

PREPARATION METHOD OF HIGH-PURITY, LOW-URANIUM, SUBMICRON-SIZED SPHERICAL SILICA MICROPOWDER

CROSS REFERENCE TO RELATED APPLICATION

[0001] This patent application claims the benefit and priority of Chinese Patent Application No. CN202111460463.2 filed with the China National Intellectual Property Administration on December 2, 2021 and entitled “PREPARATION METHOD OF HIGH-PURITY, LOW-URANIUM, SUBMICRON-SIZED SPHERICAL SILICA MICROPOWDER”, the disclosure of which is incorporated by reference herein in its entirety as part of the present application.

TECHNICAL FIELD

[0002] The present disclosure belongs to the technical field of thermal conductive fillers, and relates to a preparation method of a high-purity, low-uranium, submicron-sized spherical silica micropowder.

BACKGROUND

[0003] With the continuous development of the small and thin electronic equipment, fillers for semiconductor packaging have smaller and smaller particle sizes. Meanwhile, in order to increase the filling amount and fluidity of fillers in semiconductor packaging, it is necessary to add submicron-sized fillers with high sphericity (generally considered to be 0.1-1 μm). However, with the continuous improvement of the integrity of very large-scale integrated circuits, the conductor space becomes smaller and smaller, so that soft errors of signal transmission are generated in packaging materials when the α -ray is strong, thereby reducing the reliability of integrated circuits. Therefore, packaging materials used in very large-scale integrated circuits and memory chips present higher demands for the α -ray. Uranium (U) in the natural mine is the leading factor influencing the α -ray. Therefore, it is necessary to control the uranium content and further the strength of the α -ray.

[0004] Chinese Patent Application No. CN 101570332 A uses an organic silica source to prepare a silica sol and obtains a spherical silicon micropowder having a U content of <1 ppm through a series of processes including granulation. Chinese Patent Application No. CN 104556076 A obtains a spherical silicon micropowder free of α -ray through a series of processes including purification of organic silane and emulsification. However, the above method is mainly achieved by chemical synthesis, by which a high-purity, low-uranium spherical silica micropowder is prepared with a high-purity organic silica source and a solvent, and there are

problems of high energy consumption, severe pollution, and high cost.

[0005] Chinese Patent Application No. CN 112591756 A prepares a product having a U content of no greater than 1 ppb by combusting the natural quartz having a low U content of around 1 ppb. However, the method is only suitable to produce a micron-sized spherical silica micropowder, but cannot further obtain a submicron-sized product, which is obtained by treating through complicated processes including continuous grading.

[0006] Chinese Patent Application No. CN 101274365 A prepares a product having a U content of 0.4-5.0 ppb by controlling the content of phosphorus (P) and U in silicon (Si) raw material, but the method is strict with the Si raw material and raw materials are not readily available.

[0007] In conclusion, the existing preparation methods of low-uranium spherical silica micropowders have the following problems: high-purity and low-uranium products can be chemically synthesized by selecting high-purity organic silica sources and solvents, but the method may cause environmental protection problems; micron-sized products are merely obtained by selecting low-uranium (around 1 ppm) natural quartz alone and present higher demands for raw materials, so it is difficult to prepare products having a U content of no greater than 0.5 ppb; the U content is not stable in the products prepared by simple acid treatment of strictly screened Si raw materials.

SUMMARY

[0008] An objective of the present disclosure is to provide a preparation method of a high-purity, low-uranium, submicron-sized spherical silica micropowder.

[0009] The technical solution to achieve the objective of the present disclosure is as follows:

[0010] A preparation method of a high-purity, low-uranium, submicron-sized spherical silica micropowder is provided, including the following steps:

[0011] step 1, under an inert atmosphere, calcining a raw material in a 700-1,400°C high-temperature furnace for 10-20 h; after calcining, quenching the raw material in water, crushing the raw material into sand aggregates of no more than 1 mm, settling and drying the sand aggregates; repeating a calcining-crushing-settling-drying step to obtain the sand aggregates, where the raw material is an elemental silicon or a silicon-containing inorganic compound block having a purity of at least 99.5%, a uranium content of 5-20 ppb, and a grain size of 30-100 mm;

[0012] step 2, mixing the sand aggregates with water in a mass ratio of (1-3):(2-5), adding a hydrofluoric acid (HF) solution equivalent to 0.1‰-0.5‰ of a mass of the water, and conducting wet ball milling to obtain a slurry having an average powder particle size of 5-40 μm;

[0013] step 3, mixing the HF solution with a hydrochloric acid (HCl) solution in a concentration ratio of (1-300):1, adding an equivalent mass of each of the HF solution and the

HCl solution to the slurry, simultaneously adding hydrogen peroxide equivalent to 0.1%-0.5% of a total mass of the HF solution and the HCl solution (a mass of a mixed acid solution), recovering uranium by adding a flotation agent and a collector, and stirring at 30-60°C to obtain a slurry;

[0014] step 4, filter-pressing, washing, and drying the slurry obtained in step 3 to obtain a powder having a uranium content of no greater than 1.0 ppb; and

[0015] step 5, by means of flame spheroidization, introducing a carrier gas, a combustible gas, and a combustion improver, igniting, spheroidizing the powder obtained in step 4 at a high temperature of 1,800-2,400°C, and collecting a submicron-sized spherical silica micropowder.

[0016] Preferably, in step 1, the silicon-containing inorganic compound may be one or a mixture of at least two selected from the group consisting of silicon nitride, silicon carbide, and silica.

[0017] Preferably, in step 2, the wet ball milling may be conducted for 5 -30 h.

[0018] Preferably, in step 2, the HF solution may have a mass concentration of 1.5%.

[0019] Preferably, in step 3, the HF solution and the HCl solution may have a concentration ratio of (1-3):1.

[0020] Preferably, in step 3, the HCl solution may have a mass concentration of 0.005%-1.5%.

[0021] Preferably, in step 3, the stirring may be conducted for 12-72 h.

[0022] Preferably, in step 5, the carrier gas may be one selected from the group consisting of oxygen, air, nitrogen, and argon; the combustible gas may be one selected from the group consisting of liquefied natural gas (LNG), liquefied petroleum gas (LPG), and hydrogen (H₂); the combustion improver is one selected from the group consisting of the air and the oxygen.

[0023] Preferably, in step 5, the submicron-sized spherical silica micropowder may have an average particle size (D50) of 0.1-1.5 μm, a uranium (U) content of <1.0 ppb, and a silica (SiO₂) purity of ≥99.90%.

[0024] Compared with the prior art, the present disclosure has the following advantages:

[0025] In the present disclosure, the submicron-sized spherical silica micropowder having low and stable U content is prepared by water quenching, wet purification, and special mixed acid treatment of oxidized elemental U. The method provided by the present disclosure has low requirements for raw materials and is suitable for various industrial grade silicon sources.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0026] The present disclosure will be further described below with reference to specific examples.

[0027] Example 1

[0028] (1) Under an argon atmosphere, 10 kg of elemental silicon (purity: 99.6%; U content: 15 ppb) with a grain size of 80 μm was calcined in a 1,250°C high-temperature furnace for 15 h. After calcining, the elemental silicon was quenched in water and crushed into sand aggregates of no more than 1 mm, and the sand aggregates were settled and dried. The calcining-crushing-settling-drying step was repeated once. Dried sand aggregates were collected several times for later use.

[0029] (2) 250 kg of dried sand aggregates were weighed and added to 230 kg of water, 0.05 kg of 1.5% (w/w) HF solution was added, and wet ball milling was conducted to obtain a slurry having an average powder particle size of 35 μm .

[0030] (3) The slurry was transferred into a reaction still, 15 kg of 1.5% (w/w) HF solution and 15 kg of 0.5% (w/w) HCl solution were added, hydrogen peroxide equivalent to 0.1% of the mass of the mixed acid solution was simultaneously added, uranium was recovered by adding a flotation agent and a collector, and a slurry was obtained by stirring at 60°C for 24 h.

[0031] (4) The slurry was filter-pressed, washed, and dried to obtain a powder having a U content of no greater than 1.0 ppb.

[0032] (5) The powder was spheroidized at a high temperature of 2,000°C under oxygen-enriched conditions to obtain a high-purity, low-uranium, submicron-sized spherical silica micropowder having a particle size of 0.3 μm , a U content of 0.2 ppb, and a SiO₂ purity of 99.95%.

[0033] Example 2

[0034] (1) Under an argon atmosphere, 10 kg of silicon nitride (purity: 99.8%) and elemental silicon (purity: 99.6%) each with a grain size of 35 μm were calcined in a 900°C high-temperature furnace for 5 h. After calcining, the silicon nitride and the elemental silicon were quenched in water and crushed into sand aggregates of no more than 1 mm, and the sand aggregates were settled and dried. The calcining-crushing-settling-drying step was repeated once. Dried sand aggregates were collected several times for later use.

[0035] (2) 250 kg of dried sand aggregates were added to 230 kg of water, 0.05 kg of 1.5% (w/w) HF solution was added, and wet ball milling was conducted to obtain a slurry having an average powder particle size of 30 μm .

[0036] (3) The slurry was transferred into a reaction still, 15 kg of 1.5% (w/w) HF solution and 15 kg of 0.5% (w/w) HCl solution were added, hydrogen peroxide equivalent to 0.3% of the mass of the mixed acid solution was simultaneously added, uranium was recovered by adding a flotation agent and a collector, and a slurry was obtained by stirring at 60°C for 24 h.

[0037] (4) The slurry was filter-pressed, washed, and dried to obtain a powder having a U content of no greater than 1.0 ppb.

[0038] (5) The powder was spheroidized at a high temperature of 2,000°C under oxygen-enriched conditions to obtain a high-purity, low-uranium, submicron-sized spherical silica micropowder having a particle size of 0.3 μm , a U content of 0.3 ppb, and a SiO_2 purity of 99.91%.

[0039] Example 3

[0040] (1) Under an argon atmosphere, 10 kg of silicon nitride (purity: 99.6%) with a grain size of 70 μm was calcined in a 850°C high-temperature furnace for 15 h. After calcining, the silicon nitride was quenched in water and crushed into sand aggregates of no more than 1 mm, and the sand aggregates were settled and dried. The calcining-crushing-settling-drying step was repeated once. Dried sand aggregates were collected several times for later use.

[0041] (2) 250 kg of dried sand aggregates were added to 230 kg of water, 0.05 kg of 1.5% (w/w) HF solution was added, and wet ball milling was conducted to obtain a slurry having an average powder particle size of 35 μm .

[0042] (3) The slurry was transferred into a reaction still, 15 kg of 1.5% (w/w) HF solution and 15 kg of 1.5% (w/w) HCl solution were added, hydrogen peroxide equivalent to 0.1% of the mass of the mixed acid solution was simultaneously added, uranium was recovered by adding a flotation agent and a collector, and a slurry was obtained by stirring at 35°C for 12 h.

[0043] (4) The slurry was filter-pressed, washed, and dried to obtain a powder having a U content of no greater than 1.0 ppb.

[0044] (5) The powder was spheroidized at a high temperature of 2,000°C under oxygen-enriched conditions to obtain a high-purity, low-uranium, submicron-sized spherical silica micropowder having a particle size of 0.3 μm , a U content of 0.9 ppb, and a SiO_2 purity of 99.93%.

[0045] Example 4

[0046] The present example was substantially the same as Example 1, but the only difference was that the calcination temperature was 700°C. The prepared high-purity, low-uranium, submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 0.9 ppb, and a SiO_2 purity of 99.90%.

[0047] Example 5

[0048] The present example was substantially the same as Example 1, but the only difference was that the calcination temperature was 1,400°C. The prepared high-purity, low-uranium, submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 0.2 ppb, and a SiO_2 purity of 99.96%.

[0049] Example 6

[0050] The present example was substantially the same as Example 1, but the only difference

was that the HF solution had a mass concentration of 1.5% and the HCl solution had a mass concentration of 1.5%. The prepared high-purity, low-uranium, submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 0.3 ppb, and a SiO_2 purity of 99.95%.

[0051] Example 7

[0052] The present example was substantially the same as Example 1, but the only difference was that the HF solution had a mass concentration of 1.5% and the HCl solution had a mass concentration of 0.005%. The prepared high-purity, low-uranium, submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 0.8 ppb, and a SiO_2 purity of 99.88%.

[0053] Comparative Example 1

[0054] The present comparative example was substantially the same as Example 1, but the only difference was that only 1.5% (w/w) HF solution, rather than the mixed acid solution, was added during acid treatment. The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 2.5 ppb, and a SiO_2 purity of 99.85%.

[0055] Comparative Example 2

[0056] The present comparative example was substantially the same as Example 1, but the only difference was that the mixed acid treatment was not conducted. The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 13 ppb, and a SiO_2 purity of 99.80%.

[0057] Comparative Example 3

[0058] The present comparative example was substantially the same as Example 1, but the only difference was that the calcination temperature was 500°C. The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 3.3 ppb, and a SiO_2 purity of 99.90%.

[0059] Comparative Example 4

[0060] The present comparative example was substantially the same as Example 1, but the only difference was that the HCl solution was replaced with CH_3COOH . The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 2.6 ppb, and a SiO_2 purity of 99.84%.

[0061] Comparative Example 5

[0062] The present comparative example was substantially the same as Example 1, but the only difference was that the HCl solution was replaced with HNO_3 . The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 1.9 ppb, and a SiO_2 purity of 99.87%.

[0063] Comparative Example 6

[0064] The present comparative example was substantially the same as Example 1, but the only difference was that the 0.5% (w/w) HCl solution was replaced with the 0.003% (w/w) HCl solution. The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 2.4 ppb, and a SiO_2 purity of 99.91%.

[0065] Comparative Example 7

[0066] The present comparative example was substantially the same as Example 1, but the only difference was that the 1.5% (w/w) HF solution was replaced with the 0.05% (w/w) HF solution. The prepared submicron-sized spherical silica micropowder had a particle size of 0.3 μm , a U content of 2.7 ppb, and a SiO_2 purity of 99.83%.

[0067] The above description of examples is merely provided to help understand the method of the present disclosure and a core idea thereof. It should be noted that, several improvements and modifications may be made by a person of ordinary skill in the art without departing from the principle of the present disclosure, and these improvements and modifications should also fall within the protection scope of the present disclosure. A plurality of modifications to these examples are apparent to those skilled in the art, and the general principle defined herein may be practiced in other examples without departing from the spirit or scope of the present disclosure. Therefore, the present disclosure is not limited to the examples shown herein but falls within the widest scope consistent with the principles and novel features disclosed herein.

WHAT IS CLAIMED IS:

1. A preparation method of a high-purity, low-uranium, submicron-sized spherical silica micropowder, comprising the following steps:

step 1, under an inert atmosphere, calcining a raw material in a 700-1,400°C high-temperature furnace for 10-20 h; after calcining, quenching the raw material in water, crushing the raw material into sand aggregates of no more than 1 mm, settling and drying the sand aggregates; repeating a calcining-crushing-settling-drying step to obtain the sand aggregates, wherein the raw material is an elemental silicon or a silicon-containing inorganic compound block having a purity of at least 99.5%, a uranium content of 5-20 ppb, and a grain size of 30-100 μm ;

step 2, mixing the sand aggregates with water in a mass ratio of (1-3):(2-5), adding a hydrofluoric acid (HF) solution equivalent to 0.1%-0.5% of a mass of the water, and conducting wet ball milling to obtain a slurry having an average powder particle size of 5-40 μm ;

step 3, mixing the HF solution with a hydrochloric acid (HCl) solution in a concentration ratio of (1-300):1, adding an equivalent mass of each of the HF solution and the HCl solution to the slurry, simultaneously adding hydrogen peroxide equivalent to 0.1%-0.5% of a total mass of the HF solution and the HCl solution, recovering uranium by adding a flotation agent and a collector, and stirring at 30-60°C to obtain a slurry;

step 4, filter-pressing, washing, and drying the slurry obtained in step 3 to obtain a powder having a uranium content of no greater than 1.0 ppb; and

step 5, by means of flame spheroidization, introducing a carrier gas, a combustible gas, and a combustion improver, igniting, spheroidizing the powder obtained in step 4 at a high temperature of 1,800-2,400°C, and collecting a submicron-sized spherical silica micropowder.

2. The preparation method according to claim 1, wherein in step 1, the silicon-containing inorganic compound is one or a mixture of at least two selected from the group consisting of silicon nitride, silicon carbide, and silica.

3. The preparation method according to claim 1, wherein in step 2, the wet ball milling is conducted for 5-30 h.

4. The preparation method according to claim 1, wherein in step 2, the HF solution has a mass concentration of 1.5%.

5. The preparation method according to claim 1, wherein in step 3, the HF solution and the HCl solution have a concentration ratio of (1-3):1.

6. The preparation method according to claim 1 or 5, wherein in step 3, the HCl solution has a mass concentration of 0.005%-1.5%.

7. The preparation method according to claim 1, wherein in step 3, the stirring is conducted for 12-72 h.

8. The preparation method according to claim 1, wherein in step 5, the carrier gas is one selected from the group consisting of oxygen, air, nitrogen, and argon.

9. The preparation method according to claim 1, wherein in step 5, the combustible gas is one selected from the group consisting of liquefied natural gas (LNG), liquefied petroleum gas (LPG), and hydrogen (H_2).

10. The preparation method according to claim 1, wherein in step 5, the combustion improver is one selected from the group consisting of the air and the oxygen.

11. The preparation method according to claim 1, wherein in step 5, the submicron-sized spherical silica micropowder has an average particle size (D50) of 0.1-1.5 μm , a uranium (U) content of <1.0 ppb, and a silica (SiO_2) purity of $\geq 99.90\%$.