

DESCRIPTION

TITLE OF THE INVENTION: SPHERICAL CRYSTALLINE SILICA PARTICLES,
SPHERICAL SILICA PARTICLE MIXTURE, AND COMPOSITE MATERIAL

TECHNICAL FIELD

[0001]

The present invention relates to spherical crystalline silica particles having excellent dielectric properties, which are suitable for forming a semiconductor encapsulant for high frequencies corresponding to a high frequency signal having a frequency of 3 GHz or more and forming a wiring substrate, and to a spherical silica particle mixture containing the same and to a composite material obtained by combining the same with a resin.

BACKGROUND ART

[0002]

The frequency for communication technology is increasing due to the increase in the amount of information accompanying the sophistication of communication technology and the rapid expansion of use of millimeter-wave bands such as millimeter-wave radar. Semiconductors that handle these high-frequency signals and circuit boards that transmit them are composed of electrodes and dielectrics that form a circuit pattern. Since suppression of signal propagation delay is important for high-speed signal transmission, a low relative dielectric constant (ϵ_r) is required. In addition, in order to suppress energy loss during signal transmission, it is necessary that the dielectric loss tangent ($\tan \delta$) of the dielectric material is small. For low dielectric loss, the dielectric material must have a low polarity and a low dipole moment. In addition to these dielectric properties, when

mounting the substrate, thermal properties such as heat generation from IC chips, suppression of thermal expansion mismatch with the electrode material, thermal conductivity and coefficient of thermal expansion, and mechanical properties such as high bending strength, etc. are also important.

[0003]

As the dielectric material, ceramic fillers, resins, and composites obtained by combining them are mainly used. In particular, with the recent expansion of the use of the millimeter wave band, ceramic fillers and resins having even lower ϵ_r and lower $\tan \delta$ are required. The resin has a relatively small ϵ_r and is suitable for high frequencies, but has a $\tan \delta$ and a coefficient of thermal expansion larger than those of the ceramic filler. For this reason, in the composite in which the filler for the millimeter wave band and the resin are combined, it is suitable that (1) the ceramic filler itself has a low ϵ_r and low $\tan \delta$, and that (2) the ceramic filler is highly filled and the amount of the resin showing a large $\tan \delta$ is reduced.

[0004]

Silica (SiO_2) particles have been conventionally used as ceramic fillers. If the shape of the silica particles is angular, the fluidity, dispersibility, and filling property in the resin are deteriorated, and the manufacturing equipment is also worn. In order to improve these properties, spherical silica particles are widely used. It is considered that the closer the spherical silica filler is to a true sphere, the better the filling property, fluidity, and mold wear resistance, and a filler having a high circularity has been pursued. In addition, further improvement of filling property has been studied by optimizing the particle diameter distribution of the filler. However, if the filling rate is increased too much by spheroidizing the filler shape

and optimizing the particle diameter distribution, the fluidity of the composite as an encapsulant is lowered and its moldability is deteriorated. In order to secure high fluidity, it is difficult to achieve the silica filler filling rate of 85% by mass or more, and conventionally, it has been limited to less than 85% by mass.

[0005]

Thermal spraying is known as a method for producing a spherical silica. In thermal spraying, crushed silica particles as a raw material are passed through a flame at 2000 °C or higher to melt the particles, and the shape of the particles becomes spherical due to surface tension. The molten spheroidized particles are transported by air flow so that they do not fuse with each other and are collected, and the particles after thermal spraying are rapidly cooled. This silica (molten silica) has an amorphous structure because it is rapidly cooled from the molten state.

[0006]

Since this spherical molten silica is amorphous, its coefficient of thermal expansion and thermal conductivity are low. The coefficient of thermal expansion of amorphous silica is 0.5 ppm/K, and the thermal conductivity is 1.4 W/mK. These physical properties are substantially the same as the coefficient of thermal expansion of quartz glass, which has an amorphous structure and does not have a crystal structure. Therefore, by mixing with a resin having a high coefficient of thermal expansion, the effect of lowering the thermal expansion of the encapsulant itself can be obtained. By setting the coefficient of thermal expansion of the composite as an encapsulant to a value close to Si, deformation due to thermal expansion behavior can be suppressed when the IC chip is encapsulated.

[0007]

However, the encapsulant (composite) excessively highly filled with amorphous silica which has a low coefficient of thermal expansion, may have a smaller coefficient of thermal expansion than Si. Due to the heating temperature during reflow and the operating temperature of the semiconductor device, warpage or cracks may occur. Further, due to the low thermal conductivity, heat dissipation from the semiconductor device is also a problem.

[0008]

As described above, the characteristics required for a silica filler compatible with high frequencies of 3 GHz or higher include excellent dielectric properties, as well as all the other required properties such as filling property, fluidity, thermal properties, mechanical strength performance and mold wear resistance so that it can be blended in a large amount with a resin to maintain the performance as an encapsulant. However, such a silica filler and a silica-resin composite has not existed.

[0009]

In view of such circumstances, the present inventors aimed to provide ceramic fillers (spherical silica particles) with excellent dielectric properties in devices and substrates for 5G (fifth generation mobile communication system) having a frequency of 3 GHz or more, and in-vehicle radars using a millimeter wave band of 60 GHz or more.

CITATION LIST

PATENT LITERATURE

[0010]

Patent Literature 1: International Publication WO2016/031823

Patent Literature 2: International Publication WO2018/186308

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0011]

An object of the present invention is to provide a spherical silica particle, a spherical silica particle mixture, and a composite material, which have excellent dielectric properties and can also have excellent thermal properties and fluidity.

SOLUTION TO PROBLEM

[0012]

The present inventors have conducted diligent research for the purpose of solving the above problems. As a result, it was found that in order to obtain silica particles having excellent dielectric properties such as low dielectric constant and low dielectric loss tangent and excellent thermal properties such as high thermal conductivity and high thermal expansion coefficient, it is effective to heat-treat and crystallize spherical molten (amorphous) silicas to obtain a specific crystal structure. That is, it was confirmed for the first time that the spherical silica particles of the present invention had a low dielectric loss tangent at a high frequency of 3 GHz or higher, which was significantly lower than that of amorphous particles, and exhibited high thermal conductivity to complete the present invention.

ADVANTAGEOUS EFFECT OF INVENTION

[0013]

Since the spherical silica particles according to the present invention have a specific crystal structure, they have excellent dielectric properties (low dielectric constant and dielectric loss tangent), and also shows excellent thermal properties as compared with conventional spherical crystalline silica particles. Further, since the

particles are spherical, have a narrow particle diameter distribution, and can have a high circularity, both high flow/high dispersibility and high filling property can be achieved. Therefore, they can be suitably used as a filler for semiconductors, substrates, etc. performing high-frequency signal transmission.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

[FIG. 1]

Fig. 1 is a diagram for explaining the photographing area and the calculation of the peripheral length of the particles.

MODES FOR CARRYING OUT THE INVENTION

[0015]

The present invention provides the following aspects.

[1]

Spherical silica particles, characterized in that they comprise at least 60% in total of crystalline cristobalite phase and crystalline quartz phase, and an average diameter of polycrystalline grains constituting the crystalline cristobalite phase or the quartz phase is 2 μm or more, and they have a dielectric loss tangent at 10 GHz of 0.0020 or less which is determined by a cut-off circular waveguide method (JIS R1660-1:2004).

[2]

The spherical silica particles according to item [1], wherein they contain aluminum in an oxide equivalent of more than 0.5% by mass and 2.0% by mass or less.

[3]

The spherical silica particles according to item [1] or [2], wherein the ratio of the crystalline quartz phase in the spherical silica particles is 30% or more.

[4]

The spherical silica particles according to any one of items [1] to [3], wherein the particles having a particle diameter of 10 μm or more in the spherical silica particles have a circularity of 0.83 or more.

[5]

A spherical silica particle mixture comprising the spherical silica particles according to any one of items [1] to [4] in an amount of 95% by mass or more and 99.9% by mass or less, and ultrafine particles having an average particle diameter of 0.1 μm or less in an amount of 0.1% by mass or more and 5% by mass or less.

[6]

A composite material characterized in that it contains 85% by mass or more and 95% by mass or less of the spherical silica particles according to any one of items [1] to [4] in a resin.

[0016]

The crystal structure of silica (SiO_2) includes cristobalite, quartz, tridymite and the like. Silica having these crystal structures has a higher coefficient of thermal expansion and thermal conductivity than amorphous silica. Therefore, by replacing the molten (amorphous) silica with crystalline silica in an appropriate amount, it is possible to improve the thermal conductivity of the resulting silica while suppressing its difference in thermal expansion from IC chip. Further, by optimizing the particle diameter distribution of the molten (amorphous) silica and the crystalline silica, it is possible to obtain a silica filler (spherical silica particles) showing higher filling

property.

[0017]

The spherical silica particles of the present invention contain, in total, 60% or more of a crystalline cristobalite phase and a crystalline quartz phase (hereinafter, collectively referred to as “crystalline phase”). That is, the content of the crystalline phase in the spherical silica particles is 60% or more. If it is 60% or more, excellent dielectric properties are exhibited. In general, the higher the proportion of crystalline silica, the better the dielectric properties. Silica other than crystalline silica is amorphous. The crystalline phase may be either a crystalline cristobalite phase or a crystalline quartz phase, or both the crystalline cristobalite phase and the crystalline quartz phase in combination. The spherical silica particles of the present invention may contain crystalline tridymite in addition to the crystalline cristobalite phase and the crystalline quartz phase.

[0018]

The abundance ratio of crystalline phases such as cristobalite and quartz can be measured by, for example, X-ray diffraction (XRD). When measuring by XRD, it can be calculated by the following formula from the sum of the integrated intensities of the crystalline peaks (I_c) and the integrated intensities of the amorphous halo portion (I_a).

[0019]

X (crystal phase ratio) = $I_c / (I_c + I_a) \times 100$ (%)

[0020]

Unless otherwise specified, the ratio of various crystal phases in the crystal phase contained in the spherical silica particles according to the present invention

is measured by XRD as described below. Using the peak data of PDF 33-1161 for the crystalline quartz phase, PDF11-695 for the crystalline cristobalite phase, and PDF18-1170 for the crystalline tridymite phase, the ratio of each crystal is obtained as a mass ratio by calculating from the sum of the integrated intensities. In addition, since the peak positions of the maximum intensities derived from the cristobalite phase and the tridymite phase are close to each other, the intensities are calculated by separating each peak, or the peaks of the second and subsequent intensities can be corrected based on the intensity ratio of the pdf data, and used for calculation.

[0021]

The crystalline cristobalite phase and the crystalline quartz phase are composed of a large number of microcrystals, that is, polycrystalline grains. In the spherical silica particles of the present invention, the average diameter of the polycrystalline grains is 2 μm or more. Here, the average diameter was obtained by cutting the cross section after filling the sample with a resin and averaging the area of the polycrystalline grain appearing on the cross section with area weighting. Crystalline silica can be expected to have higher thermal conductivity than amorphous silica, but if the grain size of polycrystalline silica is too small, sufficient thermal conductivity cannot be obtained because of scattering due to grain boundaries. Therefore, in order to obtain sufficient thermal conductivity, the average diameter of the polycrystalline grain size needs to be 2 μm or more.

[0022]

In the spherical silica particles of the present invention, the polycrystalline grain size (average diameter) is measured by dispersion-filling crystalline powder in an epoxy resin, cutting out a cross section thereof, and measuring it by an EBSD

method (Electron Back Scatter Diffraction Pattern).

[0023]

Further, in order to verify the effect of improving the thermal conductivity by the spherical silica particles of the present invention, a heat conductive sheet can be prepared by kneading a resin and the spherical silica particles of the present invention, and the thermal conductivity of the resulting sheet can be measured. First, the spherical silica particles are mixed with a silicone resin (CY52-276A/B manufactured by Dow Corning Corporation) at a filler ratio of 80% by mass, the mixture is vacuum degassed to 5 Torr or less, and kneaded. Then, it is molded with a mold. The mold is heated to 120 °C, the mixture is compressed at 6 to 7 MPa, and molded for 40 minutes. The resin composition is taken out from the mold and cured at 140 °C for 1 hour. After cooling to room temperature, the resin composition is sliced to a thickness of 1.5, 2.5, 4.5, 6.5, 7.5 and 8.5 mm, respectively, and processed into a 2 cm square sheet-shaped sample. The thermal resistance of each sample was measured according to ASTM D5470. The sample is sandwiched between blocks made of SUS304, compressed at 0.123 MPa, and the thickness after compression is recorded. The relationship between the thermal resistance value and the thickness after compression obtained in this way can be linearly approximated, and the thermal conductivity can be derived from the slope.

[0024]

The spherical silica particles of the present invention have a dielectric loss tangent at 10 GHz of 0.0020 or less obtained by the blocking cylindrical waveguide method (JIS R1660-1: 2004). Although not bound by a particular theory, it is considered that the spherical silica particles of the present invention have the above-

mentioned crystal structure (crystal phase ratio and polycrystalline grain size), so that they can achieve dielectric loss tangent significantly lower than that of amorphous particles, and a high thermal conductivity.

[0025]

A method for measuring the dielectric constant and the dielectric loss tangent of the spherical silica particles of the present invention will be described. The measurement is performed using a composite material. The composite material is prepared by using a powder of spherical silica particles and an epoxy resin (YX-4000H manufactured by Mitsubishi Chemical Corporation), and kneading the spherical silica particles in an amount of 0, 30, 50 and 83 to 89% by mass based on the epoxy resin at a temperature of 100 °C with two roll mills. The sample after kneading was crushed with a mortar and pestle. The crushed sample was filled in a mold (50φ) and set in a press. After pressurizing at a molding temperature of 175 °C for about 1 minute at 1 MPa, the pressure was maintained at 5 MPa for 9 minutes. Then, the mold was transferred to a water-cooled press, cooled for about 10 minutes, and then the cured spherical silica particles-epoxy resin plate (silica-resin plate) was taken out from the mold. The produced silica-resin plate was cut with an outer peripheral blade and processed to a size of about 10 mm × 10 mm. In order to change the thickness of the cured silica-resin plate, it was ground by high-precision surface grinding (SGM-5000 manufactured by Shuwa Kogyo Co., Ltd.), and the thickness was varied between 0.2 mm and 1.0 mm.

The dielectric properties were measured by measuring the silica-resin composite in the 10 GHz frequency band based on the blocking cylindrical waveguide method (JIS R1660-1: 2004). From the relationship between the composite of

spherical silica particles in an amount of 0, 30, 50 and 83 to 89% by mass with respect to the epoxy resin and the dielectric loss tangent, the numerical value of 100% spherical silica particles is extrapolated, and the obtained numerical value was used as the dielectric loss tangent of the silica particles.

[0026]

The method for producing spherical silica particles according to the present invention will be described.

[0027]

The spherical silica particles according to the present invention can be prepared by filling an alumina container with silica particle powder (amorphous) produced by a thermal spraying method in the air and heat-treating it at a temperature range of 800 °C to 1600 °C for a heat treatment time of 50 minutes to 16 hours in an air atmosphere. The preferred heat treatment time is 1-12 hours. If it is less than 1 hour, crystallization may not be sufficient. If the heat treatment time exceeds 12 hours, the burden of manufacturing cost becomes large. When accelerating the crystallization of cristobalite, it is advisable to add a small amount of Al and to perform treatment at 900 °C to 1600 °C. By adjusting the treatment temperature and time, the abundance ratio of amorphous and crystalline silica (cristobalite phase and quartz phase) can be controlled.

[0028]

Here, the amount of Al added is preferably more than 0.5% by mass and 2.0% by mass or less in terms of oxide. Within this range, a sufficient degree of crystallinity can be obtained, and spherical silica particles in which an increase in alkali content and an increase in specific gravity due to Al are suppressed can be

obtained. If it is 0.5% by mass or less, the crystallinity tends to decrease, and if it exceeds 2.0% by mass, the alkali content and the specific gravity increase remarkably, and as a result, the resin curing characteristics are adversely affected. In addition, it tends to be difficult to apply to mobile devices and in-vehicle applications that require weight reduction.

[0029]

In Patent Document 1 and Patent Document 2, the amount of aluminum added is limited to 5000 mass ppm (0.5 mass%) or less in terms of oxide, and heat treatment at a higher temperature for a longer period of time was required to achieve sufficient crystallization, and the particles were sometimes likely to be fused to each other.

[0030]

To promote the crystallization of quartz, if a small amount of alkali metal or alkaline earth metal is added and the powder is treated at 800 to 1150 °C, which is lower than the cristobalite crystallization temperature, quartz appears as the main phase. The amount of the alkali metal or alkaline earth metal added may be 0.1 to 3% by mass in terms of oxide. If it is too small, quartz formation will not be promoted, and if it is too large, the purity of silica particles will decrease. Examples of alkali metals and alkaline earth metals include lithium, sodium, potassium, rubidium, cesium, francium, beryllium, magnesium, calcium, strontium, barium and radium. From the viewpoint of the efficiency of promoting quartz formation, Li and Ca are more preferable. The contents of aluminum, alkali metal and alkaline earth metal can be measured by, for example, atomic absorption method or ICP mass analysis (ICP-MS).

[0031]

In one aspect of the present invention, the ratio of the crystalline quartz phase in the spherical silica particles may be 30% by mass or more. Since cristobalite has a phase transition point between a low temperature phase and a high temperature phase at 200-250 °C, it is effectively accompanied by a large thermal expansion, which may be an obstacle depending on the intended use. When such a point is significant concern, it is desirable that the quartz phase is contained in an amount of 30% by mass or more. Quartz does not pose a practical obstacle because the phase transition point between the low temperature phase and the high temperature phase is 500 °C or higher. Within this range, spherical silica particles having thermal expansion characteristics suitable for a semiconductor package can be obtained. If it is less than 30% by mass, the thermal expansion due to the phase transition of the cristobalite phase becomes too large.

[0032]

The spherical silica particles (amorphous) powder, which is the raw material of the spherical silica particles of the present invention, can be produced by a thermal spraying method. Specifically, spherical silica particle (amorphous) powder was produced by thermal spraying using a device wherein a burner with a tubular structure consisting of a flammable gas supply pipe, a flame supporting gas supply pipe, and a crushed high-purity silica (quartz) supply pipe is installed at the top of the production furnace, while a collection system (the produced powder was sucked with a blower and collected with a bag filter) is connected to the lower part of the production furnace. LPG was supplied from the flammable gas supply pipe and oxygen was supplied from the flame supporting gas supply pipe to form a high-

temperature flame in the production furnace. Crushed silica powder (quartz) was supplied from the silica supply pipe, and spherical silica powder was collected by the bag filter. The spherical silica particles obtained by thermal spraying can have a circularity of 0.83 or more. The higher the circularity, the higher the fluidity. Therefore, the circularity is preferably 0.83 or more. With a thermal spraying means, particles having a high circularity can be easily obtained. In order to make the circularity of the spherical silica particles obtained by thermal spraying 0.83 or more, it is necessary to melt the raw material silica powder to make it spherical, so the temperature of the flame at the time of thermal spraying must be higher than the melting temperature of silica. In order to obtain spherical silica having a higher circularity, it is desirable that the flame temperature is 2000 °C or higher.

In addition, when silica particles in thermal spraying come into contact with each other, the particles tend to bond with each other to form a distorted shape. Therefore, it is desirable that the supply amount of the raw material into the flame is adjusted by dispersing and supplying the raw material into the gas flow.

[0033]

Further, the spherical silica particles of the present invention can maintain the circularity of the spherical silica particles (amorphous) obtained by thermal spraying without reducing the circularity of most of the spherical silica particles before and after the heat treatment for crystallization described above.

[0034]

In the present specification, unless otherwise specified, the circularity is measured for 6000 pieces of particles having 10 um or more in diameter using FPIA-3000 manufactured by Malvern PANalytical, Ltd. When measuring including

particles having a diameter of 10 μm or less, the resolution of the measuring device is generally insufficient, and the circularity may be calculated higher. In that case, the circularity cannot be adopted as an index of fluidity. Therefore, the circularity is measured for particles having a diameter of 10 μm or more. First, 10 g of a powder sample such as silica particles to be measured and 200 ml of distilled water are placed in a beaker, and the sample is subject to a dispersion treatment for 30 seconds or more with ultrasonic waves set to 150 to 500 W at a frequency of 20 to 30 kHz by an ultrasonic homogenizer for a sufficient dispersion. After dispersion, the beaker is allowed to stand still for 1 minute, discard 180 ml in the supernatant side, and add a fresh distilled water to 200 ml. The required amount is taken out from here with a pipette or the like and measured with an optical measuring device. The particle diameter is defined as a circular equivalent diameter. This is a diameter of a circle with an area equal to the projected area on the measured image, which is calculated by

[Formula 1]

$$\text{Circular Equivalent Diameter} = 2 \times \sqrt{\text{Particle Projected Area} / \pi}$$

The projected area is calculated by image processing, but as shown in FIG. 1, the particles are image-processed such as binary imaging, and the centers of respective pixel cells in the outline of the particle are connected by a straight line and the surrounded area is defined as the projected area. The objective lens of the measuring device was selected to be about 0.5-1 μm / pixel according to the number of pixels.

[0035]

In one aspect of the present invention, a mixture of spherical silica particles

including 95% by mass or more and 99.9% by mass or less of the spherical silica particles as described above and 0.1% by mass or more and 5% by mass or less of ultrafine particles having an average particle diameter of 0.1 μm or less is provided.

If ultrafine particles of 0.1 μm or less are appropriately blended with the spherical silica particles of the present invention, the filling rate can be improved when the spherical silica particles are used as a filler. This is because the ultrafine particles enter the gaps between the spherical silica particles and the volume occupied by the gaps is reduced, so that the filling rate is improved. The blending ratio of the spherical silica particles and the ultrafine particles is preferably 95% by mass or more and 99.9% by mass or less of the spherical silica particles, and 0.1% by mass or more and 5% by mass or less of the ultrafine particles. If the ratio of the ultrafine particles is too low, the gaps between the spherical silica particles will not be filled and the filling rate will not be improved. If the ratio of the ultrafine particles is too high, they will be overflowed from the gaps between the spherical silica particles and the total volume will increase.

Here, the ultrafine particles refer to spherical silica particles having a particle diameter of 0.1 μm or less. In the process of producing spherical silica particles, those having a particle diameter of 0.1 μm or less (ultrafine particles) can be separated, and a predetermined amount of the ultrafine particles can be blended at the time of final product production.

It is also possible to adjust the particle diameter distribution of the spherical silica particles. By adjusting the particle diameter distribution of the crushed silica powder (quartz) used as the thermal spraying raw material, the particle diameter distribution of the spherical silica particles (amorphous) after thermal spraying can

be adjusted. The spherical silica particles obtained by the heat treatment for crystallization may have a particle diameter distribution slightly different from that of the spherical silica particles (amorphous). However, the particle diameter distribution of the spherical silica particles of the present invention can also be adjusted by predicting an extent of change in the particle diameter distribution or by sieving the particles in the subsequent step. The silica particles of the present invention may have an average particle diameter (D50) of 1 to 100 μm . If the average particle diameter exceeds 100 μm in the case where the particles are used as a filler for semiconductor encapsulants, the particle diameter may become too coarse to be likely to cause gate clogging or mold wear. If the average particle diameter is less than 1 μm , the particles may become too fine to be filled in a large amount. A more preferable upper limit of the average particle diameter is 50 μm , and even more preferably 40 μm . On the other hand, the more preferable lower limit of the average particle diameter is 3 μm , and more preferably 5 μm . The average particle diameter here can be obtained by measuring the particle diameter distribution by a wet laser diffraction method (laser diffraction/ scattering method).

The average particle diameter referred to here is called the median diameter, and the particle diameter distribution is measured by a laser diffraction method, and the particle diameter at which the cumulative frequency of particle diameters is 50% is defined as the average particle diameter (D50).

[0036]

In the present specification, unless otherwise specified, the average particle diameter related to the particle diameter distribution of spherical silica particles, ultrafine particles, etc. is determined by measuring the particle diameter

distribution by a laser diffraction method or the like. The particle diameter distribution by the laser diffraction method can be measured by, for example, CILAS 920 manufactured by CILAS. The average particle diameter referred to here is called the median diameter, and the particle diameter at which the cumulative frequency of particle diameters is 50% by measuring the particle diameter distribution by a method such as laser diffraction is the average particle diameter (D50).

[0037]

Further, in one aspect of the present invention, a composite material of the spherical silica particles as described above and a resin is provided.

In order to improve the dielectric properties of the composite material, it is effective to increase the filling rate (filler filling rate) of the silica filler in the resin composite and reduce the amount of the resin having inferior low dielectric constant properties (for example, epoxy resin). In the composite material of the present invention, a filler filling rate of 85% by mass or more and less than 95% by mass can be achieved, while maintaining high fluidity. In order to ensure high fluidity, it is difficult to make the silica filler filling rate more than 85% by mass in the past, and conventionally it was limited to less than 85% by mass. However, it is possible to further enhance the filling rate by appropriately blending ultrafine particles of 0.1 μm or less into the silica particles of the present invention. Generally, when the filler filling rate is increased, the fluidity decreases, but when the addition amount of ultrafine particles of 0.1 μm or less is 0.1% by mass or more and 5% by mass or less, both high filling property and high fluidity can be realized. This makes it possible to obtain a composite of a silica filler and a resin having a low dielectric constant and low dielectric loss tangent suitable for increasing the frequency. However, when the

silica filler filling rate exceeds 95% by mass, the amount of resin is relatively small, and it becomes difficult to obtain a resin composite.

[0038]

In one aspect of the present invention, a composite material of the spherical silica particles as described above and a resin is included. The composition of the composite material will be described. When a resin substrate such as a packaging substrate or an interlayer insulating film is produced using a slurry composition, it is preferable to use an epoxy resin as the resin. The epoxy resin is not particularly limited, and examples thereof include a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a biphenyl type epoxy resin, a phenol novolac type epoxy resin, a naphthalene type epoxy resin, and a phenoxy type epoxy resin. One of these types can be used alone, two or more types having different important molecular weights can be used in combination, or one type or two or more types can be used. Among these epoxy resins, the bisphenol A type epoxy resin is particularly preferable from the viewpoint of availability and handleability.

[0039]

For example, when manufacturing a semiconductor-related material such as a packaging substrate or an interlayer insulating film, a known resin can be applied as the resin used in the resin composite composition, but it is preferable to adopt an epoxy resin. The epoxy resin is not particularly limited, but for example, 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 and the like, can be used. One of these can be used alone, or two or more having different molecular weights can be used in

combination. Among these, an epoxy resin having two or more epoxy groups in one molecule is preferable from the viewpoint of curability, heat resistance and the like. Specifically, biphenyl type epoxy resin, phenol novolac type epoxy resin, orthocresol novolac type epoxy resin, epoxidized phenols and aldehydes novolac resin, glycidyl ethers such as bisphenol A, bisphenol F and bisphenol S, glycidyl ester acid epoxy resin obtained by the reaction of polybasic acids such as phthalic acid or dimer acid with 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, and an epoxy resin into which a halogen such as bromine, etc. is introduced to further impart flame retardancy can be mentioned. Among the epoxy resins having two or more epoxy groups in one of these molecules, the bisphenol A type epoxy resin is particularly preferable.

[0040]

Further, as a resin used for a resin composite composition such as a prepreg for a printed circuit board and various engineering plastics for applications other than a composite material for a semiconductor encapsulant, a resin other than an epoxy-based resin can also be applied. Specifically, in addition to epoxy resin, silicone resin, phenol resin, melamine resin, urea resin, unsaturated polyester, fluororesin, polyamides such as polyimide, polyamideimide, polyetherimide, etc.; polyester such as polybutylene terephthalate, polyethylene terephthalate, etc.; polyphenylene sulfide, aromatic polyester, polysulfone, liquid crystal polymer, polyether sulfone, polycarbonate, maleimide modified resin, ABS resin, AAS (acrylonitrile-acrylic rubber/styrene) resin, AES (acrylonitrile/ ethylene/ propylene/ diene rubber-

styrene)) resin can be mentioned.

[0041]

A known curing agent may be used to cure the resin, but a phenol-based curing agent can be used. As the phenol-based curing agent, a phenol novolac resin, an alkylphenol novolac resin, polyvinylphenols and the like can be used alone or in combination of two or more.

[0042]

The amount of the phenolic curing agent blended is preferably less than 1.0 and 0.1 or more in equivalent ratio with the epoxy resin (phenolic hydroxyl group equivalent / epoxy group equivalent). As a result, the unreacted phenol curing agent does not remain, and the hygroscopic heat resistance is improved.

[0043]

The amount of the spherical silica particles blended in the composite material is preferably large from the viewpoint of heat resistance and coefficient of thermal expansion. It is usually suitable to be 70% by mass or more and 95% by mass or less, preferably 80% by mass or more and 95% by mass or less, and more preferably 85% by mass or more and 95% by mass or less with respect to the total mass of the composite material. This is because if the amount of the silica powder blended is too small, it is difficult to obtain effects such as improving the strength and suppressing thermal expansion of the encapsulant material. Conversely, this is because if it is too large, regardless of the surface treatment of the silica powder, segregation due to aggregation of the silica powder is likely to occur in the composite material, and the viscosity of the composite material becomes too large, which makes it difficult to put it into practical use as an encapsulant material.

[0044]

In addition, as for the silane coupling agent, a known coupling agent may be used, but one having an epoxy-based functional group is preferable.

EXAMPLES

[0045]

The present invention will be described through the following examples and comparative examples. However, the present invention is not construed as being limited to the following examples.

[0046]

[Examples 1 to 4]

Spherical molten (amorphous) silica particles having an average particle diameter of 29 μm were prepared by a thermal spraying method. Calcium oxide and alumina were blended to the raw material powder at the time of thermal spraying so that the calcium concentration and the aluminum concentration in the silica particles were 1% by mass and 0.6% by mass in terms of oxides, respectively. The prepared silica particles were placed in an alumina container and a heat-treatment at 1400-900 $^{\circ}\text{C}$ was performed. The conditions of each of examples and the measurement results obtained are shown in detail in Table 1.

[0047]

[Examples 5 to 8]

The silica particles prepared in the same manner as in Examples 1 to 4 except that spherical molten (amorphous) silica particles having an average particle diameter of 9 μm (the addition amount of ultrafine particles of 0.1 μm or less is 3.0 % by mass) were prepared by a thermal spraying method, were placed in an alumina

container and a heat-treatment at 1400-900 °C was performed. The conditions of each of examples and the measurement results obtained are shown in detail in Table 1.

[0048]

[Comparative Examples 1 to 4]

Spherical molten (amorphous) silica particles having an average particle diameter of 29 μm were prepared by a thermal spraying method. Calcium oxide and alumina were blended to the raw material powder at the time of thermal spraying so that the calcium concentration and the aluminum concentration in the silica particles were <0.01% by mass and 0.1% by mass, respectively, in terms of oxides. The prepared silica particles were placed in an alumina container and heat-treatment at 1400-900 °C was performed. The conditions of each of comparative examples and the measurement results obtained are shown in detail in Table 2.

[0049]

[Comparative Examples 5 to 8]

Spherical molten (amorphous) silica particles having an average particle diameter of 9 μm were prepared by a thermal spraying method. Calcium oxide and alumina were blended to the raw material powder at the time of thermal spraying so that the calcium concentration and the aluminum concentration in the silica particles were <0.01% by mass and 0.1% by mass, respectively, in terms of oxides. The prepared silica particles were placed in an alumina container and heat-treatment at 1400-900 °C was performed. The conditions of each of comparative examples and the measurement results obtained are shown in detail in Table 2.

[0050]

[Examples 3, 9-10, and Comparative Example 9]

Spherical silica particles were prepared under the same conditions as in Example 3 except for the heat treatment time. Further, the prepared spherical silica particles were filled in a silicone resin in an amount of 80% by mass as described above, and the polycrystalline grain diameter distribution was measured by EBSD of the cross-sectional sample. Moreover, the thermal conductivity was measured from the sample cut out from the same sample. Under the conditions of Comparative Example 9, the growth of crystal grains was insufficient, resulting in a slightly inferior thermal conductivity, but in Examples 3, 9 and 10, sufficient thermal conductivity was obtained. Table 3 summarizes these conditions and measurement results.

[0051]

[Comparative Examples 10 to 11]

By changing the amount of the aluminum concentration to 0.4% by mass (Comparative Example 10) and 0.2% by mass (Comparative Example 11) in terms of oxides blended to the thermal sprayed silica which is the same as that used in Example 3, crystallization was carried out under the same heat treatment conditions as in Example 3. As a result, in Comparative Examples 10 and 11, the amorphous ratio was high.

[0052]

[Table 1]

				Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	Ex.8
Average Particle Diameter Before Heat Treatment			μ m	29	29	29	29	9	9	9	9
C a O			%	1	1	1	1	1	1	1	1
A l ₂ O ₃			%	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Heat Treatment Temperature			°C	1400	1300	1100	900	1400	1300	1100	900
Time			h	1	1	1	6	1	1	1	6
Phase Ratio After Heat Treatment	cristobalite	%	90	82	38	12	88	80	35	15	
	quartz	%	5	8	31	81	4	7	27	79	
	tridymite	%	2	4	5	5	5	4	4	5	
	amorphous	%	3	6	26	2	3	9	34	1	
Average Particle Diameter After Heat Treatment			μ m	30	31	31	31	11	11	12	12
Circularity After Heat Treatment				0.84	0.85	0.85	0.85	0.93	0.94	0.94	0.95
Dielectric Loss Tangent			X0.0001	4	5	15	12	7	12	18	17

[0053]

[Table 2]

			Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6	Comp. Ex.7	Comp. Ex.8
Average Particle Diameter Before Heat Treatment		$\mu\text{ m}$	29	29	29	29	9	9	9	9
C a O		%	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
A l ₂ O ₃		%	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Heat Treatment Temperature		°C	1400	1300	1100	900	1400	1300	1100	900
Time		h	1	1	1	6	1	1	1	6
Phase Ratio After Heat Treatment	cristobalite	%	53	31	6	2	50	40	9	6
	quartz	%	3	4	4	5	3	4	12	13
	tridymite	%	6	4	5	6	7	3	4	5
	amorphous	%	38	61	85	87	40	53	75	76
Average Particle Diameter After Heat Treatment		$\mu\text{ m}$	31	32	32	33	10	10	11	11
Circularity After Heat Treatment			0.85	0.86	0.86	0.86	0.95	0.95	0.94	0.95
Dielectric Loss Tangent		X0.0001	15	26	24	29	24	32	38	38

[0054]

[Table 3]

		Ex.10	Ex.9	Ex.3	Comp.Ex.9
Heat Treatment Temperature	°C	1100	1100	1100	1100
Time	h	16	4	1	0.5
Average Grain Size	μ m	6.5	6.0	2.1	0.9
Thermal Conductivity	W/mK	1.1	1.0	0.8	0.5

[0055]

[Table 4]

			Ex.3	Comp.Ex.10	Comp.Ex.11
Average Particle Diameter Before Heat Treatment		μm	29	29	29
C a O		%	1	1	1
A l ₂ O ₃		%	0.6	0.4	0.2
Heat Treatment Temperature		°C	1100	1100	1100
Time		h	1	1	1
Phase Ratio After Heat Treatment	Cristobalite	%	38	29	22
	Quartz	%	31	25	20
	Tridymite	%	5	3	1
	Amorphous	%	26	43	57
Average Particle Diameter After Heat Treatment		μm	31	30	30
Circularity After Heat Treatment			0.85	0.85	0.85
Dielectric Loss Tangent		X0.0001	15	22	39

CLAIMS

[Claim 1]

Spherical silica particles, characterized in that the spherical silica particles comprise at least 60% in total of crystalline cristobalite phase and crystalline quartz phase, and an average diameter of polycrystalline grains constituting the crystalline cristobalite phase or the quartz phase is 2 μm or more, and the spherical silica particles have a dielectric loss tangent at 10 GHz of 0.0020 or less which is determined by a cut-off circular waveguide method (JIS R1660-1:2004).

[Claim 2]

The spherical silica particles according to claim 1, wherein the spherical silica particles contain aluminum in an oxide equivalent of more than 0.5% by mass and 2.0% by mass or less.

[Claim 3]

The spherical silica particles according to claim 1 or 2, wherein the ratio of the crystalline quartz phase in the spherical silica particles is 30% or more.

[Claim 4]

The spherical silica particles according to any one of claims 1 to 3, wherein the particles having a particle diameter of 10 μm or more in the spherical silica particles have a circularity of 0.83 or more.

[Claim 5]

A spherical silica particle mixture comprising the spherical silica particles according to any one of claims 1 to 4 in an amount of 95% by mass or more and 99.9% by mass or less, and ultrafine particles having an average particle diameter of 0.1

μm or less in an amount of 0.1% by mass or more and 5% by mass or less.

[Claim 6]

A composite material characterized by containing 85% by mass or more and 95% by mass or less of the spherical silica particles according to any one of claims 1 to 4 in a resin.