

DESCRIPTION

TITLE

SPHERICAL SILICA PARTICLES, RESIN COMPOSITE COMPOSITION CONTAINING
SAME, AND PRODUCTION METHOD THEREOF

FIELD

[0001]

The present invention relates to spherical silica particles, in particular spherical silica particles excellent in fluidity by having, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles of 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles of 100 ppm or less, and a specific surface area by the BET method of 5.0 m^2/g or more and 20 m^2/g or less, a resin composite composition containing the same, and a method for producing the same.

BACKGROUND

[0002]

ICs, CPUs, and other semiconductor packages are being made increasingly smaller in size and greater in thinness. Along with this, the need for finer bonding wires and narrower pitches has been rising. On the other hand, due to the higher performance of semiconductor apparatuses and the accompanying increase in the amount of heat generated, improvement of the heat dissipation ability of semiconductor packages has become more important. The need for a sealing material used for semiconductor packages has also been rising. To raise the ability to fill narrow parts, higher fluidity sealants are being sought and higher thermal conductivity is being demanded. As the sealant of semiconductor packages, a resin composite composition comprised of an epoxy resin in which silica particles are contained as a filler is being used. In recent years, there has been a rising need for higher fluidity, therefore spherical particles are being used in large amounts for the silica particles used as a filler. Due to use of such spherical silica particles, it has become possible to remarkably raise the fluidity of the sealant compared with conventional crushed type silica particles.

[0003]

However, along with the rising need for higher thermal conductivity of sealants, it has also become necessary to raise the filling rate of fillers with a high thermal conductivity compared with a resin to raise the thermal conductivity of the sealants. Further, it has become necessary to raise the filling rate of fillers even when aiming at raising the strength of sealants and lowering the thermal conductivity. However, if raising the filling rate of fillers, the fluidity ends up falling,

therefore attempts have been made to optimize the particle size distribution etc. Further, the method of blending parts having several types of particle size distribution so as to raise the spatial filling rate of filler particles is also being generally used.

5 [CITATIONS LIST]

[PATENT LITERATURE]

[0004]

[PTL 1] Japanese Unexamined Patent Publication No. 2022-037681

[PTL 2] Japanese Unexamined Patent Publication No. 2007-015884

10 [PTL 3] Japanese Unexamined Patent Publication No. 2022-90679

SUMMARY

[TECHNICAL PROBLEM]

[0005]

15 In this way, resin composite compositions forming sealants or the fillers for the same are being studied from various viewpoints such as fluidity, fillability, heat dissipation (thermal conductivity), and strength.

[0006]

For example, PTL 1 proposes obtaining a high fluidity of a resin composite composition by suitably adjusting the particle size distribution of the amorphous silica powder contained in the resin composite composition and its specific surface area. More specifically, it discloses amorphous silica powder with a most frequent size in the particle size frequency distribution of within 1 to 10 μm in range, with a frequency of less than 0.50 μm particle size particles of 1.0% or more, and with a 1 to 12 m^2/g specific surface area.

25 **[0007]**

Further, PTL 2 relates to a method of production of spherical inorganic fine powder comprising flame melting a starting material powder into a flame to make it spheroidal and proposes to keep the obtained powder (particles) from becoming coarser and make it become a desired particle size range. More specifically, it discloses mixing a dispersion-type surface treatment agent to an inorganic starting material powder with a specific average particle size, then flame melting the mixture to enable prevention of enlargement of particles at the time of flame melting due to agglomeration of the starting material powder.

30 **[0008]**

Further, PTL 3 discloses spherical silica powder formed by a process including forming spherical silica particles by the sol-gel method, then firing the spherical silica particles and crushing the fired material.

[0009]

However, further improvement of the properties of a resin composite composition forming a sealant and a filler of the same is being sought. In particular, along with the smaller size of semiconductor packages in recent years, smaller particle size of the filler used for the sealant is being sought, but there is an issue that the fluidity falls due to the smaller particle size of the filler.

[0010]

The present invention was made in consideration of the above situation and has as its object the provision of spherical silica particles excellent in fluidity, a resin composite composition containing the same, and a method of production of the same.

[SOLUTION TO PROBLEM]

[0011]

The inventors discovered that the above problem is resolved by precisely removing coarse particles in the particle size distribution of spherical silica particles, more specifically limiting the coarse particles having a specific particle size or more by number level.

[0012]

Based on the above discovery, the gist of the present invention is as follows:

[0013]

[1] Spherical silica particles wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles is 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles is 100 ppm or less, and a specific surface area by the BET method is 5.0 m^2/g or more and 20 m^2/g or less.

[2] Spherical silica particles according to [1], wherein a D50 by a laser diffraction/scattering method is 0.4 or more and 3.0 μm or less.

[3] Spherical silica particles according to [1] or [2], wherein a roundness is 0.85 or more.

[4] Spherical silica particles according to any one of [1] to [3], wherein, among the number of 1 μm or more and 30 μm or less particles detected by a Coulter counter, when designating the number frequency of 1 to 2 μm articles as "A" and the number frequency of 2 to 30 μm particles as "B", B/A is 0.002 or more and 0.20 or less.

[5] Spherical silica particles according to any one of [1] to [4], wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, the 10 μm or more particles are less than 10 ppm.

[6] A resin composite composition containing spherical silica particles according to any one of [1] to [5].

[7] A resin composite composition according to [6], further containing at least one type of

inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, alumina particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber.

[8] A method of production of spherical silica particles according to any one of [1] to [5] wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles is 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles is 100 ppm or less, and a specific surface area by the BET method is 5.0 m^2/g or more and 20 m^2/g or less, comprised of a step of running natural silica through a flame to make it melt, then cooling it to make it spheroidal and a step of classifying it by joint use of a classifier and/or sieve after the step for spheroidization.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0014]

The spherical silica particles according to the present invention and the resin composite composition containing the same having a particle size distribution of spherical silica particles, in particular a number frequency of 3 μm or more particles and a number frequency of 5 μm or more particles, controlled to a specific region. For this reason, they are excellent in fluidity, that is, excellent in fillability in narrow parts. As a result, it is possible to lower the defect rate in semiconductor products, in particular a wafer level package (WLP) or other of the recent small sized or thin type semiconductor products. Further, it is possible to obtain the spherical silica particles by the method of production of spherical silica particles according to the present invention.

DESCRIPTION OF EMBODIMENTS

[0015]

The spherical silica particles according to the present invention are characterized in that, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles is 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles is 100 ppm or less, and a specific surface area by the BET method is 5.0 m^2/g or more and 20 m^2/g or less.

[0016]

A Coulter counter measures particles by the electrical resistance method called the “Coulter principle”. It is free from the errors in surface morphology, internal structure, refractive index, color, etc. of the particles seen in an optical measurement method and enables high measurement precision. In particular, the particle size obtained by this method can be expressed by the number distribution. Precise management of the particle size distribution becomes possible.

[0017]

In a 200 ml glass beaker, spherical silica particles and 150 ml of an electrolyte were placed. An ultrasonic homogenizer (Ultrasonic Homogenizer UH-300 made by SMT) was used to make the particles disperse for 30 seconds. Furthermore, this dispersion was added to an electrolyte prepared in a separate beaker to adjust the concentration. The dispersion adjusted in concentration was measured by a Coulter counter (Multisizer 3 made by Beckman Coulter) using an aperture size of 50 μm to measure the individual particle sizes of the spherical silica particles. At this time, the number of particles measured per measurement was made about 100,000. The same sample was measured repeatedly three times. Among the 1 μm or more and 30 μm or less particles detected by the Coulter counter, the numbers of particles with a particle size of 3 and 5 μm or more were calculated and made the frequency of coarse particles (ppm) with respect to the total number.

[0018]

By measurement of this Coulter counter, the number frequency of 3 μm or more particles with respect to the total number of the spherical silica particles of 1 μm or more and 30 μm or less is 300 ppm or more and 50000 ppm or less and the number frequency (ratio) of 5 μm or more coarse particles becomes 100 ppm or less. "100 ppm or less" means the case where when there are 100,000 1 μm or more and 30 μm or less particles, there are 10 or less 5 μm or more particles among them. The fact that if the number frequency of 5 μm or more coarse particles is more than 100 ppm, such coarse particles clog the narrow parts between the mounting board and chip and the fluidity falls and the fact that, otherwise, the defect rate at semiconductor products filled with the particles can be lowered were first discovered by the inventors.

[0019]

The smaller the number frequency of 5 μm or more coarse particles, the more the fluidity is improved, so the more preferable. For this reason, the number frequency may be 90 ppm or less, 80 ppm or less, 70 ppm or less, 60 ppm or less, or 50 ppm or less. The number frequency of 5 μm or more coarse particles may also be 0 ppm, but by completely removing the coarse particles, that is, making them 0 ppm, sometimes production control becomes heavy in load and difficult, therefore it is several ppm, specifically may be 1 ppm or more and may be 5 ppm or more. The lower limit of the number frequency may also be adjusted in accordance with the actual application or the target yield. For example, it may also be 10 ppm or more, 20 ppm or more, or 30 ppm or more.

[0020]

On the other hand, the number frequency of 3 μm or more coarse particles has to be controlled so as to suitably secure the fluidity as a resin composite composition. If the number frequency is less than 300 ppm, the number of particles with a less than 3 μm large specific

surface area becomes greater and the viscosity rises, therefore the fluidity falls. On the other hand, if the number frequency is more than 50000 ppm, it becomes difficult to prevent the entry of 5 μm or more particles, clogging at the narrow parts between the mounting board and chip occurs, and the fluidity falls. The preferable upper limit of the number frequency is 30000 ppm, more preferably 20000 ppm. Further, the lower limit of the number frequency is preferably 500 ppm, more preferably 1000 ppm, still more preferably 2000 ppm.

[0021]

Further, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, the number frequency of 10 μm or more particles is preferably less than 10 ppm. The smaller the number frequency of 10 μm or more coarse particles, the more improved the fluidity, therefore the more preferable. If the number frequency of 10 μm or more coarse particles is 10 ppm or more, such coarse particles clog the narrow parts between the mounting board and chip and the fluidity falls. More preferably it is less than 5 ppm, still more preferably it is less than 1 ppm, even more preferably less than 0.1 ppm, most preferably zero.

[0022]

Further, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, when designating the number frequency of 1 to 2 μm articles as “A” and the number frequency of 2 to 30 μm particles as “B”, B/A is preferably 0.002 or more and 0.20 or less. This means that it is preferable to include 1 to 2 μm particles in excess compared with the 2 to 30 μm particles, but if the large surface area 1 to 2 μm particles are too numerous, the fluidity deteriorates. By making the ratio this range, the fluidity as a resin composite composition is suitably secured and the filling (mixing) effect of the filler is sufficiently obtained. The more lower limit of B/A is preferably 0.01, more preferably 0.03, still more preferably 0.05, even more preferably 0.10. On the other hand, the more preferable upper limit of B/A is 0.19.

[0023]

To obtain the desired particle size distribution, the particles may also be classified. The classification may be performed by employing a conventionally known method. It may be either of wet classification or dry classification. Further, it may be any of gravity classification, inertial classification, or centrifugal classification. In the case of centrifugal classification, it may be based on the free vortex type or forced vortex type. Preferably, for example, the method of using a precision air classifier (also referred to as an “air classifier”) to remove the coarse powder side and fine powder side can be illustrated. However, in the present invention, in classification control, the number frequency by the Coulter counter is measured. By precision control of the particle size distribution, it is possible to contribute to better properties, for example, fluidity, of the spherical silica particles.

[0024]

The spherical silica particles of the present invention enable the effects of the invention without regard as to the crystallinity. However, amorphous silica is lower in thermal conductivity than crystalline silica, therefore to more effectively lower the thermal conductivity of the resin composition, the crystallinity is preferably 20% or less, more preferably 10% or less, still more preferably 5% or less. Even more preferably, it is 1% or less, still more preferably 0.1% or less.

Here, the “crystallinity” means the ratio of the amorphous and crystalline silica in the spherical silica particles. The crystallinity can be found by XRD. In measurement by XRD, it is possible to find the ratio of the crystal phases by calculation by the following formula from the sum (I_c) of the integral intensities of the crystalline peaks and the integral intensities (I_a) of the amorphous halo parts:

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

In the present invention, measurement was performed by XRD in a $2\Theta = 10^\circ$ to 90° range. The ratio of the crystal phases was found from the sum of the crystalline peak intensities appearing in that 2Θ measurement range and the integral intensities of the halo parts due to the broad amorphous part appearing near $2\Theta = 22^\circ$.

In the present invention, an X-ray diffraction apparatus “D2 Phaser” (made by Bruker) was used.

[0025]

The spherical silica particles of the present invention 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 run through a flame so that the particles melt and the particles become spherical in shape due to their surface tension. Due to such a flame melting method, it is possible to prepare roundness 0.80 or more, preferably 0.85 or more, spherical silica particles. Further, they may also be obtained by burning a metal. For example, metal powder mixtures of silicon powder etc. can be run through a chemical flame along with a carrier gas in an atmosphere containing oxygen to obtain the targeted silica (SiO_2) microparticles. Note that the above crystallinity can be controlled by the heat treatment (melting, cooling, etc.) conditions in the process of production of the spherical silica particles.

[0026]

Note that, the spherical silica particles may also be used mixed with other inorganic fillers within a range where the desired properties are obtained. The “other inorganic fillers” here include alumina powder, magnesia powder, titania powder, or other different types of fillers and also fillers differing in particle size distribution. The types of the other inorganic fillers will be explained later.

[0027]

In one embodiment of the present invention, the spherical silica particles may also have a

D50 by the laser diffraction/scattering method of 0.4 or more and 3.0 μm or less.

[0028]

The particle size distribution of the spherical silica particles can also be determined by measuring the particle size by the laser diffraction/scattering method. As the apparatus for measurement of the particle size distribution, for example, “Mastersizer 3000” (made by Malvern) can be used in measurement. At the time of measurement, for the refractive index of the solvent water, 1.33 is used. For the refractive index of the powder, the refractive index of the material of the powder is considered. For example, for amorphous silica, measurement is performed using a refractive index of 1.54.

[0029]

The D50 (median size) means the particle size where the cumulative volume becomes 50% in the cumulative particle size distribution of the spherical silica particles. Note that D100 (maximum particle size) means the particle size where the cumulative volume becomes 100% in the cumulative particle size distribution of the spherical silica particles.

[0030]

If D50 is less than 0.4, the size of the particles become small and sometimes the viscosity of the sealant including the particles becomes too high. On the other hand, if D50 is more than 3.0 μm , there is the issue that the particles end up precipitating during storage or during filling and curing, the entry of 5 μm or more particles becomes greater, particles end up being caught in the narrow parts between the mounting board and chip, the fluidity of the sealant becomes poorer, and sometimes the shapeability falls. The more preferable lower limit is 1.0 μm . On the other hand, the more preferable upper limit is 2.0 μm .

[0031]

The spherical silica particles according to the present invention have a specific surface area by the BET method of 5 m^2/g or more and 20 m^2/g or less.

[0032]

The specific surface area of the spherical silica particles can be measured by the BET method. As the specific surface area measurement apparatus, a product name “Macorb Model HM-1208” made by Mountec Co., Ltd. is used in the measurement.

[0033]

If the specific surface area of the spherical particles is less than 5 m^2/g , it becomes difficult for the particles to form a close-packed structure, therefore sometimes the fluidity of the sealant containing the particles will fall. Preferably, the specific surface area may be 6 m^2/g or more and may be 7 m^2/g or more. On the other hand, if the specific surface area of the spherical silica particles is more than 20 m^2/g , the tendency for the particles to agglomerate increases and similarly sometimes the fluidity of the sealant will fall. Preferably, the specific surface area may

be 15 m²/g or less and may be 12 m²/g or less.

[0034]

In one embodiment of the present invention, the spherical silica particles may have a roundness of 0.85 or more. The higher the roundness of the spherical silica particles, the lower the viscosity of the resin composite composition containing the particles can be made and the more the shapeability can be improved. The roundness may also be 0.90 or more or may also be 0.93 or more. The upper limit of the roundness is theoretically 1.0, but from the viewpoint of production control, it may also be 0.98 or less or 0.95 or less.

[0035]

The roundness can be measured using an electron microscope or an optical microscope and an image analysis apparatus. For example, FPIA made by Sysmex Corporation etc. may be used. These apparatuses are used to measure the roundness of the particles (circumference of equivalent circle/circumference of projected image of particle). 100 or more particles are measured for roundness and the average value of the same is made the roundness of the powder.

[0036]

In one embodiment of the present invention, a resin composite composition containing spherical silica particles is provided. The resin composite composition can be cured to produce a resin composite. The composition of the resin composite composition will be explained below:

[0037]

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

[0038]

If producing a resin composite composition, for example, in addition to the spherical silica particles and resin, a curing agent, curing accelerator, flame retardant, silane coupling agent, etc. can be mixed in along with need and a composite formed by kneading or another known method. Further, the mixture is shaped into pellets, a film, etc. in accordance with the application.

[0039]

Further, if producing a resin composite composition, in addition to the spherical silica particles and resin, another inorganic filler may be mixed in. As the inorganic filler, amorphous spherical silica particles, amorphous spherical alumina particles, crystalline spherical silica particles, alumina particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber may be mentioned. The blending ratio of the inorganic filler can be suitably adjusted in accordance with the application of the resin composite composition, but from the viewpoint of obtaining the

effect of the spherical silica particles of the present invention, (blended weight of spherical silica particles):(blended weight of other inorganic fillers)=95:5 to 60:40 is preferable.

[0040]

Furthermore, if curing the resin composite composition to produce a resin composite, for example, heat can be applied to the resin composite composition to melt it, the composition can be worked into the shape corresponding to its application, and a heat higher than the time of melting can be applied to cause the composition to completely cure. In this case, the transfer mold method, compression mold method, or other known method can be used.

[0041]

For example, when producing a package 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 employing an epoxy resin is preferable. The epoxy resin is not particularly limited, but, for example, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, biphenyl type epoxy resin, phenol novolac type epoxy resin, cresol novolac type epoxy resin, naphthalene type epoxy resin, phenoxy type epoxy resin, etc. can be used. It is possible to use one type among these alone or to use two types or more having different molecular weights together. Among these as well, from the viewpoint of the curability, heat resistance, etc., an epoxy resin having two or more epoxy groups in a molecule is preferable. Specifically, a biphenyl type epoxy resin, phenol novolac type epoxy resin, o-cresol novolac type epoxy resin, phenol types and aldehyde types of novolac resins which are epoxylated, bisphenol A, bisphenol F, bisphenol S, and other glycidyl ethers, glycidyl ester acid epoxy resins obtained by reaction of a phthalic acid, dimic acid, or other polybasic acid and epichlorohydrin, linear aliphatic epoxy resin, alicyclic epoxy resin, heterocyclic epoxy resin, alkyl modified polyfunctional epoxy resin, β -naphthol novolac type epoxy resin, 1,6-dihydroxynaphthalene type epoxy resin, 2,7-dihydroxynaphthalene type epoxy resin, bishydroxybiphenyl type epoxy resin, an epoxy resin in which bromine or other halogen is introduced to impart flame retardance, etc. may be mentioned. Among these epoxy resins having two or more epoxy groups in a molecule, in particular a bisphenol A type epoxy resin is preferable.

[0042]

Further, as the resin used for applications other than composite materials for semiconductor sealant use, for example, prepregs for printed boards, various engineering plastics, and other resin composite compositions, resins other than epoxy types can also be applied. Specifically, in addition to epoxy resins, 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.

[0043]

As the curing agent usable in the resin composite composition, any curing agent known for curing a resin may be used, but, for example, a phenolic curing agent can be used. As a phenolic curing agent, a phenol novolac resin, alkylphenol novolac resin, polyvinyl phenol, etc. can be used alone or in combinations of two or more types.

[0044]

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

[0045]

The amount of addition of the spherical silica particles in the resin composite composition is preferably large from the viewpoint of the heat resistance and thermal expansion coefficient, but usually 70 mass% or more and 95 mass% or less, preferably 80 mass% or more and 95 mass% or less, and more preferably 85 mass% or more and 95 mass% or less are suitable. This is because if the blended amount of spherical silica particles is too small, the effects of improvement of the strength of the sealant, suppression of thermal expansion, etc. become hard to obtain. Further, if too great, despite surface treatment of the spherical silica particles, at the composite material, segregation easily occurs due to agglomeration of the spherical silica particles, the viscosity of the composite material becomes too large, and other issues arise, therefore practical application as a sealant becomes difficult. Note that when using together the “other fillers” explained above, the preferable amount of addition at the resin composite composition is the total amount of the spherical alumina particles and “other fillers”.

[0046]

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

[0047]

The fluidity of the resin composite composition containing the spherical silica particles (narrow part fluidity) is as one example measured by the following procedure.

Using a transfer molding machine equipped with a measurement use mold having a slit with a groove depth of 10 μm or less, the length of the resin composite composition containing the spherical silica particles flowing to the slit is measured. Note that the transfer molding conditions are a mold temperature of 175°C, a molding pressure of 7 MPa, and a pressure holding time of 180 seconds. The larger the length, the better the fluidity exhibited.

[0048]

Note that, the resin composite composition for measurement of fluidity is prepared by mixing spherical silica particles with a resin of predetermined conditions in a certain ratio. As one example, biphenyl-based resin (YX4000H (made by Mitsubishi Chemical Corporation) and spherical silica particles are mixed by a 25:75 (wt%) and further a curing agent, curing accelerator, and epoxy-based silane coupling agent are added for preparation.

[0049]

The method for production of the spherical silica particle according to an embodiment of the present invention comprises a step of running natural silica through a flame to make it melt, then cooling it to make it spheroidal and a step of classifying it by joint use of a classifier (for example, a precision air classifier) and/or sieve after the step for spheroidization. Due to this method of production, it is possible to produce spherical silica particles wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles is 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles is 100 ppm or less, and a specific surface area by the BET method is 5.0 m^2/g or more and 20 m^2/g or less.

EXAMPLES

[0050]

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

[0051]

(Examples 1 to 6 and Comparative Examples 1 to 4)

Natural silica was crushed and the crushed powder was run through a high temperature flame formed by combustion of LPG and oxygen to melt and make it spheroidal and obtain spherical silica particles. The conditions forming the flame, particle size of the starting material, amount of supply of the starting material, classification conditions, blending conditions, etc. were adjusted to produce various powders shown in Table 1. Specifically, the particle size distribution was adjusted by adjusting the starting material particle size, classifying the powder after the spheroidization treatment by multiple stage sieving, and classifying the powder using a precision air classifier as a final step. The number frequency of 5 μm or more particles among the 1 μm or more 30 μm or less particles detected by a Coulter counter, D50 by laser diffraction/scattering method (or mode size), specific surface area and roundness by the BET method, ratio B/A of number frequency by Coulter counter (where the number frequency of 1 to 2 μm

particles is “A” and the number frequency of 2 to 30 μm particles is “B”), number frequency of 10 μm or more particles by a Coulter counter, etc. were adjusted by adjusting the blended amounts of the several types of powder obtained by the above operation. For example, a number frequency or its ratio was adjusted by blending particles with known number frequencies in suitable ratios, the specific surface area was adjusted by addition of ultrafine powder having various particle sizes and specific surface areas, and the roundness was controlled by adjusting the flame forming conditions and amount of supply of the starting material.

[0052]

Table 1 shows the values of the physical properties of the spherical silica particles used.

[0053]

[Table 1]

Table 1

Item	Unit	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
D50	μm	1.5	1.8	0.5	2.2	0.9	0.4	2.2	2.2	0.4	2.5
D100	μm	4.0	5.2	1.5	5.3	3.9	1.4	8.7	7.6	1.8	5.6
Specific surface area	m ² /g	11.6	7.9	16.6	6.6	8.6	18.5	8	7.1	18.2	5.3
Number frequency by Coulter counter (measurement of 1 to 30 μm particles)	3 μm or more	3139	13337	309	29873	2108	410	42909	42367	225	59319
	5 um or more	0	27	33	25	52	10	2095	1555	18	56
	10 um or more	0	0	0	0	0	0	8.59	0	0	0
	A=1 to 2 um	88.5	85.7	99.6	83.6	97.7	99.9	81.4	80.7	99.7	84.7
	B=2 to 30 μm	11.5	14.3	0.4	16.4	2.3	0.1	18.6	19.3	0.3	15.3
Roundness	B/A	0.13	0.17	0.004	0.196	0.024	0.001	0.23	0.24	0.003	0.181
True specific gravity		0.95	0.95	0.96	0.93	0.95	0.96	0.96	0.95	0.96	0.93
Fluidity	g/cm ³	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
		Excellent	Excellent	Good	Excellent	Good	Good	Poor	Poor	Poor	Poor

[0054]

The methods for measurement of the different properties are explained below.

[0055]

(Measurement by Coulter Counter Method)

5 In a 200 ml glass beaker, spherical silica particles and 150 ml of an electrolyte were placed. An ultrasonic homogenizer (Ultrasonic Homogenizer UH-300 made by SMT) was used to make the particles disperse for 30 seconds. Furthermore, this dispersion was added to an electrolyte prepared in a separate beaker to adjust the concentration. The dispersion adjusted in concentration was measured by a Coulter counter (Multisizer 3 made by Beckman Coulter) using an aperture size of 10 50 μm to measure the individual particle sizes of the spherical silica particles. At this time, the number of particles measured per measurement was made about 100,000. The same sample was measured repeatedly three times. Among these, the numbers of particles with a particle size of 3 and 5 μm or more were calculated and made the frequency of coarse particles (ppm) with respect to the total number. Similarly, the number frequency A of particle size 1 to 2 μm particles, the number 15 frequency B of particle size 2 to 30 μm particles, and the number frequency of particle size 10 μm or more were also measured.

[0056]

(D50 by Laser Diffraction/Scattering Method)

20 As the particle size distribution measurement apparatus, “Mastersizer 3000” (made by Malvern) was used. At the time of measurement, for the refractive index of the solvent water, 1.33 was used. For the refractive index of the powder, the refractive index of the material of the powder was considered. For example, for amorphous silica, the refractive index of 1.54 was used for measurement.

[0057]

25 (Specific Surface Area)

The BET theory was applied to an adsorption isotherm measured by the gas adsorption method to find the specific surface area (BET value) (BET method). As the specific surface area measurement apparatus, a product name “Macrosorb Model HM-1208” made by Mountec Co., Ltd. is used in the measurement.

30 **[0058]**

(Roundness)

The roundness can be measured using an electron microscope or an optical microscope. For example, FPIA made by Sysmex Corporation etc. may be used. These apparatuses are used to measure the roundness of the particles (circumference of equivalent circle/circumference of 35 projected image of particle). 100 or more particles are measured for roundness and the average value of the same is made the roundness of the powder.

[0059]

(Fluidity (Narrow Part Fluidity))

Using a transfer molding machine equipped with a measurement use mold having a slit with a groove depth of 10 μm or less, the length of the resin composite composition containing the spherical silica particles flowing to the slit is measured. Note that the transfer molding conditions are a mold temperature of 175°C, a molding pressure of 7 MPa, and a pressure holding time of 180 seconds. The larger the length, the better the fluidity exhibited. Cases with a large length (2.5 cm or more) are indicated as “excellent”, cases of 1.5 cm or more and less than 2.5 cm as “good”, and small cases (less than 1.5 cm), as “poor”.

[0060]

Note that, the resin composite composition for measurement of the fluidity is prepared by mixing a biphenyl-based epoxy resin (YX4000H made by Mitsubishi Chemical) and spherical silica particles in a 25:75 (wt%) ratio and further adding a curing agent, curing accelerator, mold release agent, and epoxy-based silane coupling agent.

[0061]

(True Specific Gravity)

A continuous automatic powder true specific gravity measurement apparatus (product name: Auto True Denser Mat-7000 made by Seishin Enterprise Co., Ltd.) was used to measure the true specific gravity of the silica particles by the Pycnometer method (liquid phase substitution method).

[0062]

Resin composite compositions respectively containing the silica particles of Examples 1 to 6 and Comparative Examples 1 to 4 were prepared and measured for fluidity (narrow part fluidity). The measurement results are shown in Table 1. It was confirmed that in the spherical silica particles in the scope of the present invention, “excellent” or “good” fluidity was obtained.

[INDUSTRIAL APPLICABILITY]

[0063]

The spherical silica particles of the present invention and the resin composite composition containing the same exhibit good fluidity and can be used not limited to semiconductor sealants, but also used for other applications. Specifically, they can be used for prepregs for printed circuit board use, various engineering plastics, etc. Further, it is possible to obtain the above spherical silica particles by a method of production of the spherical silica particles according to the present invention.

CLAIMS

[Claim 1]

5 Spherical silica particles wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles is 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles is 100 ppm or less, and a specific surface area by the BET method is 5.0 m^2/g or more and 20 m^2/g or less.

[Claim 2]

10 Spherical silica particles according to claim 1, wherein a D50 by a laser diffraction/scattering method is 0.4 or more and 3.0 μm or less.

[Claim 3]

15 Spherical silica particles according to claim 1, wherein a roundness is 0.85 or more

[Claim 4]

20 Spherical silica particles according to claim 1, wherein, among the number of 1 μm or more and 30 μm or less particles detected by a Coulter counter, when designating the number frequency of 1 to 2 μm articles as “A” and the number frequency of 2 to 30 μm particles as “B”, B/A is 0.002 or more and 0.20 or less.

[Claim 5]

25 Spherical silica particles according to claim 1, wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, the 10 μm or more particles are less than 10 ppm.

[Claim 6]

30 A resin composite composition containing spherical silica particles according to any one of claims 1 to 5.

[Claim 7]

35 A resin composite composition according to claim 6, further containing at least one type of inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, alumina particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber.

[Claim 8]

A method of production of spherical silica particles wherein, among the 1 μm or more and 30 μm or less particles detected by a Coulter counter, a number frequency of 3 μm or more particles is 300 ppm or more and 50000 ppm or less, a number frequency of 5 μm or more particles is 100 ppm or less, and a specific surface area by the BET method is 5.0 m^2/g or more and 20 m^2/g or less, 5 comprised of a step of running natural silica through a flame to make it melt, then cooling it to make it spheroidal and a step of classifying it by joint use of a classifier and/or sieve after the step for spheroidization.