minute washing time. After the sulfuric acid washing, solid-liquid separation was performed to extract a cake 29.

In hydrofluoric acid washing, the cake 29 which is obtained by solid-liquid separation with a centrifugal separator after the sulfuric acid washing was mixed with 1.0 weight % of a hydrofluoric acid aqueous solution at a weight ratio of 1:10. Washing was performed by immersing and stirring at an ordinary temperature with a 20-minute

washing time.

After the hydrofluoric acid washing, pure water washing was performed twice to extract a solid content 32 by solid-liquid separation with a centrifugal separator.

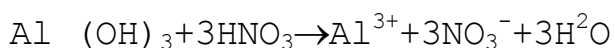
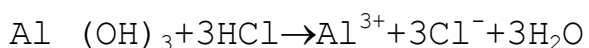
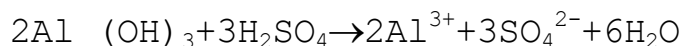
Further, the solid content 32 was dried by an airborne dryer 28 in the drying process (S04) to obtain fine silicon powder.

As shown in a Scanning Electron Microscope observation image in FIG. 6, it was confirmed that high-purity fine silicon powder obtained by the aforementioned steps had a curved scale shape having a size of about $1\text{ }\mu\text{m} \times (1\text{ to }5)\text{ }\mu\text{m} \times (0.07\text{ to }0.09)\text{ }\mu\text{m}$. It is anticipated that the fine silicon powder has a scale shape because of a processing mechanism for scraping off the silicon ingots by use of fixed abrasive grains. Conventionally, to obtain this size of fine silicon powder, micronization by a mechanical crusher, such as a ball mill or a jet mill. According to the present invention, however, high-purity scale-shaped fine silicon powder having a size of submicron to micron order can be produced in large numbers from cutting waste of the fixed abrasive grain wire saws 2 without mechanical crushing.

[0049] FIG. 7 shows a Scanning Electron Microscope observation image of a cut surface of the fixing plate 4. It is understood from FIG. 7 that coarse aluminum hydroxide particles are surrounded by a resin to be bonded. Such coarse aluminum hydroxide particles are cut by diamond

abrasive grains of the fixed abrasive grain wire saws 2 to be mixed with the silicon cutting waste in the slurry. The ingot feeding rate is set at 0.05 mm/minute to 0.5 mm/minute, which is slower than the ingot feeding rate at the time of cutting only the silicon ingots 3 as cutting conditions of the fixing plate 4 composed of aluminum hydroxide. This confirmed that the aluminum hydroxide cutting particles became fine particles of some tens of nm, which are difficult to identify its presence even by use of a high resolution Scanning Electron Microscope.

[0050] In general, aluminum hydroxide, sulfuric acid, hydrochloric acid, and nitric acid are reacted with reaction formulas each represented by the following formula to be dissolved in each solution:



As a result of inventors' acid solution experiment of aluminum hydroxide particles, in the case of any one of the aforementioned acids, however, aluminum hydroxide was not completely dissolved at an ordinary temperature and became turbid, resulting in a state in which the aluminum hydroxide particles precipitated on the bottom of the solution. On the other hand, when turbid liquids were heated at 50°C to 90°C and the heating temperature was maintained for 20 minutes to 60 minutes, only in the case of sulfuric acid, it was confirmed that the aluminum

hydroxide particles precipitated on the bottom of the solution disappeared and became turbid in a colloid state in the solution or completely became transparent to be dissolved in the solution. As mentioned above, not only when the aluminum hydroxide particles were completely dissolved but also when the aluminum hydroxide particles remained turbid in a colloid state in the solution, it was confirmed that the solid-liquid separator separated the aluminum hydroxide particles as a liquid content by heating the aluminum hydroxide particles with sulfuric acid under predetermined conditions. In other words, the aluminum hydroxide particles are separated as a liquid content by being filtered through a filter cloth of a filter pressing machine and in the case of a centrifugal separator, the aluminum hydroxide particles flow on a liquid side to be separated.

[0051] Table 1 shows analytical results of quantitative determination of metals contained in fine silicon powder obtained by the aforementioned steps by use of an ICP Emission Analyzing device. A high-frequency plasma optical emission spectrometer ICPS-8000 produced by Shimadzu Corporation was used for the ICP Emission Analyzing device.

[0052] [Table 1]

Classification	Washing process	Specific surface area BET (m ² /g)	Average particle size (μm)	Amount of impurities (ppm)		
				Fe	Al	Ca
Example 1	25% weight of sulfuric acid 1% weight of hydrofluoric acid	29.2	0.09	1	4	2
Example 2	25% weight of sulfuric acid 1% weight of hydrofluoric acid	29.2	0.09	2	3	3
Comparative Example 1	Pure water washing only	32.3	0.08	28	17,000	23
Comparative Example 2	25% weight of sulfuric acid only	22.4	0.12	7	143	4

[0053] In Examples 1 and 2, high-purity scale-shaped fine silicon powder obtained by going through the washing process (S03)<Implementation of sulfuric acid washing, implementation of hydrofluoric acid washing, and implementation of pure water washing> and the drying process (S04) shown in FIG. 5 was used as a sample in analysis.

In Comparative Example 1, fine silicon powder obtained by going through a washing process (S03)<Sulfuric acid washing was not implemented yet, Hydrofluoric acid washing

was not implemented yet, and only pure water washing was implemented> and a drying process (S04) shown in FIG. 8 was used as a sample in analysis. In pure water washing, a cake 18 containing silicon cutting waste and impurities was washed by immersing and stirring with pure water.

In Comparative Example 2, fine silicon powder obtained by going through a washing process (S03)<Sulfuric acid washing was implemented, Hydrofluoric acid washing was not implemented yet, and Pure water washing was implemented> and a drying process (S04) shown in FIG. 9 was used as a sample in analysis. In sulfuric acid washing, the cake 18 containing silicon cutting waste and impurities was mixed with 25 weight % of a sulfuric acid aqueous solution at a weight ratio of 1:10 to perform washing by immersing and stirring with a washing time for 60 minutes while maintaining the temperature at 75°C with a constant-temperature unit 23.

It was confirmed from Table 1 that metal components of impurities remained as low as some ppm and the sample used in analysis was high-purity fine silicon powder having a small amount of impurities in Examples 1 and 2. In Comparative Example 1, metal components, such as Fe and Ca remain as well as Al which is a material component of the fixing plate 4. In Comparative Example 2, while the contained components such as Fe and Ca are low, Al which is a component of the fixing plate 4 remains at a level of tens of ppm.

[0054] <Examples 3 and 4, Comparative Examples 3 and 4>

Scale-shaped fine silicon powder obtained in Examples 1 and 2 was taken by 3 g in mass to be lightly loosened. The scale-shaped fine silicon powder was placed on a boat without pressing and was put in an atmosphere furnace as a raw material for nitridation treatment to be nitrided by the direct nitridation method. As a result, fine silicon nitride powder was obtained. An external heating-type atmosphere furnace with use of a high-purity aluminum furnace core tube was used as an atmosphere furnace. After vacuuming inside the furnace, the temperature was risen up to 1,350°C at a rate of temperature rise of 300°C/hour while circulating nitrogen gas at a rate of 300 ml/minute and then was maintained at 1,350°C for 80 hours. After that, the temperature was cooled down to the room temperature at a rate of 300°C/hour.

Table 2 shows analytical results obtained by an X-ray diffraction apparatus of the fine silicon nitride powder obtained by the aforementioned steps. Ultima IV produced by Rigaku Corporation was used as a powder X-ray diffraction apparatus. BELSORP-mini produced by Japan Bell Co., Ltd. was used for specific surface area measurement.

Classification	Washing process	Shape of Si fine particles after washing process	α - Si_3N_4 content (weight %)	β - Si_3N_4 content (weight %)	Unreacted Si (weight %)	Specific surface area (m^2/g)	Average particle size (μm)	Remarks
Example 3	25% weight of sulfuric acid 1% weight of hydrofluoric acid	Scale shape	31.9	68.1	0.01	10.1	0.17	No acicular crystals
Example 4	25% weight of sulfuric acid 1% weight of hydrofluoric acid	Scale shape	21.4	77.3	1.24	10.1	0.17	No acicular crystals
Comparative Example 3	Pure water washing only	Scale shape	61.6	35.5	2.89	5.74	0.30	Acicular crystals exist
Comparative Example 4	25% weight of sulfuric acid only	Scale shape	42.2	57.2	0.60	7.28	0.24	

[0056] In Example 3, the high-purity fine silicon nitride powder obtained by nitriding the scale-shaped fine silicon powder obtained in Examples 1 and 2 under the aforementioned conditions was used as a sample in analysis. In Example 4, the high-purity fine silicon nitride powder obtained by nitriding the scale-shaped fine silicon powder obtained in Examples 1 and 2 under the conditions, in which only the retention time at 1,350°C was changed to 18 hours out of the aforementioned conditions, was used as a sample in analysis. That is, this sample is the fine silicon nitride powder obtained by going through the washing process (S03) <Implementation of sulfuric acid washing, Implementation of hydrofluoric acid washing, and Implementation of pure water washing> in FIG. 5.

In Comparative Example 3, the fine silicon nitride powder obtained by nitriding the fine silicon powder obtained in Comparative Example 1 by use of the direct nitridation method was used as a sample in analysis. That is, this sample is the fine silicon nitride powder obtained by going through the washing process <Sulfuric acid washing was not implemented yet, Hydrofluoric acid washing was not implemented yet, and only pure water washing was implemented> in FIG. 8.

In Comparative Example 4, the fine silicon nitride powder obtained by nitriding the fine silicon powder obtained in Comparative Example 2 by use of the direct nitridation method was used as a sample in analysis. That

is, this sample is the fine silicon nitride powder obtained by going through the washing process <Implementation of sulfuric acid washing, Hydrofluoric acid washing was not implemented yet, and Implementation of pure water washing> in FIG. 9.

It is understood from Example 3 in Table 2 that unreacted silicon is minute and its nitridation reaction has sufficiently progressed. As shown in the Scanning Electron Microscope observation image in FIG. 10, it was possible to confirm that the fine silicon nitride powder obtained in Example 3 was not scale shaped but formless particles having a size of submicron. As described in Table 2, the specific surface area of the fine silicon nitride powder was $3 \text{ m}^2/\text{g}$ and the average particle size of the fine silicon nitride powder was $0.58 \text{ }\mu\text{m}$ when its average particle size was converted from the specific surface area.

[0057] Since fine silicon particles after the hydrofluoric acid washing are in a scale shape, this fact is anticipated that the scale-shaped fine silicon particles are separated into formless fine silicon nitride particles by nitridation treatment. That is, there are a number of notches formed on an outer circumference portion of the scale-shaped fine silicon particles. As a result, cracks are formed by heat stress generated at the time of nitridation with these notches as a starting point. It is anticipated that this leads to the separation of the scale-shaped fine silicon

particles into the formless fine silicon nitride particles. This indicates that submicron to micron order of high-purity fine silicon nitride powder can be produced in volume at a low price by nitriding silicon cutting waste produced by cutting with the fixed abrasive grain wire saw 2 after the predetermined washing treatment.

[0058] It is possible to confirm from Comparative Example 3 that there is a number of unreacted silicon. In addition, it is possible to confirm the presence of acicular crystals from the Scanning Electron Microscope observation image in FIG. 11. The raw material of such acicular crystals is silicon cutting waste which has been subjected to only pure water washing. Impurities such as metals remain in the silicon cutting waste. It is anticipated that the acicular crystals have developed by the effects of such residual metals. It is possible to confirm that the ratio of the unreacted silicon is high, which is unsuitable for the raw material for a mold releasing agent and a sintered body.

INDUSTRIAL APPLICABILITY

[0059] According to the present invention, high-purity scale-shaped fine silicon powder can be obtained by micronizing silicon cutting waste produced without any mechanical crusher when the silicon ingot 3 is sliced. Production of high-purity fine silicon nitride powder for a mold releasing agent and a sintered body and high-purity silicon nitride ceramics at a low cost can be achieved by

using scale-shaped fine silicon powder derived from such silicon cutting waste as a starting material.

DESCRIPTION OF REFERENCE NUMERALS

[0060] 2: fixed abrasive grain wire saw; 3: silicon ingot; 4: fixing plate; 9: abrasive grains; 18; 29; 30; 31; 32: cake; 16, 19, 20, 21, 22: solid-liquid separator; 28: airborne dryer.

CLAIMS

1. A method for producing fine silicon powder,
comprising
the steps of:

preparing a silicon ingot and a fixed abrasive grain
wire saw, wherein abrasive grains are fixed to an outer
periphery of a wire;

fixing the silicon ingot to a fixing plate for
attaching the silicon ingot;

slicing the silicon ingot with the fixed abrasive
grain wire saw;

recovering a slurry including silicon cutting waste
produced in the slicing step;

separating solid and liquid to isolate a cake
including the silicon cutting waste from the slurry with a
solid-liquid separator and extract the cake;

washing the cake obtained in the solid-liquid
separation step with a washing liquid; and

drying a solid content obtained by separating the
solid and the liquid with a dryer after the washing step.

2. The method for producing fine silicon powder
according
to claim 1, wherein the fixing plate contains one of
aluminum hydroxide particles and magnesium hydroxide
particles.

3. The method for producing fine silicon powder according to any one of claims 1 to 2, wherein the abrasive grains that exist on the outer periphery of the fixed abrasive grain wire saw each have an average particle size of 1 μm to 25 μm and an abrasive grain density of 1,500 pieces/ mm^2 to 3,000 pieces/ mm^2 .

4. The method for producing fine silicon powder according to any one of claims 1 to 3, wherein the fixed abrasive grain wire saw is a resin bond wire saw.

5. The method for producing fine silicon powder according to any one of claims 1 to 4, wherein the silicon ingot has an ingot feeding rate of 0.1 mm/minute to 1.0 mm/minute when cutting the silicon ingot and has an ingot feeding rate of 0.05 mm/minute to 0.5 mm/minute when cutting the fixing plate.

6. The method for producing fine silicon powder according to any one of claims 1 to 5, wherein the washing step further includes the step of washing the cake obtained in the solid-liquid separation step with a first washing liquid and then washing the cake with a second washing liquid.

7. The method for producing fine silicon powder according to claim 6, wherein the first washing liquid is a sulfuric acid aqueous solution containing 1 weight % to 40 weight % of sulfuric acid; and the cake obtained by the solid-liquid separation step is washed while immersing and stirring the cake for 20 minutes to 60 minutes with the sulfuric acid aqueous solution that has been heated to 50°C to 90°C.

8. The method for producing fine silicon powder according to claim 6 or claim 7, wherein the second washing liquid is a hydrofluoric acid aqueous solution containing 0.5 weight % to 10 weight % of hydrofluoric acid; and the cake that has been extracted after washing with the first washing liquid and has been solid-liquid separated is washed by being immersed into the hydrofluoric acid aqueous solution for 5 minutes to 30 minutes.

9. A method for producing fine silicon powder, comprising the step of:

obtaining scale-shaped fine silicon powder by the method for producing fine silicon powder according to any one of claims 1 to 8.

10. A method for producing fine silicon powder, comprising the step of:

obtaining scale-shaped fine silicon powder having a specific surface area of $10 \text{ m}^2/\text{g}$ to $50 \text{ m}^2/\text{g}$ by the method for producing fine silicon powder according to claim 9.

11. A method for producing fine silicon nitride powder, comprising the steps of:

obtaining scale-shaped fine silicon powder by the method for producing fine silicon powder according to claim 9 or claim 10;

placing the scale-shaped fine silicon powder having a bulk density of 0.3 g/cm^3 to 0.7 g/cm^3 without pressing against a container in a nitride furnace; and

nitriding the fine silicon powder by a direct nitridation method.

12. A method for producing fine silicon nitride powder, comprising the step of:

obtaining fine silicon nitride powder having a specific surface area of $1 \text{ m}^2/\text{g}$ to $10 \text{ m}^2/\text{g}$ by the method for producing fine silicon nitride powder according to claim 11.