

DESCRIPTION

TITLE

SPHERICAL CRYSTALLINE SILICA PARTICLES, METHOD FOR PRODUCING SAME,
AND RESIN COMPOSITE COMPOSITION AND RESIN COMPOSITE CONTAINING
SAME

FIELD

[0001]

The present invention relates to spherical silica particles and a method of production of the same, in particular spherical crystalline silica particles with an amount of moisture discharged when heated to 800°C to 1000°C greater than that of conventional spherical crystalline silica particles, and a method of production of the same, and resin composite composition and resin composite containing those spherical crystalline silica particles.

BACKGROUND

[0002]

The increase in amount of information accompanying the advances in communication technology, the expansion of use of millimeter wave radar, etc. have led to higher frequencies being used. The circuit boards for transmitting these high frequency signals are comprised of electrodes forming the circuit patterns and dielectric boards. To keep down energy loss when transmitting high frequency signals, smaller dielectric dissipation factor ($\tan\delta$) of dielectric materials have become necessary. To lower the dielectric loss, dielectric materials have to have low polarity and low bipolar moment.

[0003]

As dielectric materials, mainly ceramic particles, resins, and their composites are being used. In particular, along with the increased utilization of the millimeter wave band in recent years, ceramic particles and resins with much lower dielectric dissipation factors ($\tan\delta$) are being sought. Resins have relatively small relative dielectric constants (ϵ_r) and are suited for high frequency devices, but the dielectric dissipation factors ($\tan\delta$) and thermal expansion coefficients are greater than ceramic particles. For this reason, for composites of ceramic particles and resins for millimeter wave band use, (1) lowering the dielectric dissipation factors ($\tan\delta$) of the ceramic particles themselves and (2) adding greater ceramic particles and reducing the amounts of resins exhibiting large dielectric dissipation factors ($\tan\delta$) are suitable.

[0004]

As ceramic particles, silica (SiO_2) particles have been used since the past. If the shape of

the silica particles is a shape with sharp corners, the fluidity, dispersibility, and fillability in a resin become poorer and the manufacturing apparatus is increasingly worn. To improve these, spherical silica particles are being widely used. The closer the spherical silica particles to true spheres, the more the fillability and fluidity in a resin and mold wear resistance are believed to be improved, so higher roundness of the particles have been sought. Furthermore, greater improvement of the fillability by establishment of a suitable particle size distribution of the particles has been studied.

[0005]

In general, as the method of production of spherical silica, the flame melting method is being used. In flame melting, particles are passed through a flame or other high temperature region whereby the particles melt and the particles become spherical in shape due to surface tension. The melted spherical particles are conveyed by air so that the particles do not fuse with each other and the thermally sprayed particles are rapidly cooled. Since they are rapidly cooled from the molten state, the silica does not crystallize. They become glassy particles having amorphous structures and are generally called “quartz glass”.

[0006]

The spherical silica particles formed by the flame melting method are amorphous, so are low in thermal expansion coefficient and thermal conductivity. The thermal expansion coefficient of amorphous silica particles is 0.5 ppm/K, while the thermal conductivity is 1.4W/mK. The thermal expansion coefficient is generally equal to that of quartz glass not having a crystal structure but having an amorphous structure. In general, the thermal expansion coefficient of Si, which is the main material of IC chips, is 3 to 5 ppm/K. The thermal expansion coefficient of the sealing resin for sealing IC chips is extremely large compared with Si, so the difference in thermal expansion behavior of the two materials (Si and sealing resin) causes IC chips to warp and obstructs production. On the other hand, if filling spherical silica with a small thermal expansion coefficient in a resin with a large thermal expansion coefficient in a high ratio, the effect is obtained of lowering the thermal expansion of the sealant (composite of spherical silica and resin) itself. It is possible to make the thermal expansion coefficient of the sealant a value close to that of Si so as to suppress deformation derived from the thermal expansion behavior at the time of sealing the IC chip. Further, regarding the thermal conductivity, it is preferable to have a high thermal conductivity from the viewpoint of improving the heat dissipation from IC chips.

[0007]

As explained above, as the properties sought from silica particles for sealant use, in addition to the fillability, fluidity, mold wear resistance, etc. enabling performance as a composite to be maintained when mixed in the resin in a large amount, there are excellent

dielectric properties for millimeter wave band high frequencies. Dielectric properties are physical properties of the material, so it was difficult to reduce the dielectric dissipation factor of amorphous silica particles.

[0008]

On the other hand, as the crystal structures of silica, there are cristobalite, quartz, tridymite, keatite, etc. Silica having these crystal structures are known to have higher thermal expansion coefficients and thermal conductivities and lower dielectric dissipation factors compared to amorphous silica. For this reason, various methods have been proposed for crystallizing amorphous silica to raise the thermal expansion coefficient and thermal conductivity and lower the dielectric dissipation factor (PTLs 1 to 4).

[0009]

PTL 1 shows a method of production of spherical crystalline silica particles characterized by preparing silica powder to contain aluminum in 400 to 5000 ppm, thermally spraying the prepared silica powder, holding the thermally sprayed spherical silica particles at 1100°C to 1600°C for 1 to 12 hours, and cooling to obtain spherical silica particles with 80% or more crystal phase. It describes that 95% to 100% of the crystal phase is comprised of cristobalite crystal phase.

[0010]

PTL 2 describes a method of production of spherical silica filler characterized by mixing spherical amorphous silica with an average roundness of 0.90 or more and alumina powder with a specific surface area of 40 m²/g or more and a bulk density of 0.1 g/cm³ or less to give 1000 ppm to 10000 ppm by aluminum conversion and heating them to 1200°C to 1350°C for 1 to 8 hours.

[0011]

PTL 3 describes a method of production of porous powder with a main crystal phase comprised of quartz characterized by adding to silica gel with an average particle size of 0.1 to 20 μm, a Zn compound to 0.5 mass% or more by ZnO conversion and heat treating this mixture at 900 to 1100°C.

[0012]

PTL 4 shows a method of production of spherical crystalline silica particles characterized by including a step of mixing with 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 the amorphous spherical silica particles and mass of the alkali metal by oxide conversion or of heat treating at 800°C to 1300°C spherical silica particles into which an alkali earth metal is mixed in by oxide conversion with respect to the total mass of the mass of the amorphous spherical silica particles and mass of the alkali metal by oxide conversion and cooling the heat

treated spherical silica particles and by the cooled spherical silica particles having 90 mass% or more crystal phase in which quartz crystals account for 70 mass% or more of the whole.

However, with an amount of alkali metal added of less than 0.4 mass% and an alkali earth metal of less than 1 mass%, the probability of appearance of quartz becomes lower.

5

[CITATIONS LIST]

[PATENT LITERATURE]

[0013]

[PTL 1] WO2016/031823

10 [PTL 2] Japanese Unexamined Patent Publication No. 2019-19222

[PTL 3] Japanese Unexamined Patent Publication No. 2002-20111

[PTL 4] WO2018/186308

[PTL 5] Japanese Unexamined Patent Publication No. 4-114065

15

SUMMARY

[TECHNICAL PROBLEM]

[0014]

The present inventors aimed at searching for filler particles for semiconductor sealing use having excellent dielectric properties in the millimeter wave band of a frequency of 30 GHz to 80 GHz and preparing a resin composite for high frequency device applications mixed with a resin. To obtain a resin composite with a low dielectric dissipation factor, first spherical molten (amorphous) silica was heat treated to crystallize it. That is, crystalline silica was confirmed to be greatly reduced in dielectric dissipation factor in the millimeter wave band (30 GHz to 80 GHz) compared with the amorphous silica which has been conventionally widely used. As a result, the spherical crystalline silica become silica particles exhibiting excellent dielectric properties for high frequency device applications. The crystalline silica obtained by heat treatment is quartz, cristobalite, or a mixture of the same. Quartz and cristobalite differ in values of physical properties, so when used as a filler, the phase of the crystalline silica is preferably a single phase.

30

[0015]

In a conventional resin composition for semiconductor sealing use, to raise the thermal shock strength, the method has been employed of filling silica particles with a thermal expansion coefficient close to a silicon chip as a sealant of a sealing resin as much as possible. The filling rate reaches up to 70 to 90% of the resin composition as a whole by weight. At this time, raising the adhesion of a filler and resin by adding a silane coupling agent to the resin composition has become commonly used art (for example, PTL 5). However, it has been learned that in silica

35

powder obtained by heat treating spherical amorphous silica particles to make at least part crystallize, even if adding a silane coupling agent, the adhesion with a resin does not sufficiently rise.

[0016]

5 It is known that the reaction sites between a silane coupling agent and silica particles are the silanol groups (Si-OH) present at the surfaces of the silica particles. On the other hand, in the methods for making the spherical amorphous silica crystallize described in the preceding PTLs, in PTL 1, heat treatment is performed at 1100°C to 1600°C, in PTL 2, at 1200°C to 1350°C, in PTL 3, 900 to 1100°C, and further in PTL 4, 800°C to 1300°C. Due to this, as the reason why
10 even if adding a silane coupling agent, the adhesion with a resin did not sufficiently rise, it is guessed that this is because the silanol groups of the silica surface formed siloxane bonds (Si-O-Si) by a dehydration condensation reaction and the silanol groups of the reaction sites with the silane coupling agent were almost entirely consumed. The silanol groups of the particle surfaces are considered to react by dehydration condensation at the time of heating at 800°C or more. The
15 silanol groups of the particle surfaces can be measured by analyzing silica powder by a temperature programmed desorption gas analyzer and detecting the amount of moisture discharged by heating at 800°C or more. Due to these, in spherical crystalline silica particles suitable for filler applications for semiconductor sealants having excellent dielectric properties in the millimeter wave band, to raise the reactivity with a silica coupling agent, it is believed that
20 silica particles with an amount of moisture discharged when heating to 800°C or more by a temperature programmed desorption gas analyzer greater than conventional spherical crystalline silica have become necessary.

[0017]

Therefore, the present invention has as its object the provision of spherical crystalline silica
25 particles suitable for filler applications for semiconductor sealants having excellent dielectric characteristics in the millimeter wave band, that is, spherical crystalline silica particles with a high crystallinity and with a large amount of moisture discharged when heated to 800°C or more by a temperature programmed desorption gas analyzer, and a method of production of the same and a resin composite composition and resin composite containing those spherical crystalline
30 silica particles.

[SOLUTION TO PROBLEM]

[0018]

35 The present inventors proceeded with intensive research for the purpose of solving the above problem. As a result, they discovered that by heat treating a powder comprised of amorphous spherical silica particles at a temperature of 900°C or more and 1550°C or less to

make the particles crystallize, then heat treating them in at least an atmosphere containing water vapor at 450°C or more and 830°C or less temperature, the amount of moisture discharged when heating by a temperature programmed desorption gas analyzer to 800°C or more increases compared with conventional crystalline silica and can be restored to an amount equal to or greater than that of amorphous silica particles before crystallization. The crystalline silica obtained by heat treatment has a roundness of 0.80 or more. Further, the type of the crystal may be quartz, cristobalite, or a mixture of the same. Quartz and cristobalite differ in values of physical properties, so when used as a filler, the phase of the crystalline silica is preferably a single phase. The “single phase” referred to here indicates a ratio of quartz or cristobalite in the crystalline silica of 80.0% mass% or more. Note that, to differentiate the former and latter heat treatment, the former may be called the “first heat treatment” or the “heat treatment for crystallization” and the latter may be called the “second heat treatment” or “heat treatment in the atmosphere containing water vapor.”

[0019]

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

(1) Spherical crystalline silica particles having a roundness of 0.80 or more, containing crystalline silica in 50.0% or more of the whole, and having an amount of moisture discharged when heating from 800°C to 1000°C by a temperature programmed desorption gas analyzer of 4.5 $\mu\text{g}/\text{m}^2$ or more.

(2) The spherical crystalline silica particles according to (1), wherein the amount of moisture is 7.0 $\mu\text{g}/\text{m}^2$ or more.

(3) The spherical crystalline silica particles according to any of (1) to (2), wherein a ratio of quartz or a ratio of cristobalite in the crystalline silica is 80.0% mass% or more.

(4) The spherical crystalline silica particles according to any one of (1) to (3), containing the crystalline silica in 75.0% or more of the whole.

(5) The spherical crystalline silica particles according to any one of (1) to (4), wherein the amount of moisture is 50.0 $\mu\text{g}/\text{m}^2$ or less.

(6) A method of production of spherical crystalline silica particles according to any one of (1) to (5), which method of production of spherical crystalline silica particles comprising heat treating the spherical amorphous silica particles at 900°C or more and 1550°C or less temperature to make them crystallize, then heat treating them in an atmosphere containing water vapor at 450°C or more and 830°C or less temperature.

(7) A resin composite composition comprising a resin containing spherical crystalline silica particles according to any one of (1) to (5).

(8) A resin composite comprising the cured resin composite composition according to (7).

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0020]

According to the present invention, it is possible to provide spherical crystalline silica particles suitable for filler applications for semiconductor sealants having excellent dielectric characteristics in the millimeter wave band, that is, spherical crystalline silica particles with a high crystallinity and with an amount of moisture discharged when heated to 800°C or more by a temperature programmed desorption gas analyzer greater than the amount of moisture of conventional spherical crystalline silica particles, and a method of production of the same. Furthermore, it is also possible to raise the ratio of cristobalite or quartz.

DESCRIPTION OF EMBODIMENTS

[0021]

The spherical crystalline silica according to one aspect of the present invention is spherical crystalline silica particles having a roundness of 0.80 or more, containing crystalline silica in 50.0% or more of the whole, and having an amount of moisture discharged when heating from 800°C to 1000°C by a temperature programmed desorption gas analyzer of $4.5 \mu\text{g}/\text{m}^2$ or more. The phase of the crystalline silica being 50.0% or more referred to here means the ratio of the phase of crystalline silica at the spherical silica particles. The method of finding it will be explained later. Further, the moisture (H_2O) discharged when heating the silica particles from 800°C to 1000°C by a temperature programmed desorption gas analyzer is quantified.

[0022]

As the crystal structure of silica (SiO_2), there are cristobalite, quartz, etc. Silicas having these crystal structures have higher thermal conductivities compared with amorphous silica. For this reason, in a filler for sealing semiconductors, it is possible to replace amorphous silica with a suitable amount of crystalline silica to therefore improve the heat dissipation from an IC chip. Furthermore, crystalline silica is low in dielectric dissipation factor in the millimeter wave band, so in a filler for sealing semiconductors, the more amorphous silica is replaced with crystalline silica, the more the dielectric dissipation factor of the semiconductor sealant falls. In the past, spherical crystalline silica was prepared by heat treating and crystallizing spherical amorphous silica. The obtained crystalline silica does not sufficiently rise in adhesion with a resin even if reacting with a silane coupling agent. At the time of crystallization of spherical amorphous silica, the material is fired at a high temperature of 800°C or more, so the silanol groups at the silica surface are subjected to a dehydration condensation reaction and the silanol groups are decreased or eliminated. As a result, it has been believed that almost all of the reaction sites with the silane coupling agent are eliminated.

[0023]

On the other hand, the crystalline silica of the present invention can be produced by heat treatment at 900°C or more and 1550°C or less temperature to cause crystallization, then heat treatment in an atmosphere containing water vapor at a 450°C or more and 830°C or less temperature. This spherical crystalline silica can be adjusted to an amount of moisture discharged when heated from 800°C to 1000°C by a temperature programmed desorption gas analyzer of 4.5 $\mu\text{g}/\text{m}^2$ or more. The greater the amount of moisture discharged, the more the concentration of silanol groups (Si-OH) at the silica surface increases, so the reaction sites when performing silane coupling treatment increase, so this is preferable. For this reason, the amount of moisture discharged is more preferably 7.0 $\mu\text{g}/\text{m}^2$ or more. On the other hand, if the amount of moisture discharged becomes too great, the increase in functional groups causes the dielectric dissipation factor to increase and sometimes the effect of reduction of the dielectric dissipation factor by introduction of crystalline silica ends up being lost. For this reason, the upper limit of the amount of moisture may be 50 $\mu\text{g}/\text{m}^2$ or less, more preferably may be 30 $\mu\text{g}/\text{m}^2$ or less equal to spherical amorphous silica. Note that, the spherical amorphous silica powder formed by the prior art flame melting method had an amount of moisture discharged of 7.4 $\mu\text{g}/\text{m}^2$ to 27.9 $\mu\text{g}/\text{m}^2$ when heated to 800°C to 1000°C by a temperature programmed desorption gas analyzer.

[0024]

(Spherical Amorphous Silica Particles)

The amorphous spherical silica particles used as a material can be prepared by the flame melting method or other method. In the flame melting method, natural silica powder crushed to adjust it to a desired particle size is made to pass through a flame so that the particles melt and the particles become spherical in shape due to surface tension. Due to such a flame melting method, it is possible to prepare spherical amorphous silica particles.

The composition of the spherical amorphous silica particles is not particularly limited so long as the main constituent is silica and the finally obtained spherical crystalline silica particles become the desired range. As one aspect, the composition of the spherical amorphous silica particles may comprise 98.0 mass% or more silica (SiO_2). Further, as trace elements, Ca, Li, Al, Na, Mg, Ba, Zn, etc. may be contained.

[0025]

(Method of Production of Spherical Crystalline Silica Particles)

[Heat Treatment for Crystallization]

The spherical crystalline silica particles of the present invention are produced by heat treatment of spherical amorphous silica. To accelerate the crystallization to quartz, for example it is also possible to produce them by mixing in a calcium element or lithium element and heat treating that mixture (also referred to as a “mixed material”). The crystallization temperature to

quartz is suitably 900°C or more and 1200°C or less. The crystallization temperature differs in preferable range depending on the type of the crystallization agent. If adding a calcium element, the crystallization temperature may be 1050°C to 1200°C in range. If a lithium element is added, the crystallization temperature may be 950°C to 1100°C. On the other hand, crystallization to cristobalite can proceed even without adding a crystallization agent if the heat treatment temperature becomes more than 1200°C. Provided, however, that if the temperature is more than 1550°C, the particles end up being sticking to each other due to sintering. For this reason, for crystallization to cristobalite, a 1250°C to 1500°C heat treatment temperature is preferable. The heat treatment atmosphere for crystallization can be made the air or other oxidizing atmosphere and nitrogen, argon, or other inert gas atmosphere. The atmospheric pressure is preferably the air pressure since the heat treatment is performed industrially in large amounts. On the other hand, a hot isostatic press etc. can be used to raise the atmospheric pressure. Typically, if the atmospheric pressure is 125 MPa or more and 200 MPa or less, by making the heat treatment temperature 1125°C or more and 1300°C or less, it is possible to raise the crystallinity to quartz without using lithium or another alkali metal element as a crystallization agent. The heat treatment time for crystallization can be suitably adjusted. It is 0.5 hour to 24 hours, preferably is 1 hour to 12 hours. Note that, the temperature elevation rate and the cooling rate at the time of heat treatment for crystallization do not greatly affect the formation of spherical crystalline silica particles when using an electric furnace for heat treatment.

[0026]

[Heat Treatment in Atmosphere containing Water vapor]

The spherical crystalline silica particles of the present invention can be produced by making the spherical amorphous silica crystallize by heat treatment, then performing heat treatment in an atmosphere including water vapor for at least 450°C or more and 830°C or less temperature. The heat treatment in an atmosphere containing water vapor may be performed separately from the heat treatment for crystallization. It is also possible to introduce water vapor into the atmosphere in the process of lowering the temperature in the heat treatment for crystallization. The water vapor pressure has a maximum value determined by the gas temperature. At a pressure over this value, presence in the state of water vapor is not possible. This maximum value is called the “saturated water vapor atmosphere.” The saturated water vapor pressure (Pa) can be calculated approximately from the formula of Tetens.

$$Pa \text{ (hPa)} = 6.1078 \times 10^{7.5 T / (T + 237.3)}$$

T: temperature [°C]

The water vapor atmosphere at the time of heat treatment can be formed by running air through a bubbling apparatus with a temperature adjustment function. This can be supplied to inside a furnace. By controlling the temperature of the bubbling apparatus in this way, it is

possible to make the volume ratio of the water vapor 5% to 90% in ratio with respect to the total of volumes of the atmospheric gas and water vapor (content of water vapor). If considering the changes in water vapor pressure with respect to the bubbling temperature, the water vapor content is preferably 10% to 70% in range. The heat treatment in an atmosphere containing water vapor can also be performed under pressure, but industrially, it is preferably the air pressure. The heat treatment time at the water vapor atmosphere is 1 hour to 48 hours. Preferably it is 5 hours to 25 hours.

[0027]

(Quartz Crystallization Agent)

(Calcium Material)

The calcium material, for example, may be mixed with the spherical amorphous silica particles and heat treated. The composition and mixed amount of the calcium material are not particularly limited so long as the finally obtained spherical crystalline silica particles become the desired range and are suitably adjusted. The calcium material may be calcium hydroxide, calcium oxide, etc. present stably in the air and may be natural minerals. The calcium material can be added in the state of a powder, 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 the trace elements contained in the spherical amorphous silica particles. For example, if the spherical amorphous silica particles sufficiently contain calcium and the desired calcium content is achieved by the finally obtained spherical crystalline silica particles, the spherical amorphous silica particles may also be used jointly as the calcium material. Further, if the spherical amorphous silica particles contain calcium, but not sufficiently, a calcium material can be added so that the desired calcium content is achieved by the finally obtained spherical crystalline silica particles.

[0028]

(Lithium Material)

The lithium material, for example, may be mixed with the spherical amorphous silica particles and heat treated. The composition and mixed amount of the lithium material are not particularly limited so long as the finally obtained spherical crystalline silica particles become the desired range and are suitably adjusted. The lithium material may be oxides, carboxides, hydroxides, nitrates, etc. The form added is not particularly limited. It can be added in the state of a powder, aqueous solution, etc. so as to be uniformly mixed with the spherical amorphous silica particles. Further, at least part of the lithium material may be the trace elements contained in the spherical amorphous silica particles. For example, if the spherical amorphous silica particles sufficiently contain lithium and the desired lithium content is achieved by the finally obtained spherical crystalline silica particles, the spherical amorphous silica particles may also

be used jointly as the lithium material. Further, if the spherical amorphous silica particles contain lithium, but not sufficiently, a lithium material can be added so that the desired lithium content is achieved by the finally obtained spherical crystalline silica particles.

[0029]

5 (Mixing with Crystallization Agent)

The spherical amorphous silica particles may be mixed with one or both of a calcium material and lithium material. Note that, the calcium material and/or lithium material may also be contained in the spherical amorphous silica. The method of mixing is not particularly limited so long as the different materials are evenly dispersed and mixed. The mixing may also be performed by a powder mixer. Due to the mixing, at least part of the spherical amorphous silica is contacted by the calcium material and lithium material and crystallization of the spherical amorphous silica, in particular crystallization to quartz, is accelerated in the following heat treatment step.

Note that, the mixing makes at least part of the spherical amorphous silica be contacted by the calcium material and lithium material. It does not accelerate crushing of the spherical amorphous silica, so the roundness does not fall much at all before and after mixing.

[0030]

The roundness of the spherical crystalline silica of the present invention sometimes falls somewhat before and after heat treatment for crystallization and heat treatment in a water vapor atmosphere. The amorphous silica particles sometimes join together by melt bonding or sintering and fall greatly in roundness, but the spherical crystalline silica particles of the present invention are rendered crystalline (already are not amorphous), so the particles can be kept from joining by melt bonding or sintering.

[0031]

25 (Circularity)

The spherical crystalline silica particles have a roundness of 0.80 or more. If the roundness is less than 0.80, if utilized as silica particles of a resin composite composition for semiconductor sealing material use etc., sometimes the fluidity, dispersibility, and fillability are not sufficient or wear of the equipment for manufacturing the sealing material is promoted. The spherical amorphous silica particles obtained by the flame melting method can give particles high in average roundness. The roundness of silica particles changes somewhat after heat treatment for crystallization and heat treatment in a water vapor atmosphere, but in the present invention, after heat treatment, the roundness of the spherical amorphous silica particles before heat treatment is adjusted to give a roundness of 0.80 or more. From the viewpoint of improvement of the fluidity, dispersability, and fillability and reduction of wear of equipment, the higher the roundness after heat treatment, the better. It may be 0.85 or more or may be 0.90 or more. On the other hand,

making the roundness 1.0, that is, a perfect circle, is sometimes difficult, so the upper limit of the roundness may be 0.99 or less or 0.97 or less.

[0032]

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

[0033]

(Properties of Crystal)

The spherical crystalline silica particles of the present invention contain a phase of crystalline silica. The ratio of the phase of crystalline phase silica in the spherical crystalline silica particles (overall) is 50.0 % or more. If the silica particles obtained by the heat treatment are comprised of amorphous and crystalline silica, the ratios of presence of the amorphous and crystalline silica (indicating so-called “degree of crystallization” and sometimes also called such in this Description) and the types of the crystalline silica and their ratios can be found by XRD. In XRD measurement, it is possible to find the ratio of the crystal phase by calculation by the following formula from the sum (I_c) of integrated intensities of the crystalline peaks and the integrated intensities (I_a) of the amorphous halo parts. More specifically, the ratio of the phase of crystalline silica contained in spherical crystalline silica particles can be found.

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

In the present invention, the XRD measurement was performed in the range of $2\Theta = 10^\circ$ to 90° . The ratio of the crystal phase 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 $2\Theta = 22^\circ$. In the spherical crystalline silica of the present invention, the ratio of quartz or the ratio of cristobalite in the phase of crystalline silica may be 80.0 mass% or more. The types of the quartz, cristobalite, and other crystal phase and their ratios (mass%) can be found by quantitative analysis by X-ray diffraction.

In the present invention, the quantitative analysis by X-ray diffraction was quantitative analysis using a method of analysis by the Rietveld method and without using a standard sample. In the present invention, an X-ray analysis apparatus "D2 PHASER" (made by Bruker) was used. The quantitative analysis of the crystal phase using the Rietveld method was performed by the crystal structure analysis software "TOPAS" (made by Bruker).

[0034]

The spherical crystalline silica particles of the present invention contain a phase of crystalline silica, the ratio of the phase of the crystalline silica in the spherical crystalline silica particles (overall) is 50.0 % or more, that is, a 50.0% or more high crystallinity, and the dielectric dissipation factor is preferably much lower compared with amorphous silica. From the viewpoint of reducing the dielectric dissipation factor, the higher the crystallinity, the more preferable. It may be 70.0% or more, more preferably may be 75.0% or more, still more preferably may be 90.0% or more.

[0035]

The spherical crystalline silica particles of the present invention contain a phase of crystalline silica. The ratio of the quartz or cristobalite in that phase of the crystalline silica is high and may be 80.0 mass% or more. The phase may also be substantially a single phase of quartz or cristobalite. For this reason, the thermal expansion coefficient, thermal conductivity, and other various properties of spherical crystalline silica particles are substantially determined by the properties of the quartz or cristobalite, that is, do not fluctuate. Use for a filler etc. is preferable. From the above viewpoint, the higher the ratio of quartz or cristobalite, the more preferable. The ratio may also be 85.0 mass% or more, more preferably may be 90.0 mass% or more.

[0036]

(Average Particle Size)

In one aspect of the present invention, the average particle size (D50) of the spherical crystalline silica particles may be 1 to 100 μm . If the average particle size is less than 1 μm , the agglomeration ability of particles becomes greater and the fluidity remarkably falls, so this is not preferable. If the average particle size is more than 100 μm , space between particles easily remains and it becomes difficult to raise the fillability, so this is not preferable. An average particle size of 2 to 50 μm is a more preferable range.

[0037]

The average particle size (D50) was measured by the laser diffraction-scattering type particle size distribution measurement method. In the volume-based particle size distribution, the median size D50 of a cumulative volume of 50% 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 are made to disperse 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 Cilas) was used.

Note that, the average particle size can be similarly found for the spherical amorphous silica particles.

[0038]

(Specific Surface Area)

The specific surface area was measured by the BET method using a Tristar II made by Micromeritics. The BET method is a method of analysis making nitrogen gas molecules powder particles with known adsorption occupancy areas of the surface be adsorbed at the surface of the powder particles and finding the specific surface area of the sample from the amount.

[0039]

(Temperature Programmed Desorption Gas Analysis)

The amount of moisture discharged when heating the silica particles was found by the temperature programmed desorption gas analysis method. The temperature programmed desorption gas analysis method is a mass analysis method enabling the gas generated for each temperature when heating/raising the temperature in a high vacuum to be monitored. For the temperature programmed desorption gas analyzer, a TDS1200 model made by ESCO Ltd. was used. A silica powder sample was placed in a sample holder made of quartz, then was placed on a sample stage and heated by a halogen lamp from the bottom of the stage in a high vacuum (10^{-7} Pa). In the temperature programmed desorption gas analyzer, a TDS1200 model made by ESCO Ltd., there are two types of thermocouples: a thermocouple inserted in the sample stage and a thermocouple placed above the sample stage. The heating was controlled using the sample stage thermocouple. Further, the sample temperature was measured using the thermocouple (W-Re) set above the stage. The tip of the thermocouple was made to contact the floor inside the quartz holder. The amount of gas discharged from a quartz board was measured (blank measurement) in advance. The amount of moisture of the gas generated by the heating was calculated by cumulatively adding the ion current strength of m/z 18 obtained by a quadrupole mass analyzer and using a TDS1200 model analysis software (TDS data processing application Ver5.2.0.5). The amount of moisture was quantified from room temperature to 1000°C. The amount of moisture derived from dehydration condensation of the silanol groups at the silica surface is discharged by heating at 800°C or more, so the amount of moisture discharged at 800°C to 1000°C was focused on.

[0040]

(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 resin and further a resin composite obtained by curing the resin composite composition. The composition of the resin composite composition will be explained below:

[0041]

It is possible to use a slurry composition including the spherical crystalline silica particles and resin to obtain a semiconductor sealant (in particular a solid sealing agent), interlayer insulating film, or other resin composite composition. Furthermore, by making these resin composite compositions harden, it is possible to obtain a sealant (cured article), a board for a semiconductor package, or other resin composite.

[0042]

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, silane coupling agent, etc. can be added according to need and compounded by kneading or another known method. Further, it is possible to form it into pellets, film, etc. according to the application.

[0043]

Further, when producing the resin composite composition, in addition to the spherical crystalline silica particles and resin, other inorganic fillers may be added. As the inorganic filler, amorphous spherical silica particles, alumina particles, titania particles, magnesia particles, aluminum nitride particles, boronitride particles, barium titanate particles, and calcium titanate particles may be mentioned. The ratio of mixture of the inorganic fillers can be suitably adjusted according to the application of the resin composite composition.

[0044]

Furthermore, when curing the resin composite composition to produce a resin composite, for example, the resin composite composition can be heated to melt it and then worked into the shape for its application and then be heated higher than when melted to make it completely cure. In this case, a transfer mold or other known method can be used.

[0045]

For example, when producing a package use board or interlayer insulating film or other semiconductor related material, as the resin used for the resin composite composition, a known resin can be used, but it is preferable to employ an epoxy resin. 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. Among these, single types can be used alone or two types or more having different molecular weights can be

used together. Among these as well, from the viewpoint of curability, heat resistance, etc., an epoxy resin having two or more epoxy groups in its 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 resins which have been epoxylated, bisphenol A, bisphenol F, bisphenol S, and other glycidyl ethers, glycidyl ester acid epoxy resin obtained by a reaction of phthalic acid or dimer acid or other polybasic acid and epichlorohydrin, linear aliphatic epoxy resin, alicyclic epoxy resins, heterocyclic epoxy resin, alkyl-modified functional epoxy resin, β -naphthol novolac type epoxy resin, 1,6-dihydroxynaphthalene type epoxy resin, 2,7-dihydroxynaphthalene type epoxy resin, bishydroxybiphenyl type epoxy resin, and further epoxy resins in which bromine or another halogen is introduced for imparting flame resistance etc. may be mentioned. Among these epoxy resins having two or more epoxy groups in their molecules, in particular a bisphenol A type epoxy resin is preferable.

[0046]

Further, as a resin used for applications other than a composite material for sealing semiconductors, for example, prepregs for printed boards, various engineering plastics and other resin composite compositions, a resin other than an epoxy based one can also be used. Specifically, in addition to an epoxy resin, a silicone resin, phenol resin, melamine resin, urea resin, unsaturated polyester, fluororesin, polyimide, polyamide imide, polyether imide, or other polyamide; polybutylene terephthalate, polyethylene terephthalate, or other polyester; polyphenylene sulfide, aromatic polyester, polysulfone, liquid crystal polymer, polyether sulfone, polycarbonate, maleimide modified resin, ABS resin, AAS (acrylonitrile-acryl rubber styrene) resin, and AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resin may be mentioned.

As the curing agent used for the resin composite composition, a curing agent known for curing the resin 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 phenol type, etc. can be used alone or in combinations of two types or more.

[0047]

The amount of the phenol curing agent mixed in is preferably 0.1 or more and less than 1.0 by equivalent ratio with the epoxy resin (phenolic hydroxy group equivalent/epoxy group equivalent). Due to this, unreacted phenol curing agent no longer remains and the moisture absorption heat resistance is improved.

[0048]

The amount of addition of the spherical crystalline silica particles of the present invention in a resin composite composition is preferably large from the viewpoint of the heat resistance and thermal expansion coefficient, but is usually suitably 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 added is too small, the effects of improvement of strength, suppression of thermal expansion, etc. of the sealing material are hard to obtain. Further, if conversely too great, regardless of surface treatment of the silica powder, in the composite material, segregation easily occurs due to agglomeration of silica powder, the viscosity of the composite material becomes too great, and other problems arise, so practical use as a sealing material becomes difficult.

[0049]

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

EXAMPLES

[0050]

The present invention will be explained through the following examples and comparative examples. Provided, however, that the present invention shall not be interpreted as limited to the following examples.

[0051]

(Example 1 to Example 6)

Amorphous silica particles were prepared by the flame melting method. Into the spherical amorphous silica particles (average particle size d₅₀: 3.5 μm), calcium hydroxide particles were mixed, then the particles were filled in an alumina container and heat treated using an electric furnace SUPER-BURN (made by Motoyama) in an air atmosphere (atmospheric pressure). The amount of calcium hydroxide mixed was made 0.9 mass%, by oxide conversion, with respect to the mass of the total of the mass of the spherical amorphous silica and the mass of calcium by oxide conversion. The particles were raised in temperature by a temperature elevation rate of 300°C/h to 1080°C and held there for 24 hours. After that, they were cooled by a temperature lowering rate of about 100°C/h until room temperature. By heat treatment in the air, silica powder containing crystalline silica was obtained. The silica powder was packed in an alumina crucible and reheated by an electric furnace with a Siliconit heating element having a water vapor bubbling device. The temperature elevation rate was made 250°C/h. At the point when the furnace temperature reached 100°C, air gas containing water vapor was made to flow into the furnace through a water vapor bubbling device. The maximum temperature of the furnace was 500°C (Example 1), 700°C (Examples 2, 5, 6), 750°C (Example 3), and 800°C (Example 4), and the holding time at the peak temperature was made 24 hours (Example 1 to Example 5) and 6 hours (Example 6). The water vapor content in the air gas introduced into the furnace was made 50% (Examples 1 to 4 and Example 6) and 10% (Example 5). The particles were cooled by a

temperature lowering rate of about 100°C/h down to room temperature. Air containing water vapor was introduced into the furnace until cooled to room temperature.

[0052]

(Example 7 and Example 8)

Amorphous silica particles were prepared by the flame melting method to obtain spherical amorphous silica particles (average particle size d50: 10.4 μm). No crystallization agent was added. The particles were filled in an alumina container and heat treated using an electric furnace SUPER-BURN (made by Motoyama) in an air atmosphere (atmospheric pressure). The particles were raised in temperature by a temperature elevation rate of 300°C/h to 1300°C and held there for 24 hours. After that, they were cooled by a temperature lowering rate of about 100°C/h until room temperature. By heat treatment in the air, silica powder containing crystalline silica was obtained. The silica powder was packed in an alumina crucible and heated by an electric furnace with a Siliconit heating element having a water vapor bubbling device. The temperature elevation rate was made 250°C/h. At the point when the furnace temperature reached 100°C, air gas containing water vapor was made to flow into the furnace through a water vapor bubbling device. The maximum temperature of the furnace was 700°C (Example 7) and 800°C (Example 8), and the holding time at the peak temperature was made 24 hours. The water vapor content in the air gas introduced into the furnace was made 50%. The particles were cooled by a temperature lowering rate of about 100°C/h down to room temperature. Air containing water vapor was introduced into the furnace until cooled to room temperature.

[0053]

(Example 9 to Example 12)

Amorphous silica particles were prepared by the flame melting method. Into the spherical amorphous silica particles (average particle size d50: 15.4 μm), calcium hydroxide particles and lithium carbonate particles were mixed. The calcium hydroxide particles were mixed in by 0.6 mass% by oxide conversion and the lithium carbonate particles were mixed in by 0.05 mass% by oxide conversion with respect to the mass of the total of the mass of the spherical amorphous silica and the mass of calcium by oxide conversion and lithium by oxide conversion. The particles were raised in temperature by a temperature elevation rate of 300°C/h to 1050°C (Example 9), 1100°C (Example 10), 1150°C (Example 11), and 1230°C (Example 12) and held there for 24 hours. After that, they were cooled by a temperature lowering rate of about 100°C/h until room temperature. By heat treatment in the air, silica powder containing crystalline silica was obtained. The silica powder was packed in an alumina crucible and reheated by an electric furnace with a Siliconit heating element having a water vapor bubbling device. The temperature elevation rate was made 250°C/h. At the point when the furnace temperature reached 100°C, air gas containing water vapor was made to flow into the furnace through a water vapor bubbling

device. The maximum temperature of the furnace was 750°C (Example 9) and 700°C (Example 10 to Example 12) and the holding time was made 24 hours. The particles were cooled by a temperature lowering rate of about 100°C/h down to room temperature. Air containing water vapor was introduced into the furnace until cooled to room temperature.

[0054]

(Example 13)

Amorphous silica particles were prepared by the flame melting method. In the flame melting, a powder obtained by mixing crushed shaped silica and calcium hydroxide was thermally sprayed. The mixed powder was powder obtained by mixing calcium in 0.80 mass% by oxide conversion with respect to the mass of the total of the mass of the crushed shaped silica and mass of the calcium by oxide conversion. The average particle size d50 of the spherical amorphous silica particles obtained by flame melting was 39.0 μm. The powder was packed into a container made of BN and heat treated by a hot isostatic pressing (HIP) device to obtain silica powder containing crystalline silica. The atmospheric gas was nitrogen, the pressure was 196 MPa, the peak temperature was 1250°C, and the holding time was 24 hours. The obtained silica powder containing crystalline silica was packed in an alumina crucible and reheated by an electric furnace with a Siliconit heating element having a water vapor bubbling device. The temperature elevation rate was made 250°C/h. At the point when the furnace temperature reached 100°C, air gas containing water vapor was made to flow into the furnace through a water vapor bubbling device. The maximum temperature of the furnace was 700°C and the holding time was made 24 hours. The particles were cooled by a temperature lowering rate of about 100°C/h down to room temperature. Air containing water vapor was introduced into the furnace until cooled to room temperature.

[0055]

(Comparative Example 1 to Comparative Example 3)

Amorphous silica particles were prepared by the flame melting method. Into the spherical amorphous silica particles (average particle size d50: 3.5 μm), calcium hydroxide particles were mixed, then the particles were filled in an alumina container and heat treated using an electric furnace SUPER-BURN (made by Motoyama) in an air atmosphere (atmospheric pressure). The amount of calcium hydroxide mixed was made 0.9 mass%, by oxide conversion, with respect to the mass of the total of the mass of the spherical amorphous silica and the mass of calcium by oxide conversion. The particles were raised in temperature by a temperature elevation rate of 300°C/h to 1080°C and held there for 24 hours. After that, they were cooled by a temperature lowering rate of about 100°C/h until room temperature. By heat treatment in the air, silica powder containing crystalline silica was obtained. The silica powder was packed in an alumina crucible and reheated by an electric furnace with a Siliconit heating element having a water

vapor bubbling device. The temperature elevation rate was made 250°C/h. At the point when the furnace temperature reached 100°C, air gas containing water vapor was made to flow into the furnace through a water vapor bubbling device. The maximum temperature of the furnace was 400°C (Comparative Example 1), 860°C (Comparative Example 2), and 900°C (Comparative Example 3), and the holding time at the peak temperature was made 24 hours. The water vapor content in the air gas introduced into the furnace was made 50%. The particles were cooled by a temperature lowering rate of about 100°C/h down to room temperature. Air containing water vapor was introduced into the furnace until cooled to room temperature.

[0056]

(Comparative Example 4 and Comparative Example 5)

Amorphous silica particles were prepared by the flame melting method. These were spherical amorphous silica particles (average particle size d50: 10.4 μm). No crystallization agent was added. The particles were filled in an alumina container and heat treated using an electric furnace SUPER-BURN (made by Motoyama) in an air atmosphere (atmospheric pressure). They were raised in temperature by a temperature elevation rate of 300°C/h to 1300°C and held there for 24 hours. After that, they were cooled by a temperature lowering rate of about 100°C/h until room temperature. By heat treatment in the air, silica powder containing crystalline silica was obtained. The silica powder was packed in an alumina crucible and heated by an electric furnace with a Siliconit heating element having a water vapor bubbling device. The temperature elevation rate was made 250°C/h. At the point when the furnace temperature reached 100°C, air gas containing water vapor was made to flow into the furnace through a water vapor bubbling device. The maximum temperature of the furnace was 400°C (Comparative Example 4) and 900°C (Comparative Example 5) and the holding time at the peak temperature was made 24 hours. The water vapor content in the air gas introduced into the furnace was made 50%. The particles were cooled by a temperature lowering rate of about 100°C/h down to room temperature. Air containing water vapor was introduced into the furnace until cooled to room temperature.

[0057]

(Reference Example 1 to Reference Example 4)

Amorphous silica particles were prepared by the flame melting method. The average particle sizes of the spherical amorphous silica particles were d50: 2.2 μm (Reference 1), d50: 10.2 μm (Reference 2), d50: 15.2 μm (Reference 3), and d50: 37.0 μm (Reference 4).

[0058]

The ratios of presence of the amorphous and crystalline silica and the types of the crystalline silica and their ratios of the silica particles obtained by heat treatment (Example 1 to Example 13 and Comparative Example 1 to Comparative Example 4) were found by XRD. In the present

invention, an X-ray diffraction apparatus “D2 PHASER” (made by Bruker) was used. Quantitative analysis of the crystal phase by the Rietveld method was performed by the crystal structure analysis software “TOPAS” (made by Bruker).

[0059]

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

[0060]

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 Cilas) was used.

[0061]

(Temperature Programmed Desorption Gas Analysis)

The amount of moisture discharged when heating the silica particles was found by the temperature programmed desorption gas analysis method. The temperature programmed desorption gas analysis method is a mass analysis method enabling the gas generated for each temperature when heating/raising the temperature in a high vacuum to be monitored. For the temperature programmed desorption gas analyzer, a TDS1200 model made by ESCO Ltd. was used. A silica powder sample was placed in a sample holder made of quartz, then was placed on a sample stage and heated by a halogen lamp from the bottom of the stage in a high vacuum (10^{-7} Pa). In the temperature programmed desorption gas analyzer made by ESCO Ltd., there are two types of thermocouples: a thermocouple inserted in the sample stage and a thermocouple placed above the sample stage. The heating was controlled using the sample stage thermocouple. Further, the sample temperature was measured using the thermocouple (W-Re) set above the stage. The tip of the thermocouple was made to contact the floor inside the quartz holder. The amount of gas discharged from a quartz board was measured (blank measurement) in advance. The amount of moisture of the gas generated by the heating was calculated by cumulatively adding the ion current strength of m/z 18 obtained by a quadrupole mass analyzer and using a TDS1200 model analysis software (TDS data processing application Ver5.2.0.5). The amount of moisture from room temperature to 1000°C was quantified. The amount of moisture derived from the dehydration condensation of the silanol groups at the silica surface was discharged by heating at 800°C or more, so the amount of moisture discharged was calculated at 800°C to 1000°C.

[0062]

(Amount of Moisture Discharged Per Unit Area)

The surface area per unit weight is known from the measurement of the specific surface area by BET. Further, by temperature programmed dehydration gas analysis, the amount of moisture discharged per weight can be quantified, so it is possible to calculate the amount of moisture discharged per unit area ($\mu\text{g}/\text{m}^2$).

[0063]

In the spherical crystalline silica particles obtained by the examples according to the present invention, in each case, the roundness is 0.80 or more, crystalline silica is contained in 50.0% or more of the whole, and the amount of moisture discharged when heated from 800°C to 1000°C by a temperature programmed desorption gas analyzer (after heat treatment in the atmosphere containing water vapor) is $4.5 \mu\text{g}/\text{m}^2$ or more. Further, the ratio of the quartz or cristobalite in the crystalline silica is 80.0% mass% or more.

The average particle sizes of the spherical crystalline silica particles of the present invention using spherical amorphous silica particles of $3.5 \mu\text{m}$ as a material (Examples 1 to 6) were $3.4 \mu\text{m}$ to $3.6 \mu\text{m}$. Further, the average particle sizes of the spherical crystalline silica particles of the present invention using spherical amorphous silica particles of $10.4 \mu\text{m}$ as a material (Examples 7 to 8) were $10.3 \mu\text{m}$ and $10.4 \mu\text{m}$.

Still further, the particle sizes of the spherical crystalline silica particles of the present invention using spherical amorphous silica particles of $15.4 \mu\text{m}$ as a material (Examples 9 to 12) were $15.2 \mu\text{m}$ to $15.6 \mu\text{m}$.

Further, the average particle size of the spherical crystalline silica particles of the present invention using spherical amorphous silica particles of $39.0 \mu\text{m}$ as a material (Example 13) was $39.5 \mu\text{m}$.

[0064]

Comparing Example 1 to Example 4 and Comparative Examples 1 to 3, it is learned that by heat treating spherical amorphous silica particles with a roundness of 0.80 or more at a 900°C or more and 1550°C or less temperature to cause them to crystallize, then heat treating them in an atmosphere containing water vapor at a 450°C or more and 830°C or less temperature range, the amount of moisture discharged when heating to 800°C to 1000°C by a temperature programmed desorption gas analyzer (after heat treatment in the atmosphere containing water vapor) becomes $4.5 \mu\text{g}/\text{m}^2$ or more. In Comparative Example 1, the heat treatment temperature in the water vapor atmosphere is 400°C while in Comparative Example 2 and Comparative Example 3, the temperatures are respectively 860°C and 900°C, but if the temperature is less than 450°C or a higher temperature than 830°C, the amount of moisture (after heat treatment in the atmosphere containing water vapor) does not increase compared with before the water vapor atmosphere and is less than $4.5 \mu\text{g}/\text{m}^2$. The ratios of crystalline silica in Examples 1 to 4 and Comparative Example 1 to Comparative Example 3 are 77% of the whole, while the ratio of quartz in the

crystalline silica is 84.5%.

[0065]

If comparing Example 2 and Example 5, even if changing the water vapor atmosphere of the heat treatment in the atmosphere containing water vapor to a water vapor content of 10% or 50%, the spherical crystalline silica of the present invention can be obtained. Further, if comparing Example 2 and Example 6, it is learned that the spherical crystalline silica of the present invention can be obtained both if the treatment time in the heat treatment in the atmosphere containing water vapor is 24 hours and 6 hours.

[0066]

If comparing Example 7 to Example 8 and Comparative Examples 4 to 5, it is learned that by heat treating spherical amorphous silica particles with a roundness of 0.80 or more at 1300°C temperature to crystallize them, then heat treating them in an atmosphere containing water vapor in a 450°C or more and 830°C or less temperature range, the amount of moisture discharged when heated to 800°C to 1000°C by a temperature programmed desorption gas analyzer (after heat treatment in the atmosphere containing water vapor) becomes 4.5 $\mu\text{g}/\text{m}^2$ or more. In Comparative Example 4, the heat treatment temperature in the water vapor atmosphere is 400°C, while in Comparative Example 5, it is 900°C, but if the temperature is less than 450°C or higher than 830°C, the amount of moisture (after heat treatment in the atmosphere containing water vapor) will not increase compared with before the water vapor atmosphere but will be less than 4.5 $\mu\text{g}/\text{m}^2$. The ratios of crystalline silica in Examples 7 to 8 and Comparative Examples 4 to 5 were 90.2% of the whole while the ratio of cristobalite in the crystalline silica was 100%.

[0067]

Example 9 to Example 13 are spherical crystalline silicas of the present invention obtained by changing the ratios in the crystalline silica as a whole and ratios of quartz or cristobalite in the crystalline silica. It is learned that by heat treating spherical amorphous silica particles with a roundness of 0.80 or more at 1050 to 1250°C temperature to crystallize them, then heat treating them in an atmosphere containing water vapor in a 450°C or more and 830°C or less temperature range, the amount of moisture discharged when heated to 800°C to 1000°C by a temperature programmed desorption gas analyzer (after heat treatment in the atmosphere containing water vapor) becomes 4.5 $\mu\text{g}/\text{m}^2$ or more.

[0068]

Spherical amorphous silica powders produced by the prior art flame melting method are shown in Reference Example 1 to Reference Example 4. The amounts of moisture detected by 800°C to 1000°C temperature programmed desorption gas analysis were 7.4 to 27.9 $\mu\text{g}/\text{m}^2$. When analyzing by TDS the silicas heat treated for crystallizing spherical crystalline silica described in Example 1 to Example 13, the amounts of moisture discharged in the 800°C to

1000°C temperature range (before treatment in water vapor atmosphere) were 0.0 to 3.5 $\mu\text{g}/\text{m}^2$ or less than the amount of moisture 4.5 $\mu\text{g}/\text{m}^2$ of the present invention.

[0069]

[Table 1]

Table 1. Examples and Comparative Examples

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13
Silica before heat treatment in water vapor atmosphere													
Amorphous silica %	23.0	23.0	23.0	23.0	23.0	23.0	9.8	9.8	47.9	39.9	24.4	14.5	13.3
Crystalline silica %													
Breakdown %													
Quartz	77.0	77.0	77.0	77.0	77.0	77.0	90.2	90.2	52.1	60.1	75.6	85.5	86.7
Crystobalite	65.1	65.1	65.1	65.1	65.1	65.1	0	0	51.6	58.4	60.3	19.2	81.3
	11.9	11.9	11.9	11.9	11.9	11.9	90.2	90.2	0.5	1.7	15.3	66.3	5.8
Ratio of quartz in crystal phase	84.5	84.5	84.5	84.5	84.5	84.5	0.0	0.0	99.0	97.2	79.8	22.5	93.8
Ratio of crystobalite in crystal phase	15.5	15.5	15.5	15.5	15.5	15.5	100.0	100.0	1.0	2.8	20.2	77.5	6.7
Roundness	0.99	0.99	0.99	0.99	0.99	0.99	0.94	0.94	0.91	0.93	0.93	0.88	0.9
d50 μm	3.5	3.5	3.5	3.5	3.5	3.5	10.4	10.4	15.4	15.4	15.4	15.4	39.0
Specific surface area (m^2/g)	4.2	4.2	4.2	4.2	4.2	4.2	0.7	0.7	0.9	0.9	0.9	0.9	0.8
Heat treatment in water vapor atmosphere													
Water vapor atmosphere (%)	50	50	50	50	10	50	50	50	50	50	50	50	50
Treatment temp. ($^{\circ}\text{C}$)	500	700	750	800	700	700	700	800	750	700	700	700	700
Treatment time (hr)	24	24	24	24	24	6	24	24	24	24	24	24	24
Amount of moisture discharged													
800 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$													
Before heat treatment in water vapor atmosphere ($\mu\text{g}/\text{m}^2$)	2.7	2.7	2.7	2.7	2.7	2.7	0.0	0.0	3.5	3.0	1.8	0.6	2.0
After heat treatment in water vapor atmosphere ($\mu\text{g}/\text{m}^2$)	6.1	12.3	9.3	4.6	11.2	8.8	5.2	4.5	56.7	20.2	8.9	5.8	13.5
Roundness after heat treatment in water vapor atmosphere	0.93	0.93	0.93	0.93	0.93	0.93	0.92	0.92	0.9	0.91	0.89	0.86	0.87
d50 μm after heat treatment in water vapor atmosphere	3.6	3.5	3.6	3.5	3.4	3.5	10.3	10.4	15.2	15.6	15.5	15.4	39.5
Specific surface area after heat treatment in water vapor atmosphere (m^2/g)	4.2	4.2	4.2	4.2	4.2	4.2	0.7	0.9	0.9	0.9	0.9	0.9	0.8

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5
Silica before heat treatment in water vapor atmosphere					
Amorphous silica %	23.0	23.0	23.0	9.8	9.8
Crystalline silica %	77.0	77.0	77.0	90.2	90.2
Breakdown %	82.0 18.0	82.0 18.0	63.1 13.9 82.0 18.0 63.1 13.9	0 100	0 100
Quartz				90.2	90.2
Crystobalite					
Ratio of quartz in crystal phase	82.0	82.0	82.0	0	0
Ratio of cristobalite in crystal phase	18.0	18.0	18.0	100	100
Roundness	0.99	0.99	0.99	0.94	0.94
d50 μm	3.5	3.5	3.5	10.4	10.4
Specific surface area (m^2/g)	4.2	4.2	4.2	0.7	0.7
Heat treatment in water vapor atmosphere					
Water vapor atmosphere (%)	50	50	50	50	50
Treatment temp. ($^{\circ}\text{C}$)	400	860	900	400	900
Treatment time (hr)	24	24	24	24	24
Amount of moisture discharged					
800 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$					
Before heat treatment in water vapor atmosphere ($\mu\text{g}/\text{m}^2$)	2.7	2.7	2.7	0	0
After heat treatment in water vapor atmosphere ($\mu\text{g}/\text{m}^2$)	2.7	2.3	1.9	0	0
Roundness after heat treatment in water vapor atmosphere	0.97	0.95	0.94	0.92	0.90
d50 μm after heat treatment in water vapor atmosphere	3.5	3.5	3.5	10.4	10.4
Specific surface area after heat treatment in water vapor atmosphere (m^2/g)	4.2	4.2	4.2	0.7	0.7

Ref. Ex. 1	Ref. Ex. 2	Ref. Ex. 3	Ref. Ex. 4
100	100	100	100
0	0	0	0
0.99	0.93	0.92	0.89
2.2	10.2	15.2	37.0
7.3	3.2	0.9	0.8
74	10.0	21.1	27.9
2.2	10.2	15.2	37.0

INDUSTRIAL APPLICABILITY

[0070]

The spherical crystalline silica particles of the present invention are not limited to materials for sealing semiconductors. They may also be used for other applications. Specifically, they can
5 be used for prepregs for printed circuit boards and various engineering plastics etc.

CLAIMS

[Claim 1]

5 Spherical crystalline silica particles having a roundness of 0.80 or more, containing crystalline silica in 50.0% or more of the whole, and having an amount of moisture discharged when heating from 800°C to 1000°C by a temperature programmed desorption gas analyzer of 4.5 $\mu\text{g}/\text{m}^2$ or more.

[Claim 2]

10 The spherical crystalline silica particles according to claim 1, wherein the amount of moisture is 7.0 $\mu\text{g}/\text{m}^2$ or more.

[Claim 3]

15 The spherical crystalline silica particles according to claim 1 or 2, wherein a ratio of quartz or a ratio of cristobalite in the crystalline silica is 80.0% mass% or more.

[Claim 4]

20 The spherical crystalline silica particles according to any one of claims 1 to 3, containing the crystalline silica in 75.0% or more of the whole.

[Claim 5]

The spherical crystalline silica particles according to claim 1, wherein the amount of moisture is 50.0 $\mu\text{g}/\text{m}^2$ or less.

[Claim 6]

25 A method of production of spherical crystalline silica particles according to any one of claims 1 to 5, which method of production of spherical crystalline silica particles comprising heat treating the spherical amorphous silica particles at 900°C or more and 1550°C or less temperature to make them crystallize, then heat treating them in an atmosphere containing water
30 vapor at 450°C or more and 830°C or less temperature.

[Claim 7]

35 A resin composite composition comprising a resin containing spherical crystalline silica particles according to any one of claims 1 to 5.

[Claim 8]

A resin composite comprising the cured resin composite composition according to claim 7.