

DESCRIPTION

TITLE

SPHERICAL CRYSTALLINE SILICA PARTICLES AND METHOD OF PRODUCING
SAME

FIELD

[0001]

The present invention relates to spherical crystalline silica particles and a method of producing the same, more particularly relates to spherical crystalline silica particles with a high ratio of quartz and a method of producing the same.

BACKGROUND

[0002]

Due to the increase in the amount of information accompanying the advances made in communications technology and the rapid expansion of utilization of the millimeter wave band by millimeter wave radar etc., the frequencies used have been made increasingly higher. The circuit boards for transmitting these high frequency signals are comprised of electrodes forming circuit patterns and dielectric boards. To keep down the energy loss at the time of transmission of high frequency signals, it is necessary that the dielectric loss tangent ($\tan\delta$) of the dielectric material be small. To lower the dielectric loss, the dielectric material has to have low polarity and low dipole moment.

[0003]

As the dielectric material, mainly ceramic particles, resins, and composites combining these have been used. In particular, along with the expansion of utilization of the millimeter wave band in recent years, much lower low dielectric loss tangent ($\tan\delta$) ceramic particles and resins have been sought. Resins are suitable for high frequency devices where the relative permittivity (ϵ_r) is relatively small, but their dielectric loss tangents ($\tan\delta$) and coefficients of thermal expansion are larger than those of ceramic particles. For this reason, for composites of ceramic particles and resins for use in the millimeter wave band, it is suitable to (1) lower the dielectric loss tangent ($\tan\delta$) of the ceramic particles themselves and (2) increase the ratio of ceramic particles incorporated and decrease the amount of resins exhibiting a large dielectric loss tangent ($\tan\delta$).

[0004]

As the ceramic particles, silica (SiO_2) particles have conventionally been used. If silica particles are angular in shape, their fluidity, dispersibility, and fillability in resins become poor and wear of the manufacturing equipment progresses. To improve on these points, spherical

silica particles have been widely used. It is believed that the closer spherical silica particles are to true spheres, the more their fillability and fluidity in resins and the die wear resistance is improved. Particles with high degree of roundness have therefore been sought. Furthermore, greater improvement of the fillability by adjusting the particle size distribution of particles has also been studied.

[0005]

In general, the thermal spraying method has been used as the method for producing spherical silica. In thermal spraying, particles are passed through a high temperature region of a flame etc. to make the particles melt and render the particles spherical in shape by their surface tension. The particles melted to make them spherical are recovered by being conveyed by a flow of gas so that the particles do not fuse with each other, but after thermal spraying, the particles are rapidly cooled. Since they are rapidly cooled from the melted state, the silica does not crystallize but has a noncrystalline (amorphous) structure and becomes glass-like particles generally called “quartz glass”.

[0006]

Since the spherical silica particles obtained by the thermal spraying method are amorphous, they are low in coefficient of thermal expansion and thermal conductivity. The coefficient of thermal expansion of amorphous silica particles is 0.5 ppm/K, while the thermal conductivity is 1.4W/mK. These physical properties are generally equivalent with the coefficient of thermal expansion of quartz glass not having a crystalline structure, but having an amorphous structure. In general, the coefficient of thermal expansion of Si, which forms the main material of IC chips, is 3 to 5 ppm/K. The coefficient of thermal expansion of encapsulation resin for encapsulation IC chips is much larger compared with Si, so the difference in thermal expansion behavior of the two materials (Si and encapsulation resin) causes warping in the IC chips which in turn obstructs production. On the other hand, if filling a resin with a large coefficient of thermal expansion in spherical silica with a small coefficient of thermal expansion in a high ratio, the effect will be obtained of lowering the thermal expansion of the encapsulation material (composite of spherical silica and resin) itself. By making the coefficient of thermal expansion of the encapsulation material a value close to Si, it is possible to suppress deformation occurring due to the thermal expansion behavior at the time of encapsulation IC chips.

[0007]

As has been stated above, as the properties sought from silica particles for encapsulation use, in addition to the fillability, fluidity, die wear resistance, etc. enabling performance of the composite to be maintained when the particles are mixed into the resin in a large amount, there is an excellent dielectric property of high frequency waves of the millimeter wave band. A dielectric property is a physical property of the material, so it was difficult to decrease the

dielectric loss tangent of amorphous silica particles.

[0008]

PTL 1 describes a method of producing a porous powder comprised of a main crystalline phase of quartz characterized by adding a Zn compound in 0.5 mass% or more converted to ZnO to silica gel having an average particle size of 0.1 to 20 μm and heat treating that mixture at 900 to 1100°C.

[0009]

PTL 2 shows a method of producing spherical crystalline silica particles characterized by including the steps of mixing into amorphous spherical silica particles a compound of an alkali metal in a ratio of 0.4 to 5 mass% by oxide conversion with respect to the total mass of the mass of amorphous spherical silica particles and the mass of the alkali metal by oxide conversion or mixing an alkali earth metal in a ratio of 1 to 5 mass% by oxide conversion with respect to the total mass of the mass of amorphous spherical silica particles and the mass of the alkali earth metal by oxide conversion, heat treating the obtained spherical silica particles at 800°C to 1300°C, and cooling the heat treated spherical silica particles, wherein the cooled spherical silica particles have 90 mass% or more of crystal phases and quartz crystals account for 70 mass% or more of the whole. However, with less than 0.4 mass% of addition of alkali metal or less than 1 mass% of addition of alkali earth metal, the probability of appearance of quartz becomes lower.

[0010]

NPL 1 studied the effect of crystallization and phase transition due to additives when systematically adding an alkali metal oxide to synthesized amorphous spherical silica and shaping it into pellets, then performing heat treatment. According to this, it is shown that if the additive is lithium oxide (Li_2O), quartz is obtained if adding 0.5 mass% or more and firing at 800°C or more.

[0011]

NPL 2 investigated the effects of positive ions on the crystallization and phase transition of a silica substance. In this, it is shown to add, by mass, 10% of LiCl to synthesized amorphous silica and heat treat the mixture at 800°C to get quartz to form as the most dominant phase.

[CITATIONS LIST]

[PATENT LITERATURE]

[0012]

[PTL 1] Japanese Unexamined Patent Publication No. 2002-20111

[PTL 2] WO2018/186308

[NONPATENT LITERATURE]

[0013]

[NPL 1] Journal of Ceramics Society of Japan, 105, [5], 385 to 390 (1997)

[NPL 2] Abstracts of Kagoshima University Faculty of Science, Geology and Biology, vol. 24, pp. 1 to 22 (1991)

5 [NPT 3] High Pressure Research, 28, (4), 641 to 650 (2008)

SUMMARY

[TECHNICAL PROBLEM]

[0014]

10 The inventors aimed at finding filler particles for semiconductor encapsulation use having an excellent dielectric property in the millimeter wave band of a frequency of 30 GHz to 80 GHz and at fabrication of a resin composite for high frequency device applications obtained by mixing these into resins. As a result, they discovered that to obtain a resin composite with a low dielectric loss tangent, it is effective to first heat treat spherical molten (amorphous) silica to
15 make it crystallize. That is, they confirmed that crystalline silica has a dielectric loss tangent in the millimeter wave band (30 GHz to 80 GHz) which is greatly reduced compared with the conventionally widely used amorphous silica. As a result, spherical crystalline silica particles become silica particles exhibiting an excellent dielectric property for high frequency device applications. The crystalline silica obtained by heat treatment is comprised of quartz, cristobalite,
20 or a mixture of the same. Quartz and cristobalite differ in values of physical properties, so when used as a filler, there is preferably a single crystalline silica phase.

[0015]

Further, if crystallizing cristobalite, since the coefficient of thermal expansion of cristobalite becomes 3 times or more that before heat treatment and furthermore there is an inflection point
25 near 250°C, various problems arise in use. In particular, if used as a filler for semiconductor encapsulation use, peeling ends up occurring at the interface of the semiconductor device and encapsulation material due to the mismatch in thermal expansion behavior with the device. For such an application, even among the crystalline silica, quartz, which has an inflection point of the thermal expansion outside the mounting temperature region, is suitable. If using quartz as a
30 filler for semiconductor encapsulation use, it is possible to lower the dielectric loss and realize a suitable coefficient of thermal expansion while trying to improve the mounting reliability.

[0016]

As the method for making spherical amorphous silica crystallize to obtain quartz, PTL 1 discloses adding a zinc compound in 0.5 mass% or more by oxide conversion and heat treating
35 this mixture at 900 to 1100°C. However, as a result of reproducibility tests by the inventors, at a 950°C or less heat treatment temperature, the crystallization itself did not proceed and the silica

remained amorphous. If performing heat treatment at more than 950°C, crystallization starts to proceed, but even at 1100°C, the degree of crystallinity was only about 20%. Further, the crystal phase which appeared was mainly cristobalite. It was not possible to obtain a single phase of quartz at a high content.

[0017]

PTL 2 shows a method of producing spherical crystalline silica particles characterized by including a step of heat treating at 800°C to 1300°C spherical silica particles in which alkali earth metals are mixed in 1 to 5 mass% by oxide conversion with respect to the total mass of the masses by oxide conversion and cooling the heat treated spherical silica particles, the cooled spherical silica particles having 90 mass% or more of crystal phases, and having quartz crystal accounting for 70 mass% or more of the whole. In the examples, as an alkali earth metal, calcium is shown, but if in a comparative example adding calcium in 0.5 mass% by oxide conversion and heat treating the mixture at 1100°C, quartz appears by a low amount of less than 30%. Further, if adding calcium in less than 1 mass% by oxide conversion, spherical crystalline silica with a high quartz content cannot be obtained.

[0018]

Further, PTL 2, NPL 1, and NPL 2 similarly show lithium as an element promoting quartz crystallization. PTL 2 shows mixing lithium in 0.5 to 5 mass% by oxide conversion and heat treating the mixture at 800°C to 1300°C. NPL 1 shows that if adding lithium oxide in 0.5 mass% or more to synthesized amorphous spherical silica and firing the mixture at 800°C or more, quartz is obtained. Furthermore, NPL 2 shows to add 10 mass% of lithium chloride (LiCl) to synthesized amorphous silica and heat treating the mixture at 800°C so that quartz appears as the most dominant phase.

[0019]

However, calcium and other alkali earth metals or lithium and other alkali metals are not preferable as elements to be added to a semiconductor encapsulation material. From the viewpoints of normal operation of a semiconductor device and maintenance of mounting reliability, the amounts of addition of alkali earth metal and alkali metal elements have to be reduced.

[0020]

As factors affecting the crystallization of amorphous silica, the temperature, pressure, and impurity elements are well known. Regarding the effect of pressure, for example, NPL 3 describes that crystallization to quartz occurs if performing heat treatment at a pressure of 20,000 to 30,000 atms at 300°C to 1200°C, but there are limits to the processing of pressurizing apparatuses of tens of thousands of atmospheric pressure and large scale industrial production is difficult, so this is not preferable. Up until now, there have been many reports of crystallization

tests using temperature and impurity elements as variable factors, but spherical crystalline silica with a content of crystalline silica of 40% or more and a ratio of quartz in the crystalline silica of 80 mass% or more has not been obtained. From the viewpoints of normal operation of a semiconductor device and maintenance of mounting reliability, it had been sought to obtain silica particles reduced in lithium and calcium to respectively less than 0.40 mass% and less than 1.0 mass% by oxide conversion while having high degree of crystallinity and a substantially single quartz phase.

[0021]

The present invention has as its object to provide spherical silica particles suitable for an application as a filler for semiconductor encapsulation use having an excellent dielectric property in the millimeter wave band, that is, spherical crystalline silica particles with contents of alkali metals and alkali earth methods kept low while having a high degree of crystallinity and high ratio of quartz, and a method of producing the same.

[SOLUTION TO PROBLEM]

[0022]

The inventors engaged in in-depth research for the purpose of solving the above problem. As a result, they mixed into a powder material comprised of amorphous silica particles with a degree of roundness of 0.80 or more both of a calcium material containing calcium in 0.004 or more and less than 1.0 mass% by oxide conversion and a lithium material containing lithium in 0.02 mass% or more and less than 0.40 mass% by oxide conversion and heated the mixed material powder at a heat treatment temperature of 850°C to 1150°C and thereby succeeded in reducing the respective contents of lithium and calcium compared with the past while promoting quartz crystallization. While not constrained to a specific theory, it is believed that by lithium metal and calcium metal being simultaneously added into the silica, a synergistic effect is exhibited on the quartz crystallization and the crystallization of quartz is promoted despite reducing the amounts of addition compared with the case of addition of the elements alone. The crystalline silica particles obtained by 850 to 1150°C heat treatment include phases of crystalline silica. The phases of crystalline silica are substantially a single phase of quartz. The “single phase” referred to here indicates a ratio of quartz in the phases of crystalline silica of 80 mass% or more, preferably 85.0 mass% or more, more preferably 90.0 mass% or more.

[0023]

According to the present invention, the following spherical silica particles and methods of producing the same are provided.

- (1) Spherical crystalline silica particles having a degree of roundness of 0.80 or more, containing lithium in 0.02 mass% or more and less than 0.40 mass% by oxide conversion,

containing calcium in 0.004 mass% or more and less than 1.0 mass% by oxide conversion, and containing phases of crystalline silica, in which spherical crystalline silica particles, a ratio of the phases of crystalline silica in the spherical crystalline silica particles is 40.0% or more and a ratio of quartz in the phases of crystalline silica is 80.0 mass% or more.

(2) The spherical crystalline silica particles according to (1), wherein the ratio of the phases of crystalline silica is 70.0% or more and the ratio of quartz in the phases of crystalline silica is 85.0 mass% or more.

(3) The spherical crystalline silica particles according to (2), wherein the ratio of the phases of crystalline silica is 80.0% or more and the ratio of quartz in the phases of crystalline silica is 90.0 mass% or more.

(4) The spherical crystalline silica particles according to any one of (1) to (3), wherein an average particle size (D50) is 3 to 100 μm .

(5) A method of producing the spherical crystalline silica particles according to any one of (1) to (4), which method of producing spherical crystalline silica particles including mixing a calcium material and a lithium material with spherical amorphous silica particles having a degree of roundness of 0.80 or more and heat treating the obtained mixed powder at 850°C to 1150°C.

(6) A method of producing the spherical crystalline silica particles according to any one of (1) to (4), which method of producing spherical crystalline silica particles including mixing a lithium material with spherical amorphous silica particles having a degree of roundness of 0.80 or more and containing a calcium constituent and heat treating the obtained mixed powder at 850°C to 1150°C.

(7) A method of producing the spherical crystalline silica particles according to any one of (1) to (4), which method of producing spherical crystalline silica particles including mixing a calcium material with spherical amorphous silica particles having a degree of roundness of 0.80 or more and containing a lithium constituent and heat treating the obtained mixed powder at 850°C to 1150°C.

(8) A method of producing the spherical crystalline silica particles according to any one of (1) to (4), which method of producing spherical crystalline silica particles including heat treating spherical amorphous silica particles having a degree of roundness of 0.80 or more and containing a calcium constituent and a lithium constituent at 850°C to 1150°C.

(9) The method of producing the spherical crystalline silica particles according to any one of (5) to (8), wherein a temperature of the heat treatment is 875°C to 1100°C.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0024]

According to the present invention, it is possible to provide spherical crystalline silica

particles suitable for application as a filler for semiconductor encapsulation use having an excellent dielectric property in the millimeter wave band, that is, spherical crystalline silica particles with contents of alkali metals and alkali earth methods kept low while having a high degree of crystallinity and high ratio of quartz, and a method of producing the same.

5

BRIEF DESCRIPTION OF DRAWINGS

[0025]

[FIG. 1] FIG. 1 shows XRD patterns of amorphous silica before heat treatment and silica of one aspect of the present invention (after heat treatment).

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DESCRIPTION OF EMBODIMENTS

[0026]

The spherical crystalline silica according to one aspect of the present invention comprises spherical crystalline silica particles having a degree of roundness of 0.80 or more, containing lithium in 0.02 mass% or more and less than 0.40 mass% by oxide conversion, containing calcium in 0.004 mass% or more and less than 1.0 mass% by oxide conversion, and containing phases of crystalline silica, in which spherical crystalline silica particles, a ratio of the phases of crystalline silica in the spherical crystalline silica particles is 40.0% or more and a ratio of quartz in the phases of crystalline silica is 80.0 mass% or more. The “phases of crystalline silica being 40.0% or more” referred to there is the ratio of the phases of crystalline silica in the spherical crystalline silica particles. The method of finding this will be explained later.

20

[0027]

As the crystal structures of silica (SiO_2), there are cristobalite, quartz, etc. Silica having these crystal structures has a higher thermal conductivity compared with amorphous silica. For this reason, in a filler for semiconductor encapsulation use, it is possible to improve the heat dissipation from an IC chip by replacing amorphous silica with crystalline silica in a suitable amount. Furthermore, crystalline silica has a low dielectric loss tangent in the millimeter wave band, so the more of the amorphous silica is replaced with crystalline silica in a filler for semiconductor encapsulation use, the more the dielectric loss tangent of the semiconductor encapsulation material falls.

25

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[0028]

[Method of Producing Spherical Crystalline Silica Particles]

The spherical crystalline silica particles of the present invention may be produced by mixing spherical amorphous silica with both a calcium material and lithium material and heat treating that mixture (also referred to as “mixed materials”).

35

According to one aspect, it is also possible to mix a lithium material with spherical

amorphous silica particles containing a calcium constituent and heat treat the obtained mixed materials to produce the particles.

Further, it is also possible to mix a calcium material with spherical amorphous silica particles containing a lithium constituent and heat treat the obtained mixed materials to produce the particles.

Alternatively, it is also possible to heat treat spherical amorphous silica particles containing a calcium constituent and a lithium constituent to produce the particles.

[0029]

(Spherical Amorphous Silica Particles)

The amorphous spherical silica particles used as the material can be fabricated by the thermal spraying method or other method. In the thermal spraying method, natural silica powder adjusted to a desired particle size by pulverization is passed through a flame so that the particles melt and the particles become spherical in shape by surface tension. By such a thermal spraying method, it is possible to fabricate spherical amorphous silica particles having a degree of roundness of 0.80 or more.

The composition of the spherical amorphous silica particles is not particularly limited so long as it is mainly comprised of silica and the finally obtained spherical crystalline silica particles are in the desired range. As one aspect, the composition of the spherical amorphous silica particles may be 98.0 mass% or more silica (SiO_2). Further, as elements contained in trace amounts, Ca, Li, Al, Na, Mg, Ba, Zn, etc. may be included. In one aspect, the composition of the spherical amorphous silica particles may also contain Zn in less than 0.5 mass%.

[0030]

(Calcium Material)

The calcium material is mixed with spherical amorphous silica particles and heat treated. The composition and amount of mixture of the calcium material are not particularly limited if the finally obtained spherical crystalline silica particles becomes a desired range and are suitably adjusted. The calcium material may also be calcium hydroxide, calcium oxide, etc. stably present in the atmosphere and may be natural minerals. The calcium material can be added in the state of a powder material or aqueous solution etc. so as to be uniformly mixed with the spherical amorphous silica particles. Further, at least part of the calcium material may be a trace element contained in the spherical amorphous silica particles. For example, if the spherical amorphous silica particles sufficiently contain calcium and the content of calcium in the finally obtained spherical crystalline silica particles becomes the desired one, the spherical amorphous silica particles can also be jointly used with the calcium material. Further, if the spherical amorphous silica particles contains calcium, but not sufficiently, it is possible to add a calcium material so that the content of calcium in the finally obtained spherical crystalline silica particles becomes

the desired one.

[0031]

(Lithium Material)

The lithium material is mixed with spherical amorphous silica particles and heat treated.

5 The composition and amount of mixture of the lithium material are not particularly limited if the finally obtained spherical crystalline silica particles becomes a desired range and are suitably adjusted. The lithium material may be an oxide, carbonate, hydroxide, nitrate, etc. The form of addition is not particularly limited. The material can be added in the state of a powder material or aqueous solution etc. so as to be uniformly mixed with the spherical amorphous silica particles.

10 Further, at least part of the lithium material may be a trace element contained in the spherical amorphous silica particles. For example, if the spherical amorphous silica particles sufficiently contain lithium and the content of lithium in the finally obtained spherical crystalline silica particles becomes the desired one, the spherical amorphous silica particles can also be jointly used with the lithium material. Further, if the spherical amorphous silica particles contains

15 lithium, but not sufficiently, it is possible to add a lithium material so that the content of lithium in the finally obtained spherical crystalline silica particles becomes the desired one.

[0032]

(Mixing)

The spherical amorphous silica particles are mixed with both the calcium material and

20 lithium material. Note that, the calcium material and/or the lithium material may also be contained in the spherical amorphous silica. The mixing technique is not particularly limited so long as the materials are mixed equally dispersed in the mixture. The mixing may also be performed by a powder mixer. Due to the mixing, the calcium material and lithium material contact at least part of the spherical amorphous silica and in the following heat treatment step,

25 crystallization of the spherical amorphous silica, in particular crystallization to quartz, is promoted.

At the time of mixing, the respective materials are blended and mixed so that the lithium contained in the produced spherical crystalline silica particles becomes 0.02 mass% or more and less than 0.40 mass% by oxide conversion and so that the calcium contained becomes 0.004

30 mass% or more and less than 1.0 mass% by oxide conversion. Note that, the total amounts of the blended lithium material and calcium material are not contained in the produced spherical crystalline silica particles, so it is preferable to blend them considering the rates which are contained.

Note that, “mixing” causes the calcium material and lithium material to contact at least part

35 of the spherical amorphous silica and does not promote pulverization of the spherical amorphous silica, so the degree of roundness of the same does not fall much at all between before and after

mixing.

[0033]

(Heat Treatment)

The heat treatment of the mixed materials obtained by mixing the spherical amorphous silica particles, the calcium material, and the lithium material is performed at a temperature of a 850°C to 1150°C temperature range. The atmosphere at the time of heat treatment can be made the air or other oxidizing atmosphere and a nitrogen or argon or other inert gas atmosphere. The atmospheric pressure is preferably the air pressure since the heat treatment is performed on a large industrial scale. If the heat treatment temperature is lower than 850°C, crystallization does not proceed or is remarkably slow. On the other hand, if a temperature higher than 1150°C, the crystallization of cristobalite proceeds competitively with the quartz crystallization. As a result, it no longer becomes possible to obtain spherical crystalline silica particles of a substantially quartz single phase. Here, the “substantially single phase” indicates a state of the quartz phase accounting for 80 mass% or more in the phases of crystalline silica contained in the spherical crystalline silica particles. Preferably, the heat treatment temperature is 875°C to 1110°C.

[0034]

The time of the heat treatment can be suitably adjusted so as to obtain the desired degree of crystallinity. If the lithium element and calcium element are uniformly copresent in the spherical amorphous silica particles, quartz crystallization of the spherical amorphous silica particles proceeds due to the synergistic effect of the two elements faster than the case of presence of single elements. In one aspect of the present invention, lithium may be added at the time of mixture as a lithium material (lithium carbonate etc.) or may be added in advance to the spherical amorphous silica particles. Further, calcium may be supplied at the time of mixture as a calcium material (calcium oxide etc.) or may be contained in advance in the spherical amorphous silica particles. It is believed that the lithium and calcium are uniformly present in the spherical amorphous silica particles due to dispersion by the heat dissipation step, so the spherical amorphous silica particles as a whole crystallize to quartz. For this reason, the longer the heat treatment time becomes, the more the lithium and calcium disperse inside the spherical amorphous silica particles, so the more the crystallization proceeds. Typically, in other words, if the heating and cooling rate is greater than 60°C/h, the progression of crystallization is substantially determined by the heat treatment temperature, that is, the holding time at the peak temperature, so the crystallinity can be controlled by adjusting the holding time at the peak temperature. In this case, the heat treatment time may be adjusted in the range of generally 1 hour to 48 hours. From the viewpoint of sufficient promotion of crystallization, it may be 3 hours or more or may be 6 hours or more. Further, even if excessively extending the heat treatment time, the degree of crystallinity becomes saturated, so from the viewpoint of cost reduction, the

heat treatment time may be 25 hours or less, may be 18 hours or less, or may be 12 hours or less.

Further, if the heat treatment temperature becomes higher, the coefficient of dispersion of the lithium element in the spherical amorphous silica particles becomes greater, so the quartz crystallization proceeds. However, if more than 1150°C, the cristobalite phase competitively appears and quartz no longer becomes a single phase, so there is an upper limit to the heat treatment temperature.

Further, the extent of dispersion changes depending on the types and amounts of addition of the lithium material and calcium material, so the optimal time and temperature of the heat treatment may be suitably selected in accordance with these.

Note that the heating rate and the cooling rate do not greatly affect the appearance of crystalline silica particles if performing the heat treatment in an electric furnace.

[0035]

The degree of roundness of the spherical crystalline silica of the present invention does not fall much at all between before and after heat treatment for crystallization. The spherical crystalline silica particles of the present invention were made crystalline at the relatively low temperature of the heat treatment at 850°C to 1150°C. In that temperature range, the degree of roundness does not fall much at all. If amorphous silica particles become more than 1100°C, they are sometimes joined together by fusion or sintering, but the spherical crystalline silica particles of the present invention were rendered crystallized at 850°C to 1150°C (already not amorphous), so the particles being joined together by fusion or sintering can be completely suppressed.

[0036]

[Spherical Crystalline Silica Particles]

(Degree of roundness)

The spherical crystalline silica particles of the present invention have a degree of roundness of 0.80 or more.

If the degree of roundness is less than 0.80, if utilized as silica particles of a resin composite composition for use as a semiconductor encapsulation material etc., the fluidity, dispersibility, and fillability are not sufficient. Further, sometimes wear of the equipment for fabricating the encapsulation material is promoted. The average degree of roundness of the spherical amorphous silica particles obtained by thermal spraying may be 0.80 or more. The temperature in the heat treatment step for causing crystallization is 850 to 1150°C, so the degree of roundness of the silica particles does not change much at all between before and after the heat treatment. Further, if the thermal spraying method, particles with a high average degree of roundness can be easily obtained. As a result in the method of the present invention, it is possible to realize the desired spherical crystalline silica particles with a high degree of roundness. From the viewpoint of the improvement of the fluidity, dispersibility, and fillability and reduction of wear of the

equipment, the higher the degree of roundness, the more preferable. It may be 0.85 or more or may be 0.90 or more. On the other hand, if making the circular shape one with a degree of roundness of 1.0, that is, a perfect circle, is difficult, the upper limit of the degree of roundness may be 0.99 or less or 0.97 or less.

[0037]

The degree of roundness is found by the “circumference of a circle equivalent in projected area of the captured particles ÷ circumference of the captured particle image”. The closer this value to 1, the closer to a true sphere is meant. The degree of roundness of the present invention was found by flow type particle image analysis. In the flow type particle image analysis method, spherical crystalline silica particles are poured into a liquid, the particles are captured as a still image, and the image is analyzed based on the obtained particle image to find the degree of roundness of the spherical crystalline silica particles. The average value of these plurality of degree of roundness was made the average degree of roundness. If the number of particles when measuring the average degree of roundness by the flow type particle image analysis method is too small, the average value cannot be accurately obtained. At the very least, 100 or more particles are necessary. Preferably, there are 500 or more, more preferably 1000 or more. In the present invention, the flow type particle image analysis apparatus “FPIA-3000” (made by Spectris) and about 100 particles were used. Note that, the degree of roundness of spherical amorphous silica particles are similarly found.

[0038]

(Composition)

The spherical crystalline silica particles of the present invention contain lithium in 0.02 mass% or more and less than 0.40 mass% and calcium in 0.004 mass% or more and less than 1.0 mass% based on the mass of the silica particles (100 mass%). The preferable lower limit of lithium may be 0.05 mass%, more preferably 0.10 mass%, still more preferably 0.25 mass%. Further, the preferable upper limit of lithium may be less than 0.35 mass%, more preferably less than 0.30 mass%. The preferable lower limit of calcium may be 0.20 mass%, more preferably 0.6 mass%. Further, the preferable upper limit of calcium may be 0.9 mass%, more preferably 0.8 mass%. The contents of lithium and calcium can be measured by, for example, the atomic absorption spectrometry and ICP mass spectrometry (ICP-MS). Specifically, they are measured based on JIS-K0133 using ICP-MS (“7700X” made by Agilent). An aqueous solution obtained by completely dissolving silica particles by hydrofluoric acid was used as a sample. Here, the contents of impurity elements contained in the silica particles were made the contents of impurity elements in the silica solution. The calibration line may also be obtained using a base solution of only the reagents. By performing specific heat treatment by a composition containing the above ranges of the lithium and calcium, it is possible to obtain spherical crystalline silica

particles with a high degree of crystallinity and substantially a single phase with a high ratio of quartz. The lithium and calcium become substantially present in the form of oxides through heat treatment in a 850 to 1150°C temperature range for causing crystallization. After that, the lithium and calcium react with the silica and are taken into the silica structure. The contents of these do not change much at all between before and after the heat treatment in this temperature range. If the contents of the lithium and calcium change before and after the heat treatment, it is possible to suitably adjust the composition of the material in consideration of the extent of the change so as to obtain the predetermined lithium and calcium contents in the finally obtained spherical crystalline silica particles.

[0039]

(Properties of Crystals)

The spherical crystalline silica particles of the present invention contain phases of crystalline silica. The degree of crystallinity in the spherical crystalline silica particles is 40.0 % or more and the ratio of the quartz in the phases of crystalline silica is 80.0 mass% or more.

If the silica particles obtained by the heat treatment are comprised of amorphous and crystalline silica, the ratio of presence of the amorphous and crystalline silica (indicating so-called “degree of crystallinity”, in this Description, sometimes referred to in this way) and the types of the crystalline silica and their ratios can be found by XRD. With XRD measurement, it is possible to find the ratio of the crystal phases by the following formula from the sum (Ic) of integrated intensities of the crystalline peaks and the integrated intensities (Ia) of the amorphous halo parts. More specifically, the degree of crystallinity in the spherical crystalline silica particles can be found:

$$X(\text{phase ratio of crystal phases}) = \frac{I_c}{I_c + I_a} \times 100 (\%)$$

In the present invention, the XRD measurement was performed in the range of $2\Theta = 10^\circ$ to 90° .

The ratio of the crystal phases was found from the sum of the intensities of the crystalline peaks appearing in the 2Θ measurement range and the integrated intensities of the halo parts derived from broad amorphous structures appearing near $2\Theta = 22^\circ$.

The types of the crystal phases such as cristobalite and quartz and the ratios of the same (mass%) were found by quantitative analysis by X-ray diffraction. In the present invention, the quantitative analysis by X-ray diffraction was a method of analysis using the Rietveld method. The quantitative analysis was performed without using a standard specimen. In the present invention, an X-ray diffraction apparatus “D2 PHASER” (made by Bruker) was used. The quantitative analysis of the crystal phases by the Rietveld method was performed by the crystal structure analysis software “TOPAS” (made by Bruker).

[0040]

The spherical crystalline silica particles of the present invention include phases of

crystalline silica. The degree of crystallinity in the spherical crystalline silica particles is 40.0 % or more, that is, the particles have a high degree of crystallinity of 40.0% or more and the dielectric loss tangent greatly falls compared with amorphous silica, so this is preferable. From the viewpoint of reduction of the dielectric loss tangent, the higher the degree of crystallinity, the better. It may be 70.0% or more, more preferably may be 80.0% or more.

[0041]

The spherical crystalline silica particles of the present invention include phases of crystalline silica. The ratio of quartz in the phases of crystalline silica is high and is 80.0 mass% or more. Substantially it is a quartz single phase. For this reason, the coefficient of thermal expansion, thermal conductivity, and other various properties of the spherical crystalline silica particles are substantially determined by the properties of the quartz. That is, they do not change. This is preferable in the case of use for a filler etc. From the above viewpoint, the higher the ratio of quartz, the more preferable. The ratio may be 85.0 mass% or more, more preferably may be 90.0 mass% or more.

[0042]

(Average Particle Size)

In one aspect of the present invention, the average particle size (D50) of the spherical crystalline silica particles may be 3 to 100 μm . If the average particle size is less than 3 μm , the particles become large in agglomerating ability and the fluidity remarkably falls, so this is not preferable. If the average particle size is more than 100 μm , gaps easily remain between particles and the fillability becomes difficult to raise, so this is not preferable. An average particle size of 10 to 80 μm in range is more preferable. The spherical amorphous silica particles before heat treatment do not change much at all in particle size before and after heat treatment of 850 to 1150°C in temperature range.

[0043]

For the average particle size (D50), the median size D50 of a cumulative volume of 50% in the particle size distribution measured by the laser diffraction-scattering type particle size distribution measurement method was found. Note that, the laser diffraction-scattering type particle size distribution measurement method is the method of firing a laser beam at a dispersion in which spherical crystalline silica particles were dispersed and finding the particle size distribution from the intensity distribution pattern of the diffracted and scattered light emitted from the dispersion. In the present invention, a laser diffraction-scattering type particle size distribution measurement apparatus “CILAS920” (made by Cirrus) was used. Note that, the average particle size may be similarly found for amorphous silica particles.

[0044]

(Examples of Application)

According to the present invention, it is possible to produce a composite composition of the finally obtained spherical crystalline silica particles and further a resin composite obtained by curing the resin composite composition. The composition of the resin composite composition will be explained below.

[0045]

A slurry composition containing spherical crystalline silica particles and a resin can be used to obtain a semiconductor encapsulation material (in particular, a solid encapsulation material), interlayer insulating film, or other resin composite composition. Furthermore, by curing these resin composite compositions, it is possible to obtain a encapsulation material (cured material), semiconductor package board, or other resin composite.

[0046]

If producing the resin composite composition, for example, in addition to the spherical crystalline silica particles and resin, a curing agent, curing accelerator, flame retardant, silica coupling agent, etc. are blended in accordance with need and formed into a composite by kneading or other known method. Further, the composite is shaped into pellets, a film, etc. in accordance with the application.

[0047]

Furthermore, if curing the resin composite composition to produce a resin composite, for example, heat is added to the resin composite composition to make it melt, the composition is worked into a shape suitable for the application, and a heat higher than the time of melting is applied to make the composition completely cure. In this case, it is possible to use the transfer mold method or other known method.

[0048]

For example, if producing package boards, interlayer insulating films, or other semiconductor related materials, resins known as resins used for resin composite compositions can be applied, but an epoxy resin is preferably employed. The epoxy resin is not particularly limited, but, for example, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, biphenyl type epoxy resin, phenol novolac type epoxy resin, cresol novolac type epoxy resin, naphthalene type epoxy resin, phenoxy type epoxy resin, etc. can be used. It is also possible to use single types among these alone or use two types having different molecular weights or more together. Among these in particular, from the viewpoint of the curability, heat resistance, etc., an epoxy resin having two or more epoxy groups in one molecule is preferable. Specifically, a biphenyl type epoxy resin, phenol novolac type epoxy resin, o-cresol novolac type epoxy resin, phenol type and aldehyde type novolac resin which is epoxylated, bisphenol A, bisphenol F, bisphenol S, or other glycidyl ether, a glycidyl ester acid epoxy resin obtained by a reaction of phthalic acid or dimer acid or other polybasic acid and and epichlorohydrin, linear aliphatic epoxy resin,

alicyclic epoxy resin, heterocyclic epoxy resin, alkyl-modified polyfunctional epoxy resin, β -naphthol novolac type epoxy resin, 1,6-dihydroxynaphthalene type epoxy resin, 2,7-dihydroxynaphthalene type epoxy resin, bishydroxybiphenyl type epoxy resin, further, an epoxy resin in which bromine or other halogen is introduced for imparting flame retardancy, etc. may be mentioned. Among epoxy resins having two or more epoxy groups in a single molecule, in particular a bisphenol A type epoxy resin is preferable.

[0049]

Further, as the resin used for resin composite compositions of applications other than composite materials for semiconductor encapsulation material use, for example, prepregs for printed circuit boards, various engineering plastics, etc., resins other than epoxy types can also be used. Specifically, in addition to epoxy resins, silicone resins, phenol resins, melamine resins, urea resins, unsaturated polyesters, fluororesins, polyamides, polyamide imides, polyether imides, and other polyamides; polybutylene terephthalates, polyethylene terephthalates, and other polyesters; polyphenylene sulfides, aromatic polyesters, polysulfones, liquid crystal polymers, polyether sulfones, polycarbonates, maleimide modified resins, ABS resins, AAS (acrylonitrile-acrylic rubber-styrene), and AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resins may be mentioned.

As the curing agent used for the resin composite composition, curing agents for curing the above resins may be used. For example, a phenolic curing agent can be used. As the phenolic curing agent, a phenol novolac resin, alkyl phenol novolac resin, polyvinyl phenols, etc. can be used alone or in combinations of two or more types.

[0050]

The amount of the phenol curing agent blended is preferably an equivalent ratio with the epoxy resin (phenolic hydroxy group equivalent/epoxy group equivalent) of 0.1 or more and less than 1.0. Due to this, there is no longer any residual unreacted phenolic curing agent and the hydroscopic heat resistance are improved.

[0051]

The amount of addition of the spherical crystalline silica particles of the present invention in the resin composite composition is preferably large from the viewpoint of the heat resistance and coefficient of thermal expansion, but is usually 70 mass% or more and 95 mass% or less, preferably 80 mass% or more and 95 mass% or less, more preferably 85 mass% or more and 95 mass% or less. This is because if the amount of silica powder material blended is too small, the improvement of strength of the encapsulation material, suppression of thermal expansion, and other effects are hard to obtain. Further, if too great, segregation due to agglomeration of silica powder in the composite material easily occurs regardless of the surface treatment of the silica powder material, the composite material becomes too large in viscosity, and other problems

arise. From this, practical use as a encapsulation material becomes difficult.

[0052]

Further, for the encapsulation coupling agent, a known coupling agent may be used, but one having an epoxy-based functional group is preferable.

5

EXAMPLES

[0053]

The present invention will be explained through the following examples and comparative examples. However, the present invention are not interpreted limited to the following examples.

10

[0054]

(Example 1 to Example 3)

15

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed with the spherical amorphous silica particles, then the particles were filled in a container made of aluminum and heat treated using an electric furnace SUPER-BURN (made by K.K. Motoyama) in an air atmosphere (atmospheric pressure). The amount of mixture of lithium carbonate was made 0.25 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion, and the calcium contained in the amorphous silica particles was made 0.004 mass% by oxide conversion. At a heating rate of 300°C/h, the particles were raised to 900°C (Example 1), 1000°C (Example 2), and 1100°C (Example 3) and held there for 6 hours. After that, the particles were cooled by a rate of temperature fall of about 100°C/h until room temperature.

20

[0055]

(Example 4 to Example 6)

25

Amorphous silica particles containing calcium were fabricated by the thermal spray method. The calcium contained in the amorphous silica particles was made 0.0040 mass%. Lithium carbonate was mixed in by 0.10 mass% by oxide conversion (Example 4), 0.07 mass% (Example 5), and 0.05 mass% (Example 6) with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion. At a heating rate of 300°C/h, the particles were raised to 930°C (Example 4), 1030°C (Example 5), and 1130°C (Example 6) and held there for 6 hours. After that, the particles were cooled by a rate of temperature fall of about 100°C/h until room temperature.

30

[0056]

(Example 7 to Example 9)

35

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.25 mass% by oxide conversion with

respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion. The calcium contained in the amorphous silica particles was made 0.24 mass% by oxide conversion. At a heating rate of 300°C/h, the particles were raised to 900°C (Example 7), 1000°C (Example 8), and 1100°C (Example 9) and held there for 6 hours. Except for that, heat treatment was performed in the same way as Example 1.

[0057]

(Example 10 to Example 12)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.25 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion. The calcium contained in the amorphous silica particles was made 0.66 mass% by oxide conversion. After that, at a heating rate of 300°C/h, the particles were raised to 900°C (Example 10), 1000°C (Example 11), and 1100°C (Example 12) and held there for 6 hours. After that, the particles were cooled by a rate of temperature fall of about 100°C/h.

[0058]

(Example 13 and Example 14)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.05 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion. The calcium contained in the amorphous silica particles was made 0.66 mass% by oxide conversion. After that, at a heating rate of 300°C/h, the particles were raised to 925°C in Example 13 and were raised to 1080°C in Example 14. After that, in Example 13, the particles were held there for 6 hours and in Example 14, the particles were held there for 24 hours. Except for that, heat treatment was performed in the same way as Example 1.

[0059]

(Example 15 and Example 16)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.10 mass% (Example 15) and 0.02 mass% (Example 16) by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion. The calcium contained in the amorphous silica particles was made 0.66 mass% by oxide conversion. After that, at a heating rate of 300°C/h, the particles were raised to 925°C in Example 15 and were raised to 950°C in Example 16. After that, the particles were held there for 6 hours. Except for that, heat treatment was performed in the same way as Example 1.

[0060]

(Example 17 to Example 20)

Amorphous silica particles were fabricated by the thermal spray method. Calcium hydroxide particles and lithium carbonate particles were mixed with the spherical amorphous silica particles, then the mixture was filled in a container made of aluminum and heat treated using an electric furnace SUPER-BURN (made by K.K. Motoyama) in an air atmosphere (atmospheric pressure). The amount of mixture of calcium hydroxide was made 0.48 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica, the mass of calcium by oxide conversion, and the mass of lithium by oxide conversion, while the amount of mixture of lithium carbonate was made 0.04 mass% by oxide conversion (Example 17), 0.06 mass% (Example 18), 0.08 mass% (Example 19), and 0.10 mass% (Example 20). At a heating rate of 300°C/h, the particles were raised to 925°C and held there for 12 hours. After that, the particles were cooled by a rate of temperature fall of about 100°C/h until room temperature.

[0061]

(Example 21 and Example 22)

Amorphous silica particles containing calcium and lithium were fabricated by the thermal spray method. The spherical amorphous silica particles were filled in a container made of aluminum and heat treated using an electric furnace SUPER-BURN (made by K.K. Motoyama) in an air atmosphere (atmospheric pressure). The calcium contained in the amorphous silica particles was made 0.82 mass% by oxide conversion while the lithium was made 0.08 mass% by oxide conversion. The heating rate was made 300°C/h. The temperature was raised to 950°C (Example 21) or 1050°C (Example 22) and held there for 24 hours. After that, the particles were cooled by a rate of temperature fall of about 100°C/h until room temperature.

[0062]

Further, amorphous silica particles containing lithium were fabricated by the thermal spray method. Calcium compound particles were mixed in the spherical amorphous silica particles, then the spherical amorphous silica particles were filled in a container made of aluminum and heat treated using an electric furnace SUPER-BURN (made by K.K. Motoyama) in an air atmosphere (atmospheric pressure) at 850°C to 1150°C in range.

[0063]

(Comparative Example 1)

Amorphous silica particles containing calcium in 0.004 mass% by oxide conversion were fabricated by the thermal spray method. Lithium carbonate particles were not mixed into the spherical amorphous silica particles. After that, heat treatment was performed in the same way as Example 1 except for raising the particles in temperature by a heating rate of 300°C/h until 900°C and holding them there for 6 hours.

[0064]

(Comparative Example 2)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.25 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion while the calcium contained in the amorphous silica particles was 0.004 mass% by oxide conversion. After that, heat treatment was performed in the same way as Example 1 except for raising the particles in temperature by a heating rate of 300°C/h until 1200°C and holding them there for 6 hours.

[0065]

(Comparative Example 3 and Comparative Example 4)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.25 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion while the calcium contained in the amorphous silica particles was 0.24 mass% by oxide conversion. After that, heat treatment was performed in the same way as Example 1 except for raising the particles in temperature by a heating rate of 300°C/h until 1200°C (Comparative Example 3) or 800°C (Comparative Example 4) and holding them there for 6 hours.

[0066]

(Comparative Example 5)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.25 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion while the calcium contained in the amorphous silica particles was 0.0014 mass% by oxide conversion. After that, heat treatment was performed in the same way as Example 1 except for raising the particles in temperature by a heating rate of 300°C/h until 900°C and holding them there for 6 hours.

[0067]

(Comparative Example 6)

Amorphous silica particles containing calcium were fabricated by the thermal spray method. Lithium carbonate particles were mixed in by 0.01 mass% by oxide conversion with respect to the total mass of the mass of the spherical amorphous silica and the mass of lithium by oxide conversion while the calcium contained in the amorphous silica particles was 0.66 mass% by oxide conversion. After that, heat treatment was performed in the same way as Example 1 except for raising the particles in temperature by a heating rate of 300°C/h until 925°C and holding them there for 6 hours.

[0068]

(Comparative Example 7)

Amorphous silica particles containing calcium in 0.66 mass% by metal conversion were fabricated by the thermal spray method. Lithium carbonate particles were not mixed in. After
5 that, heat treatment was performed in the same way as Example 1 except for raising the particles in temperature by a heating rate of 300°C/h until 1100°C and holding them there for 6 hours.

[0069]

The ratios of presence of amorphous and crystalline silica of the silica particles obtained by heat treatment and the types of crystalline silica and the degree of crystallinity were found by
10 XRD. In the present invention, an X-ray diffraction apparatus “D2 PHASER” (made by Bruker) was used. The quantitative analysis of the crystal phase by the Rietveld method was performed by the crystal structure analysis software “TOPAS” (made by Bruker).

[0070]

The degree of roundness was found by flow type particle image analysis. In the present
15 invention, a flow type particle image analysis apparatus “FPIA-3000” (made by Spectris) was used.

[0071]

The contents of the lithium, calcium, and other impurity elements of the spherical silica particles of the present invention were measured by ICP mass spectrometry (ICP-MS).
20 Specifically, based on JIS-K0133, an ICP-MS (“7700X” made by Agilent) was used for measurement. An aqueous solution obtained by making silica particles completely dissolve by hydrogen fluoride was used. Here, the contents of impurity elements contained in the silica particles were made the contents of impurity elements in the dissolved silica solution. The calibration line was obtained using a base solution of only the reagents.

[0072]

The average particle size (D50) of the spherical quartz particles was measured by the laser diffraction-scattering type particle size distribution measurement method. In the present
invention, a laser diffraction-scattering type particle size distribution measurement apparatus “CILAS920” (made by Cirrus) was used.

[0073]

In the spherical crystalline silica particles obtained in the examples according to the present invention, in each case, the lithium content was 0.02 mass% or more and less than 0.40 mass% in range by oxide conversion and phases of crystalline silica was contained, the degree of crystallinity in the spherical crystalline silica particles was 40.0% or more, and the ratio of quartz
35 in the phases of crystalline silica was 80 mass% or more. The spherical crystalline silica particles of the examples according to the present invention had a degree of roundness of 0.83 to 0.95.

The average particle size of spherical amorphous silica particles containing calcium in 0.004 mass% by oxide conversion was 35.1 μm , while in the case of the spherical crystalline silica particles of the present invention using this material, it was 35.2 μm to 35.6 μm .

Further, the average particle size of the spherical amorphous silica particles containing calcium in 0.24 mass% was 33.8 μm , while in the case of the spherical crystalline silica particles of the present invention using this material, it was 33.3 μm to 33.9 μm .

Furthermore, in the case of the spherical amorphous silica particles containing calcium in 0.66 mass% by oxide conversion, it was 41.1 μm , while in the case of the spherical crystalline silica particles of the present invention using this material, it was 40.9 μm to 41.5 μm .

Further, if heat treating a mixed material powder obtained by mixing a calcium material containing calcium in 0.48 mass% by oxide conversion and a lithium material containing lithium in 0.04 to 0.10 mass by oxide conversion with amorphous silica particles, the average particle size of the spherical amorphous silica particles was 32.3 μm , while in the spherical crystalline silica particles of the present invention using this mixed material powder, it was 31.6 μm to 35.1 μm .

Furthermore, in spherical amorphous silica particles containing calcium and lithium respectively in 0.82 mass% and 0.08 mass% by oxide conversion, the average particle size was 21.5 μm , while in the spherical crystalline silica particles of the present invention using this material powder, it was 20.3 μm and 21.9 μm .

[0074]

If comparing Example 1, Example 7, and Comparative Example 5, it will be understood that even with the same 0.25 mass% lithium content, it is only first when the calcium content is more than 0.004 mass% by oxide conversion that the degree of crystallinity in the spherical crystalline silica particles is more than 40.0%. It will be understood that a synergistic effect is exhibited due to the copresence of calcium and lithium elements and crystallization is promoted. Furthermore, if looking at only Comparative Example 1, even if calcium is contained in 0.004 mass% by oxide conversion, if lithium is not added, crystallization does not proceed. It will be understood that copresence of lithium and calcium is required.

[0075]

If comparing Examples 4 to 6 and Examples 13 to 16 and Comparative Example 6 and Comparative Example 7, it will be understood that the lower limit value of the amount of addition of lithium is 0.02 mass%.

[0076]

If comparing Example 1 to Example 3 and Comparative Example 2 or Example 7 to Example 9 and Comparative Example 3, it will be understood that if the heat treatment temperature becomes a high temperature, the cristobalite content increases and that at 1200°C,

the ratio of quartz in the phases of crystalline silica ends up falling below 80 mass%.

Furthermore, if comparing Example 7 to Example 9 and Comparative Example 4, it will be understood that at a heat treatment temperature of 800°C, the crystallization does not progress and the degree of crystallinity in the spherical crystalline silica particles becomes less than 40%.

5 The preferable heat treatment temperature is 850°C to 1150°C. The more preferable temperature range is 875°C to 1100°C.

[0077]

10 If comparing Example 12 and Comparative Example 7, even if calcium is contained in 0.66 mass% or more by oxide conversion, if no lithium is added, the degree of crystallinity in the spherical crystalline silica particles is 11.4% or less than 40.0%. If lithium is added in 0.02 mass% or more by oxide conversion, the degree of crystallinity in the spherical crystalline silica particles becomes more than 40% and the ratio of quartz in the phases of crystalline silica becomes more than 80 mass%. It was discovered that this high degree of quartz crystallinity is a synergistic effect of the copresence of calcium and lithium. Note that even if making the content
15 of lithium or calcium increase (to lithium of 0.02 mass% or more by oxide conversion and calcium of 0.004% or more by oxide conversion), there was no problem with the degree of crystallinity and the degree of quartzification: the degree of crystallinity in the spherical crystalline silica particles became 40.0% or more and the ratio of quartz in the phases of crystalline silica became more than 80 mass%.

20 **[0078]**

The contents of zinc of the spherical crystalline silica particles used in the examples and comparative examples of the present invention were less than 1.0 ppm by metal conversion, the totals of alkali metals other than lithium (K and Na) were 24 to 36 ppm by metal conversion, the totals of alkali earth metals other than calcium (Mg+Ba) were 1.8 to 42 ppm, and the
25 aluminum metals were 90 to 4552 ppm. Metal impurities other than these lithium and calcium may be contained in the silica if in ranges not affecting the crystallization.

[0079]

[Table 1]

Table 1

			Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Ca content	Oxide conversion	wt%			0.0040					0.24	
Li compound					Li2CO3						
Amount of addition of Li	Oxide conversion	wt%		0.25		0.10	0.07	0.05		0.25	
Chemical analysis											
Al	Metal conversion	ppm			90					110	
Na	Metal conversion	ppm			14					13	
K	Metal conversion	ppm			10					13	
Na+K total		ppm			24					26	
Mg	Metal conversion	ppm			1.4					13	
Ba	Metal conversion	ppm			0.4					0.4	
Mg+Ba total		ppm			1.8					13.4	
Zn		ppm			0.04					0.18	
Heat treatment	Holding temp.	°C	900	1000	1100	930	1030	1130	900	1000	1100
	Holding time	h	6	6	6	6	6	6	6	6	6
Atmosphere			Air	Air	Air	Air	Air	Air	Air	Air	Air
Atmosphere total pressure		Atm	1	1	1	1	1	1	1	1	1
Component phases	Amorphous	%	43.3	18.6	12.0	32.4	32.6	21.2	17.4	10.1	11.3
	Crystallinity	%	56.7	81.4	88.0	65.2	67.2	77.4	82.6	89.9	88.7
Breakdown of crystal phases	A. Phase of crystalline silica	Quartz "a", %	56.5	66.5	70.5	65	65.4	63.2	81.2	75	74
		Cristobalite "b", %	0.1	14.7	17.3	0.1	1.5	12.8	0.2	87.2	12
	B. Phases of other crystals	%	0.1	0.2	0.2	0.1	0.3	1.4	1.2	2.7	1.9
Ratio of quartz in phases of crystalline silica, 100*a/(a+b)		mass%	99.8	81.9	80.3	99.8	97.8	83.2	99.8	85.9	85.1
Average particle size		µm	35.6	35.3	35.2	35.6	35.4	35.2	33.9	33.6	33.3
Degree of roundness		—	0.91	0.89	0.88	0.92	0.90	0.83	0.91	0.88	0.84
Judgment			Good	Good	Good	Good	Good	Good	Very very good	Very good	Very good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 40.0% or more and ratio of quartz in crystalline silica of 80.0 mass% or more: Good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 70.0% or more and ratio of quartz in crystalline silica of 85.0 mass% or more: Very good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 80.0% or more and ratio of quartz in crystalline silica of 90.0 mass% or more: Very very good

[0080]

[Table 2]

Table 2

Ca compound		Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Ca content	Oxide conversion				—			
Li compound					0.66			
Amount of addition of Li					Li ₂ CO ₃			
Chemical analysis								
Al	Metal conversion	4200			4209			
Na	Metal conversion				13			
K	Metal conversion				20			
Na+K total					33			
Mg	Metal conversion				40			
Ba	Metal conversion				1			
Mg+Ba total					41			
Zn					0.34			
Heat treatment	Holding temp.	900	1000	1100	925	1080	925	950
	Holding time	6	6	6	6	24	6	6
Atmosphere		Air	Air	Air	Air	Air	Air	Air
Atmosphere total pressure		1	1	1	1	1	1	1
Component phases	Amorphous	15.2	20.5	8.4	54.2	23.8	23.9	50.0
	Crystallinity	84.8	79.5	91.6	45.8	76.2	76.1	50.0
	A. Phases of crystalline silica	83.1	71.6	83.1	43.6	68.2	74.5	47.9
	B. Phases of other crystals	0.1	6.4	6.6	0.2	74.3	0.3	0.2
Crystal phase breakdown		83.2	78.0	89.7	43.8	6.1	74.8	48.1
		1.6	1.5	1.9	2.0	1.9	1.3	1.9
Ratio of quartz in phases of crystalline silica, 100*(a/(a+b))	mass%	99.9	91.8	92.6	99.5	91.8	99.6	99.6
Average particle phase	μm	41.3	41.4	40.9	41.5	41.3	41.4	41.3
Degree of roundness	—	0.94	0.90	0.87	0.95	0.88	0.93	0.92
Judgment		Very very good	Very good	Very very good	Good	Very good	Very good	Good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 40.0% or more and ratio of quartz in crystalline silica of 80.0 mass% or more: Good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 70.0% or more and ratio of quartz in crystalline silica of 85.0 mass% or more: Very good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 80.0% or more and ratio of quartz in crystalline silica of 90.0 mass% or more: Very very good

[0081]

[Table 3]

Table 3

			Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22
Ca compound								
Ca content	Oxide conversion	wt%		Ca(OH) 2 0.48				- 0.82
Li compound				Li2CO3				-
Amount of addition of Li	Oxide conversion	wt%	0.04	0.06	0.08	0.10		0.08
	Chemical analysis							
Al	Metal conversion	ppm		1155				1650
Na	Metal conversion	ppm		18				21
K	Metal conversion	ppm		12				15
	Na+K total	ppm		30				36
Mg	Metal conversion	ppm		37				37
Ba	Metal conversion	ppm		1				1
	Mg+Ba total	ppm		38				38
	Zn	ppm		0.12				0.10
Heat treatment	Holding temp.	°C		925			950	1050
	Holding time	h		12				24
Atmosphere			Air	Air	Air	Air	Air	Air
Atmosphere total pressure		Atm	1	1	1	1	1	1
Component phases	Amorphous	%	49.8	41.7	22.6	15.7	55.0	25.8
	Crystallinity	%	50.2	58.3	77.4	84.3	45.0	74.2
	A. Phases of crystalline silica	%	49.1	57.1	76.1	83.1	44.0	72.5
	Quartz "a"	%	49.0	57.0	76.0	83.0	43.0	70.5
	Cristobalite "b"	%	0.1	0.1	0.1	0.1	1.0	2.0
	B. Phases of other crystals	%	1.1	1.2	1.3	1.2	1.0	1.7
	Ratio of quartz in phases of crystalline silica, 100*a/(a+b)	mass%	99.8	99.8	99.9	99.9	97.7	97.2
Average particle phase		μm	34.1	35.1	31.6	33.5	20.3	21.9
Degree of roundness		—	0.89	0.90	0.88	0.89	0.90	0.89
	Judgment		Good	Good	Very good	Very very good	Good	Very good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 40.0% or more and ratio of quartz in crystalline silica of 80.0 mass% or more: Good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 70.0% or more and ratio of quartz in crystalline silica of 85.0 mass% or more: Very good

Ratio of phases of crystalline silica in spherical crystalline silica particles of 80.0% or more and ratio of quartz in crystalline silica of 90.0 mass% or more: Very very good

[0082]

[Table 4]

Table 4

Ca content	Oxide conversion	wt%	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Li compound			—						
Amount of addition of Li	Oxide conversion	wt%	—	0.25	0.25	0.25	0.25	0.01	—
Chemical analysis									
Al	Metal conversion	ppm	90	110			4552		4209
Na	Metal conversion	ppm	14	13			13		13
K	Metal conversion	ppm	10	13			23		20
Na+K total		ppm	24	26			36		33
Mg	Metal conversion	ppm	1.4	13			41		40
Ba	Metal conversion	ppm	0.4	0.4			1		1
Mg+Ba total		ppm	1.8	13.4			42		41
Zn		ppm	0.04	0.18			0.45		0.34
Heat treatment	Holding temp.	°C	900	1200			800		925
Atmosphere	Holding time	h	6	6			6		6
Atmosphere total pressure		Atm	1	1			1		1
Component phases	Amorphous	%	98.5	18.9			84.4		95.5
	Crystallinity	%	1.5	81.1			16.6		4.5
Crystal phase breakdown	A. Phases of crystalline silica	Quartz "a"	1.5	52.1			14.7		29
		Cristobalite "b"	0.0	26.4			0.0		0.0
	B. Phase of other crystals		0.0	2.6			1.9		0.1
Ratio of quartz in phases of crystalline silica, 100*a/(a+b)		mass%	100.0	66.4			100.0		100.0
Average particle phase		μm	35.5	35.2			33.7		35
Degree of roundness		—	0.93	0.85			0.95		0.91
Judgment			Poor	Poor			Poor		Poor

Ratio of phases of crystalline silica in spherical crystalline silica particles of less than 40.0% and ratio of quartz in crystalline silica of less than 80.0 mass%: Poor

INDUSTRIAL APPLICABILITY

[0083]

The spherical crystalline silica particles of the present invention are not limited to semiconductor encapsulation materials and can be used for other applications as well.

- 5 Specifically, they can also be used as prepregs for printed circuit boards, various types of engineering plastics, etc.

CLAIMS

[Claim 1]

Spherical crystalline silica particles having a degree of roundness of 0.80 or more,
5 containing lithium in 0.02 mass% or more and less than 0.40 mass% by oxide conversion,
containing calcium in 0.004 mass% or more and less than 1.0 mass% by oxide conversion, and
containing phases of crystalline silica, in which spherical crystalline silica particles, a degree of
crystallinity in the spherical crystalline silica particles is 40.0% or more and a ratio of quartz in
the phases of crystalline silica is 80.0 mass% or more.

[Claim 2]

The spherical crystalline silica particles according to claim 1, wherein the degree of
crystallinity is 70.0% or more and the ratio of quartz in the phases of crystalline silica is 85.0
mass% or more.

[Claim 3]

The spherical crystalline silica particles according to claim 2, wherein the degree of
crystallinity is 80.0% or more and the ratio of quartz in the phases of crystalline silica is 90.0
mass% or more.

[Claim 4]

The spherical crystalline silica particles according to any one of claims 1 to 3, wherein an
average particle size (D50) is 3 to 100 μm .

[Claim 5]

A method of producing the spherical crystalline silica particles according to any one of
claims 1 to 4, which method of producing spherical crystalline silica particles including mixing a
calcium material and a lithium material with spherical amorphous silica particles having a degree
of roundness of 0.80 or more and heat treating the obtained mixed powder at 850°C to 1150°C.

[Claim 6]

A method of producing the spherical crystalline silica particles according to any one of
claims 1 to 4, which method of producing spherical crystalline silica particles including mixing a
lithium material with spherical amorphous silica particles having a degree of roundness of 0.80
35 or more and containing a calcium constituent and heat treating the obtained mixed powder at
850°C to 1150°C.

[Claim 7]

A method of producing the spherical crystalline silica particles according to any one of claims 1 to 4, which method of producing spherical crystalline silica particles including mixing a calcium material with spherical amorphous silica particles having a degree of roundness of 0.80 or more and containing a lithium constituent and heat treating the obtained mixed powder at 850°C to 1150°C.

[Claim 8]

A method of producing the spherical crystalline silica particles according to any one of claims 1 to 4, which method of producing spherical crystalline silica particles including heat treating spherical amorphous silica particles having a degree of roundness of 0.80 or more and containing a calcium constituent and a lithium constituent at 850°C to 1150°C.

[Claim 9]

The method of producing the spherical crystalline silica particles according to any one of claims 5 to 8, wherein a temperature of the heat treatment is 875°C to 1100°C.