DESCRIPTION

TITLE

GALLIUM-CONTAINING ALUMINA PARTICLES, AND SLURRY COMPOSITION AND RESIN COMPOSITE COMPOSITION COMPRISING SAME

FIELD

[0001]

The present invention relates to gallium-containing alumina particles, in particular alumina particles with a content of gallium measured by inductively coupled mass spectrometry (ICP-MS) of a specific range and a slurry composition and resin composite composition containing the alumina particles.

BACKGROUND

[0002]

In recent years, due to the increasingly higher functions and higher speeds of mobile phones and other electronic equipment, the amount of heat generated from the electronic components inside electronic equipment has been increasing. For normal operation of electronic equipment, efficient dissipation of the generated heat to the outside has become an important issue. For heat dissipation, much use is made of what are called “heat dissipation sheets” and “heat dissipation adhesives”. These are adhered or coated and press bonded between a heat-generating body and heat dissipating fins to eliminate the gaps between the heat-generating body and heat dissipating fins and enable efficient dispersion of the heat. Further, inside of the electronic components, the semiconductors themselves also remarkably generate heat due to their similar increasingly higher functions and speeds. A heat dissipation ability is also sought to be imparted to the encapsulants protecting the semiconductors.

[0003]

In general, heat dissipation sheets, heat dissipation adhesives, and semiconductor encapsulants are comprised of a thermal conductive inorganic filler and a resin (such mixtures of fillers and resins sometimes referred to as “resin compositions” or “resin composite compositions”). Thermally conductive inorganic fillers include inexpensive aluminum hydroxide or aluminum oxide (below, “alumina”) and further silicon carbide, boron nitride, aluminum nitride, or other such materials promising high thermal conduction. Further, as a resin, a silicone resin is generally used if a heat dissipation sheet or heat dissipation adhesive, while an epoxy resin is generally used if a semiconductor encapsulant.

[0004]

In general, thermally conductive inorganic fillers are known to become high in thermal

conductivity due to the fact that better the symmetry of the crystal structure (if alumina, the α- and θ-phases) of the particles, the smaller the scattering due to lattice imperfections (for example, NPL 1). On the other hand, if the α- and θ-phase contents are high, the smoothness of the surface profile is lost (for example, PTL 1). Further, the α-phase is high in hardness, so deterioration of the wear due to its inclusion is reported (for example, PTL 2). For example, in the kneading step of the filler and resin at the time of production of the heat dissipation sheets, problems such as wear of the kneading facilities can arise. (For example, PTLs 1 and 2). For this reason, in thermally conductive inorganic fillers, design of materials giving thermal conductivity and smoothness of the surface profile was an important technical topic.

[0005]

PTL 2 discloses to spray aluminum hydroxide powder or a slurry of aluminum hydroxide powder from a feed tube having a powerful dispersion function into a flame to obtain spherical alumina powder. It discloses that due to this technique, the main crystal phases of the spherical alumina powder become comprised of δ and α and the mold wear characteristics can be improved. However, according to PTL 1, in spherical alumina particles obtained by this technique, even with particles with an average spheroidicity of 0.90 or more, there are surface irregularities derived from the aluminum hydroxide. It is considered that there is room for improvement.

[0006]

Further, PTL 1 discloses supplying aluminum hydroxide or alumina as alumina raw materials in a specific feed amount, melting it at 2050 to 2300°C, then rapidly cooling it by dry ice to obtain spherical alumina. It discloses that by this technique, in X-ray diffraction, the ratio of the δ-phase peak intensity and θ-phase peak intensity (δ-phase peak intensity/θ-phase peak intensity) becomes 1.0 or more and high fluidity spherical alumina powder controlled in surface profile is obtained. However, it is believed that by supplying low temperature dry ice to the inside of a high temperature melting furnace for rapid cooling in a production process melting the alumina raw materials in a flame, the load on the production apparatus becomes greater and stable industrial production is difficult. Further, it is believed that there is room for improvement in control of the surface profile and mold wear characteristics.

[CITATION LIST]

[PATENT LITERATURE]

[0007]

[PTL 1] Japanese Unexamined Patent Publication No. 2011-102215

[PTL 2] Japanese Unexamined Patent Publication No. 2001-19425

[NONPATENT LITERATURE]

[0008]

[NPL 1] Kittel Introduction to Solid State Physics. Fifth Edition

SUMMARY

[TECHNICAL PROBLEM]

[0009]

As stated above, attempts have been made to design materials featuring both the high thermal conductivity of alumina particles and excellent smoothness of the surface profile, but they have not been sufficiently effective. Further improvement has been necessary. Further, from the viewpoint of stable production in industry, a method of production not placing an excessive load on the production apparatus has been sought.

[SOLUTION TO PROBLEM]

[0010]

The inventors engaged in detailed studies on alumina particles and discovered that by controlling the content of gallium in alumina particles to a specific range, in particular a high thermal conductivity and excellent smoothness of surface profile are imparted together. Further, they discovered that due to this technique, it is possible to achieve control of these properties without placing an excessive load on the production apparatuses.

[0011]

It is not desirable to be constrained by any specific theory, but it is believed that by controlling the ratio of the α-crystal phase, θ-crystal phase, and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method, in particular by making the θ-crystal phase a certain amount, the smoothness of the surface profile rises.

[0012]

The present invention tries to solve the above-mentioned issue based on the above discoveries and has as its gist the following content as described in the claims.

[1] Gallium-containing alumina particles having an average particle size of 0.5 to 30.0 μm and a content of gallium measured by inductively coupled plasma mass spectrometry (ICP-MS) of 1.0 to 60.0 ppm.

[2] The gallium-containing alumina particles according to [1], wherein a ratio of the α-crystal phase, θ-crystal phase, and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method is represented by $(\alpha+\theta)/\delta \geq 2.0$.

[3] The gallium-containing alumina particles according to [1] or [2], wherein a ratio of θ-crystal phase and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method is represented by $\theta/\delta \geq 2.0$.

[4] The gallium-containing alumina particles according to any one of [1] to [3] wherein the circularity is 0.90 or more.

[5] A slurry composition containing gallium-containing alumina particles according to any one of [1] to [4].

[6] The slurry composition according to [5], further containing at least one type or more of an inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, carbon fiber, talc, mica, kaolin, calcium oxide, zinc oxide, barium sulfate, calcium sulfate, and alkali earth basic carbonates (calcium carbonate, magnesium carbonate, etc.)

[7] A resin composite composition containing gallium-containing alumina particles according to any one of [1] to [4].

[8] The resin composite composition according to [7], further containing at least one type or more of an inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, carbon fiber, talc, mica, kaolin, calcium oxide, zinc oxide, barium sulfate, calcium sulfate, and alkali earth basic carbonates (calcium carbonate, magnesium carbonate, etc.)

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0013]

The gallium-containing alumina particles of the present invention having a content of gallium in the alumina particles controlled to a specific range particularly have both excellent thermal conductivity and a high level of smoothness of the surface profile.

Further, the gallium-containing alumina particles are extremely excellent in stable industrial productivity in the point of enabling control of these properties without imposing an excessive load on the production facilities.

Further, by controlling the content of gallium in alumina particles, it is possible to simply control the balance of thermal conductivity and smoothness of the surface profile. That is, the required level of thermal conductivity differs depending on the application, while the required level of the wear resistance of the kneading facilities differs depending on the facilities. It is possible to control the balance in accordance with these required properties.

Note that the above effects are extremely useful when using gallium-containing alumina particles for fillers for heat dissipation sheets, heat dissipation adhesives, semiconductor encapsulants, and other products where thermal conductivity is sought.

DESCRIPTION OF EMBODIMENTS

[0014]

(Content of Gallium Measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of 1.0 to 60.0 ppm)

Alumina particles provided by one embodiment of the present invention have a content of gallium measured by inductively coupled plasma mass spectrometry (ICP-MS) of 1.0 to 60.0 ppm. The upper limit is preferably 40.0, more preferably 30.0, still more preferably 20.0, even more preferably 10.0 ppm. The lower limit may be preferably 2.0, more preferably 3.0 ppm.

[0015]

By controlling the amount of gallium contained in the alumina particles to the above range, it becomes possible to obtain excellent thermal conductivity while providing low abrasiveness.

[0016]

While the details are not clear, if the amount of gallium is less than 1.0 ppm, at the time of production of alumina particles, for example, in the cooling step after melting the alumina raw materials, surface irregularities remarkably form along with crystallization. It is believed that cooling of alumina particles occurs from the surface, therefore crystallization occurs from the surface. As a result, it is believed the irregularities of the surface become remarkable and the smoothness of the surface of the alumina particles remarkably fall. That is, if the Ga content is less than 1.0 ppm, the contents of the α-phase and θ-phase with high symmetries and a readiness to surface irregularities derived from crystal habits at the time of crystallization become greater, whereby the irregularities of particle surfaces at the time of crystallization upon cooling become remarkable. For this reason, in the kneading step of alumina particles and resin, the irregularities at the alumina particle surfaces (due to low smoothness) cause wear of the kneading facilities, so-called equipment wear. Further, the fluidity of the resin composition remarkably falls.

[0017]

If the amount of gallium is more than 60.0 ppm, the contents of the α-phase and θ-phase fall, causing the thermal conductivity to fall as a tendency. It is believed particularly difficult to achieve both excellent thermal conductivity and good abrasiveness (low wear on facilities).

[0018]

That is, by controlling the Ga content at the alumina particles to a suitable range, the ratio of the α-phase, δ-phase, and θ-phase is suitably controlled and as a result particularly excellent thermal conductivity and low abrasiveness can both be achieved.

[0019]

To obtain all of the above properties (avoidance of problem of equipment wear and excellent thermal conductivity), in the past, in the cooling step at the time of particle production, dry ice had to be used for rapid cooling etc. In the present invention, surprisingly, by controlling

the Ga content, particles having all of the above properties (avoidance of problem of equipment wear and excellent thermal conductivity) were created.

[0020]

[Method of Measurement of Ga Content]

For the method of measurement of the Ga content, an ICP-MS at which the quantification of the ultrafine components (ppm order) can be secured is used. For measurement by ICP-MS, a sample has to be dissolved to obtain a solution, but alumina is a hard to dissolve substance, therefore is dissolved by a pressurized acid decomposition method. After that, this solution may be analyzed by ICP-MS.

[0021]

(Average Particle Size of 0.5 or More and 30.0 μm or Less)

The alumina particles of one embodiment of the present invention has an average particle size of 0.5 to 30.0 μm. If the average particle size is less than 0.5 μm, the agglomeration ability of the particles becomes greater and the compositions containing the alumina particles, typically the slurry composition and resin composite composition etc., sometimes fall in lubrication ability (fluidity) so this is not preferable. If the average particle size is more than 10.0 μm, in compositions containing the alumina particles, typically the slurry composition and resin composite composition etc., sometimes the miscibility with other components falls. The average particle size of the alumina particles can be suitably adjusted in accordance with the desired application and properties of the composition in which they are contained. For this reason, the lower limit of the average particle size may be 1.0 μm or may be 3.0 μm. Further, the upper limit of the average particle size may be 20.0 μm, may be 15.0 μm, or may be 10.0 μm. Note that the alumina particles according to one embodiment of the present invention can be produced by the thermal spraying method. In the thermal spraying method, by adjusting the particle size of the raw materials used, it is possible to adjust the particle size of the alumina particles after thermal spraying.

[0022]

Here, the “average particle size” indicates the average particle size (D50) and means the median size D50 with a cumulative volume of 50% in the particle size distribution based on volume measured by the laser diffraction/scattering particle size distribution measurement method. Note that the “laser diffraction/scattering particle size distribution measurement method” is the method of firing a laser at a dispersion in which spherical alumina particles are dispersed and finding the particle size distribution from the intensity distribution pattern of diffracted/scattered light emitted from the dispersion. In one embodiment of the present invention, a laser diffraction/scattering particle size distribution analyzer “Mastersizer 3000” (made by Malvern) is used. Note that the average particle size can also be found in the same way

for the starting material of the alumina particles.

[0023]

(Ratio of α-Crystal Phase, θ-Crystal Phase, and δ-Crystal Phase Measured by X-Ray Diffraction (XRD) and Analyzed by Rietveld Method Expressed as $(\alpha+\theta)/\delta \geq 2$)

The alumina particles of one embodiment of the present invention may have a ratio of the α-crystal phase, θ-crystal phase, and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method expressed as $(\alpha+\theta)/\delta \geq 2$. The upper limit of $(\alpha+\theta)/\delta$ may be less than or equal to 10.0, preferably may be less than or equal to 8.0. The lower limit of $(\alpha+\theta)/\delta$ is preferably more than or equal to 3.0, more preferably more than or equal to 4.0, still more preferably more than or equal to 5.0.

[0024]

By controlling the ratio of the α-crystal phase, θ-crystal phase, and δ-crystal phase to within the above range, the ratio of the α-phase, δ-phase, and θ-phase is suitably controlled and as a result a particularly excellent thermal conductivity and low abrasiveness can both be realized.

[0025]

[Method of Quantification of α-Phase, θ-Phase, and δ-Phase]

The α-phase, θ-phase, and δ-phase of the alumina particles are quantified by Rietveld analysis of X-ray diffraction data of the particles. The measurement of the X-ray diffraction of the alumina particles is performed using an X-ray diffraction measurement apparatus “Bruker D2PHASER” of Bruker. The obtained X-ray diffraction pattern is analyzed by the Rietveld method, the phases are quantified, and $(\alpha+\theta)/\delta$ and θ/δ are calculated. In the analysis, a data base of PDF-4 2020 (α: 04-004-2852, θ:01-086-1410, δ:04-021-8098) was referred to. In addition, the measurement conditions are as follows:

<Measurement Conditions>

Light source: CuKα (=0.1541 nm)

Scan range: 10 to 90°

Scan speed: 0.02°/s

Further, the reliability parameter Rwp value used as an indicator of the reliability of analysis in the Rietveld method is made less than 10% in each case.

[0026]

(Ratio of θ-Crystal Phase and δ-Crystal Phase Measured by X-Ray Diffraction (XRD) and Analyzed by Rietveld Method Expressed as $\theta/\delta \geq 2$)

The alumina particles of one embodiment of the present invention may have a ratio of the α-crystal phase, θ-crystal phase, and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method expressed as $\theta/\delta \geq 2$. The upper limit of θ/δ may be less than or equal to 10.0, preferably may be less than or equal to 8.0, more preferably may be less than or

equal to 6.0. The lower limit of θ/δ is preferably more than or equal to 3.0, more preferably more than or equal to 4.0, still more preferably more than or equal to 5.0.

[0027]

By controlling the ratio of the α-crystal phase, θ-crystal phase, and δ-crystal phase to within the above range, the ratio of the α-phase, δ-phase, and θ-phase is suitably controlled and as a result a particularly excellent thermal conductivity and low abrasiveness can both be realized. Note that the θ-phase and δ-phase are quantified by the method of quantification explained above.

[0028]

(Circularity of 0.90 or More)

The alumina particles according to one embodiment of the present invention can be produced based on the thermal spraying method. In the thermal spraying method, it is possible to adjust the profile of the alumina particles obtained by the amount of raw materials charged into the flame per unit time or the type of fuel gas. Spherical alumina particles can be obtained.

[0029]

Being spherical includes not only completely spherical, but also generally spherical. Specifically, the following procedure is used to judge whether something is spherical or not. First, the particles are photographed to obtain 2D images. The profiles of the 2D images (i.e., circular or generally circular) are focused on and the circularities (circumference of equivalent circle/circumference of projected image of particle) are measured. 100 or more particles are measured for circularity and the average value is calculated. An average value of circularity of 0.90 or more is deemed spherical.

[0030]

The spherical alumina particles may have a circularity of 0.90 or more.

The higher the circularity of the spherical particles, the more possible it is to lower the abrasiveness of the composition including the alumina particles, typically the slurry composition and resin composite composition, or raise the lubrication (fluidity) and in turn obtain an excellent feel during use (texture). The circularity may be 0.91 or more, may be 0.92 or more, may be 0.93 or more, may be 0.94 or more, or may be 0.95 or more. The upper limit of the circularity is theoretically 1.0, but from the viewpoint of production control, may also be 0.98 or less or 0.97 or less.

[0031]

[Method of Measurement of Circularity]

The circularity can be measured using an electron microscope or an optical microscope and an image analysis apparatus. For example, FPIA made by Sysmex Corporation is used. These apparatuses are used to obtain 2D images of the particles. The 2D images are measured for

circularity (circumference of equivalent circle/circumference of projected image of particle). 100 or more particles are measured for circularity and the average value of the same is made the circularity of the powder.

[0032]

(Slurry Composition Containing Gallium-Containing Alumina Particles)

According to an embodiment of the present invention, a slurry composition containing gallium-containing alumina particles is provided. A composition containing alumina particles and a dispersant can be used to obtain a slurry composition. The slurry composition can be used for the later explained resin composite composition etc. The slurry composition according to one embodiment of the present invention enables the abrasiveness to be lowered or the lubrication (fluidity) to be raised. Further, it enables a resin composite composition excellent in fluidity to be obtained.

[0033]

As the dispersant at the slurry composition, water or a known organic solvent can be suitably adjusted in accordance with the application of the slurry composition. A plurality of dispersants may also be jointly used. Typically, the dispersant is a liquid. Water, an organic solvent, etc. may be mentioned. As an organic solvent, hexane, heptane, octane, decane, or other alkane solvent, methanol, ethanol, propanol, or other alcoholic solvent, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, or other ketone solvent, benzene, toluene, ethylbenzene, xylene, and other aromatic solvents may be mentioned. Preferably, it is methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, or another ketone solvent. .

[0034]

If producing a slurry composition, for example, in addition to the gallium-containing alumina particles and dispersion medium, a known dispersant, pigment, fragrance, preservative, refined water, surfactant, etc. may be blended in according to need and kneading or other known method may be used for forming a composite.

[0035]

As the dispersant in the slurry composition, water or a known organic solvent can be suitably prepared in accordance with the application of the slurry composition. A plurality of dispersants may also be jointly used.

[0036]

As the dispersant, for example, a dispersant containing at least one type of dispersant selected from nonionic dispersants and cationic dispersants may be mentioned.

[0037]

The nonionic dispersant is not particularly limited. A known one can be used. For example, a polymer compound having a polyoxyethylene chain etc. may be mentioned. As the polymer

compound having a polyoxyethylene chain, for example, an alkyl polyoxyethylene ether, alkyl polyoxyethylene-polyoxypropylene ether, alkyl polyoxypropylene-polyoxyethylene ether, polyoxyethylene-polyoxypropylene ether (polyoxyethylene oxypropylene block copolymer), fatty acid polyoxyethylene ester, fatty acid polyoxyethylene sorbitan ester, fatty acid polyoxyethylene sorbitol ester, polyoxyethylene sorbitan monoalkyl ether, polyoxyethylene alkyl ether sulfuric acid ester, polyoxyethylene castor oil (hydrogenated castor oil), acetylene glycol ethylene oxide adduct etc. may be mentioned. As the alkyl polyoxyethylene ether, for example, polyoxyethylene lauryl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene octyl ether, polyoxyethylene cetyl ether, polyoxyethylene octylphenyl ether, polyoxyethylene nonylphenyl ether, etc. may be mentioned. As the fatty acid polyoxyethylene sorbitan ester, for example, polyoxyethylene sorbitan monolaurate etc. may be mentioned.

[0038]

The cationic dispersant is not particularly limited. A known one can be used. For example, an alkylamine salt, acylamine salt, quaternary ammonium salt, ammonium salt having amide bonds, ester bonds, or ether bonds, imidazoline, imidazolium salt, amine derivatives, etc. may be mentioned. The cationic dispersant may be a low-molecular-weight compound or a polymeric compound, but from the viewpoint of the dispersion of alumina particles, a polymeric compound is preferable. As such a polymeric dispersant, for example, polyethylene imine, aminoalkyl (meth)acrylate copolymer, polyvinyl imidazoline, polyvinyl pyridine derivative, polyoxyethylene alkylamine, polyoxyethylene alkylamide, etc. may be mentioned. As the polyvinyl pyridine derivative, a copolymer of vinyl pyridine and (meth)acrylic acid, copolymer of vinyl pyridine, (meth)acrylic acid, and an oxyethylene group-containing polymer compound, etc. may be mentioned. As a copolymer of vinyl pyridine, (meth)acrylic acid, and an oxyethylene group-containing polymer compound, for example, a copolymer of vinyl pyridine and (meth)acrylic acid, copolymer with polyoxyethylene, etc. may be mentioned. Among these, from the viewpoint of dispersion of alumina particles, an amine polymeric dispersant is preferable.

[0039]

Further, as the dispersant, a known surface treatment agent may be mentioned. By containing a surface treatment agent, the dispersion of the alumina particles and dispersant in the slurry composition and the dispersion or affinity with the resin in the resin composite composition are improved. For example, a compound having at least one or more functional groups selected from a methyl group, ethyl group, propyl group, butyl group, or other alkyl group, vinyl group, ethenyl group, propenyl group, or other alkenyl group, phenyl group, amino group, phenyl amino group, acryl group, methacryl group, epoxy group, and styryl group, a silane coupling agent, and silazane may be mentioned. More preferably, a silane coupling agent having SiH, SiOH, SiOR (R is a hydrocarbon group) and hexamethyldisilazane or other silazane

may be mentioned.

[0040]

As the silane coupling agent, vinyltrimethoxysilane, vinyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-aminopropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-methacryloxypropyltrimethoxysilane, and N-phenyl-3-aminopropyltrimethoxysilane may be mentioned. As an alkoxysilane compound, hexyltrimethoxysilane, octyltriethoxysilane, phenyltriethoxysilane may be mentioned. As the silazane compound, hexamethyldisilazane and trimethylsilane may be mentioned. From the viewpoint of excellent reactivity, a silazane compound is more preferable. More preferable are hexamethyldisilazane and trimethylsilane.

[0041]

The content of the gallium-containing alumina particles in the slurry composition (if containing the later mentioned “inorganic filler” or “other filler”, content combined with these) can be suitably adjusted in accordance with the application of the slurry composition. Typically, from the viewpoint of realizing the effect of the gallium-containing alumina particles of an embodiment of the present invention, it is 50 to 95 wt%. The more preferable lower limit is 55 wt%, more preferably 60 wt%, more preferably 65 wt%, more preferably 70 wt%. The more preferable upper limit is 93 wt%, more preferably 90 wt%, more preferably 85 wt%.

[0042]

(Inorganic Filler)

Further, in the case of producing the slurry composition and the later explained resin composite composition, in addition to the gallium-containing alumina particles of one embodiment of the present invention, another inorganic filler may be mixed in. As the inorganic filler, amorphous spherical alumina particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, carbon fiber, talc, mica, kaolin, calcium oxide, zinc oxide, barium sulfate, calcium sulfate, and alkali earth basic carbonates (calcium carbonate, magnesium carbonate, etc.) may be mentioned. The blending ratio of the inorganic filler can be suitably adjusted in accordance with the application of the slurry composition or resin composite composition. Typically, from the viewpoint of bringing out the effect of the gallium-containing alumina particles of one embodiment of the present invention, (blended weight of gallium-containing alumina particles):(blended weight of other inorganic filler) may be 5:95 to 90:10.

[0043]

(Resin Composite Composition Containing Gallium-Containing Alumina Particles)

According to one embodiment of the present invention, a resin composite composition containing gallium-containing alumina particles is provided. A composition containing gallium-

containing alumina particles and a resin can be used to obtain a resin composite composition.

[0044]

For example, gallium-containing alumina particles can be used to obtain a semiconductor encapsulant (in particular a solid encapsulant), interlayer insulating film, or other resin composite composition. Furthermore, by curing these resin composite compositions, a encapsulant (cured), a board for a semiconductor package, or other resin composite can be obtained. In semiconductor encapsulants, interlayer insulating films, heat dissipation sheets, heat dissipation grease, and other applications as well, by using the gallium-containing alumina particles of one embodiment of the present invention, it is possible to obtain a resin composite composition excellent in thermal conductivity, therefore this can be suitably used.

[0045]

If producing the resin composite composition, for example, in addition to the gallium-containing alumina particles and resin, a curing agent, curing accelerator, flame retardant, silane coupling agent, etc. are 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.

[0046]

Further, if producing a resin composite composition, in addition to the gallium-containing alumina particles and resin, another inorganic filler may be mixed in. As the inorganic filler to be blended into the resin composite composition (or slurry composition), amorphous spherical alumina particles, crystalline spherical silica 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 gallium-containing alumina particles of one embodiment of the present invention, (blended weight of gallium-containing alumina particles):(blended weight of other inorganic fillers)=95:5 to 60:40 is preferable.

[0047]

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

[0048]

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-dihydroxynapthalene type epoxy resin, 2,7-dihydroxynapthalene 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.

[0049]

Further, as the resin used for applications other than composite materials for semiconductor encapsulant 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.

[0050]

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.

[0051]

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

absorption and heat resistance are improved.

[0052]

The amount of addition of the gallium-containing alumina particles of one embodiment of the present invention 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 the gallium-containing alumina particles is too small, the effects of improvement of the strength of the encapsulant, suppression of thermal expansion, etc. become hard to obtain. Further, if too great, despite surface treatment of the gallium-containing alumina particles, at the composite material, segregation easily occurs due to agglomeration of the gallium-containing alumina particles, the viscosity of the composite material becomes too large, and other issues arise, therefore practical application as a encapsulant becomes difficult. Note that in the case of joint use of the above-mentioned “other filler”, the preferable amount of addition in the resin composite composition is the total amount of the gallium-containing alumina particles and “other filler”.

[0053]

Further, in addition to a resin, an added material, for example, silane coupling agent, curing agent, coloring agent, curing retardant, or other known additive can be used.

[0054]

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

[0055]

Further, the resin composite composition can be used to obtain heat dissipation sheets, heat dissipation grease, etc.

[0056]

When obtaining a heat dissipation sheet, in addition to the gallium-containing alumina particles and resin, an additive is suitably blended and the mixture is formed into a composite by kneading or other known method. The obtained composite is shaped into a sheet by a known method.

[0057]

For example, when producing a heat dissipation sheet, as the resin used for the resin composite composition, a known resin can be applied, but specifically 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. Among these as well, a silicone resin is preferably used. The silicone resin is not particularly limited, but, for example, a peroxide curable type, addition curable type, condensation curable type, ultraviolet curable type, etc. can be used.

[0058]

Further, in addition to a resin, an added material, for example, a silane coupling agent, curing agent, coloring agent, curing retardant, or other known additive can be used.

[0059]

When obtaining the heat dissipation grease, in addition to the gallium-containing alumina particles and resin, an additive is suitably blended and the mixture is formed into a composite by kneading or other known method. Here, the resin used for the heat dissipation grease is also called the “base oil”.

[0060]

For example, if producing a heat dissipation grease, as the resin used for the resin composite composition, a known resin is possible, but specifically 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, AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resin, mineral oil, synthetic hydrocarbon oil, ester oil, polyglycol oil, silicone oil, and fluorine oil may be mentioned.

[0061]

Further, in addition to the resin, an added material, for example, a silane coupling agent, coloring agent, thickener, or other known additive can be used. As the thickener, calcium soap, lithium soap, aluminum soap, calcium complex, aluminum complex, lithium complex, barium complex, bentonite, urea, PTFE, sodium terephthalate, silica gel, organic bentonite, or other known ones can be used.

[0062]

[Method of Production of Alumina Particles]

The gallium-containing alumina particles of one embodiment of the present invention are not particularly limited in method of production and can be produced by the following method of production. That method of production is a method enabling optimum production of the above-mentioned gallium-containing alumina particles and can include the following steps:

(1) a step of charging at least one of alumina, boehmite, aluminum hydroxide, etc. into a

flame to make it melt, then cooling it to produce alumina particles and

(2) a step of classifying the alumina particles by a sieve etc. after the step of producing them

[0063]

The step of producing alumina particles of (1) is a step of charging the raw materials of the alumina particles (below, also simply referred to as the "raw materials") into the flame to make them melt, then cooling them. These raw materials can be charged into the flame in a state made to float in a carrier gas. As the carrier gas, air, oxygen, propane gas, etc. can be employed.

[0064]

The flame is preferably formed inside a heat-resistant furnace. Preferably, the flame is formed at the top part of the heat-resistant furnace, the raw materials are supplied into the flame, and the melted alumina particle materials sink down due to gravity and are recovered from the bottom of the heat-resistant furnace. To prevent the raw materials from forming a flame at the bottom of the heat-resistant furnace, the alumina particle materials sinking to the bottom are cooled and form particles.

[0065]

The region at the top of the heat-resistant furnace with a flame where the raw materials are supplied and melted can be called the "melting region" and the region at the bottom of the heat-resistant furnace where the melted alumina particles are cooled can be called the "cooling region".

[0066]

The method of forming the flame is not particularly limited, but it is possible to supply fuel (propane, LPG, LNG, hydrogen, ammonia, or other known fuel) and combustion-supporting gas (air and oxygen) through respective burners to the melting region, supply a mixture of the fuel and combustion-supporting gas through a burner to the melting region, or supply a mixture of the raw materials, fuel, and combustion-supporting gas through a burner to the melting region so as to form a flame. In particular, from the viewpoint of raising the maximum temperature of the flame and increasing the temperature gradient inside the heat-resistant furnace, a method of forming a flame where a mixture of the raw materials and combustion-supporting gas or a mixture of the raw material, fuel, and combustion-supporting gas is supplied to the melting region is preferable.

[0067]

Note that, in the melting region, if possible to apply an amount of heat sufficient for melting to the particles of the raw materials, it is possible to decrease the amount of irregularly shaped particles not formed into spheres. Due to this, it is possible to adjust the bulk specific density of the alumina particles. Further, it is possible to adjust the circularity and bulk specific density by

the amount of material charged into flame per unit time or the type of fuel gas. Further, it is possible to adjust the particle size of the raw material powder used so as to adjust the particle size of alumina particles after thermal spraying.

[0068]

The raw materials of the alumina particles may be at least one of alumina, boehmite, aluminum hydroxide, etc. When these raw materials are charged into a flame, the alumina remains alumina while the boehmite and aluminum hydroxide form alumina by an oxidation or dehydration reaction.

[0069]

In the cooling region, a refrigerant may be used. The refrigerant is not particularly limited, but from the viewpoint of not causing the purity of the spherical particles to fall, air or distilled water or ion exchanged water not containing sodium ions or chlorine ions as impurities is desirable.

[0070]

In the classifying step of (2), the alumina particles obtained in the step of producing the alumina particles can be suitably classified using a sieve having predetermined mesh openings. They may also be pretreated or post-treated by a cyclone separator to classify them into coarse particles and fine particles in accordance with need. Due to this step, it is possible to obtain the desired particle size, particle size distribution, specific surface area, and bulk specific density.

[0071]

The gallium-containing alumina particles of one embodiment of the present invention need only be in a state where alumina particles having a content of Ga prescribed in the present invention are obtained in the step of the above (1).

[0072]

For example, the raw materials of the alumina particles may have the content of Ga prescribed in an embodiment of the present invention or a source of Ga such as gallium oxide, gallium hydroxide, etc. may be charged together with the raw materials when charging them into the flame.

EXAMPLES

[0073]

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

[0074]

Alumina particles were produced by charging alumina particle materials containing

predetermined amounts of gallium into a flame formed by LPG and oxygen, that is, by thermal spraying. The particle size of the charged alumina particle materials was controlled to adjust the average particle size of the alumina particles and the flame forming conditions, particle size of the raw materials, amount of supply of raw materials, classification conditions, etc. were adjusted to produce gallium-containing alumina particles having properties shown in Table 1. The properties of the obtained alumina particles are shown in Table 1.

[0075]

[Table 1]

Table 1. Properties of Alumina Particles

		Ex. 1	Ex. 2	Ex. 3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Average particle size [um]		4.6	2.5	5.1	2.1	0.5	0.8
Ga content [ppm]		50	50	5	310	85	130
Crystal phase (Rietveld method)	(α+θ)/δ	4.6	3.2	6.4	0.3	0.7	0.2
	θ/δ	2.9	2.6	4.4	0.2	0.7	0.2
Thermal conductivity		Very good	Very good	Very good	Fair	Good	Fair
Abrasiveness (hardness)		Good	Good	Fair	Very good	Good	Very good

[0076]

The methods of measurement of the physical properties are described below:

[0077]

[Average Particle Size]

A laser diffraction/scattering particle size distribution analyzer “Mastersizer3000” (made by Malvern) was used to measure the average particle size (D50).

[0078]

[Method of Measurement of Ga Content]

The Ga content was measured by the ICP-MS method. To dissolve the alumina, a step was dissolved by the pressurized acid decomposition method to obtain a solution. After that, ICP-MS was used to measure the amount of Ga and find the content.

[0079]

[Method of Quantification of α-Phase, θ-Phase, and δ-Phase]

The α-phase, θ-phase, δ-phase of the alumina particles described in the examples and comparative examples were quantified by Rietveld analysis of the X-ray diffraction data of the particles. The X-ray diffraction measurement of the alumina particles was performed using a powder X-ray diffraction measurement apparatus “Bruker D2PHASER” made by Bruker. The obtained X-ray diffraction pattern was analyzed by the Rietveld method, each phase was quantified, and (α+θ)/δ and θ/δ were calculated. In the analysis, a data base of PDF-4 2020 (α: 04-004-2852, θ:01-086-1410, δ:04-021-8098) was referred to. In addition, the measurement conditions were as follows:

<Measurement Conditions>

Light source: CuKα (=0.1541 nm)

Scan range: 10 to 90°

Scan speed: 0.02°/s

Further, the reliability parameter Rwp value used as an indicator of the reliability of analysis in the Rietveld method was less than 10% in each case.

[0080]

[Method of Evaluation of Thermal Conductivity]

Alumina particles described in each of the examples and comparative examples, a biphenyl-based epoxy resin "YX-4000H" made by Mitsubishi Chemical, and a curing agent of "2-ethyl-4-methylimidazole" made by Shikoku Chemicals were weighed out on a metal plate by a ratio of a mass ratio of 80:15:5 and kneaded on a hot plate set to 175°C while heated until the mixture became uniform. The mixture was held as is for 5 hours to prepare a sheet-shaped resin composite composition with a thickness of 5 mm. The plate-shaped resin composition cooled in a constant temperature bath of 25°C was placed on a hot plate heated to 100°C and the thermal conductivity was evaluated by the time until the surface not contacting the hot plate reached 80°C.The group with the shortest time until reaching 80°C was evaluated as "very good", the next shortest group as "good", the next shortest group as "fair", and the longest group as "poor". "Very good" means particularly excellent in thermal conductivity. Further, in industry, "good" to "fair" can be said to mean sufficient thermal conductivity.

[0081]

[Method of Measurement of Composition Hardness]

Alumina particles described in each of the examples and comparative examples and a biphenyl-based epoxy resin "YX-4000H" made by Mitsubishi Chemical were weighed out on a metal plate by a ratio of a mass ratio of 4:1 and kneaded on a hot plate set to 175°C while heated until the mixture became uniform. The mixture was cooled in a constant temperature bath of 25°C to prepare a plate-shaped resin composite composition of a thickness of 5 mm. As Asker hardness meter TYPE E was used to measure the hardness of the plate-shaped resin composition which was then used for evaluation of the abrasiveness performance. The group with the lowest hardness was evaluated as "very good", the next lowest group as "good", the next lowest group as "fair", and the highest group as "poor". "Very good" means particularly low in equipment wearability and can be said to be excellent in industrial. Further, in industry, "good" to "fair" can be said to mean sufficiently excellent thermal conductivity.

[0082]

[Circularity]

The circularity was measured using an electron microscope or an optical microscope and an

image analysis apparatus. In the examples and comparative examples, FPIA made by Sysmex Corporation was used. These apparatuses are used to measure the circularity of the particles (circumference of equivalent circle/circumference of projected image of particle). 100 or more particles are measured for circularity and the average value of the same is made the circularity of the powder.

INDUSTRIAL APPLICABILITY

[0083]

The alumina particles of one embodiment of the present invention are excellent in thermal conductivity and high in level of smoothness of the surface profile. In one embodiment of the present invention, a slurry composition and resin composite composition containing the alumina particles are also provided. In accordance with the properties of the alumina particles, excellent thermal conductivity and abrasiveness (little wear of facilities) and other effects can be obtained.

CLAIMS

[Claim 1]

Gallium-containing alumina particles having an average particle size of 0.5 to 30.0 μm and a content of gallium measured by inductively coupled plasma mass spectrometry (ICP-MS) of 1.0 to 60.0 ppm.

[Claim 2]

The gallium-containing alumina particles according to claim 1, wherein a ratio of an α-crystal phase, θ-crystal phase, and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method is represented by $(\alpha+\theta)/\delta \geq 2.0$.

[Claim 3]

The gallium-containing alumina particles according to claim 1, wherein a ratio of θ-crystal phase and δ-crystal phase measured by X-ray diffraction (XRD) and analyzed by the Rietveld method is represented by $\theta/\delta \geq 2.0$.

[Claim 4]

The gallium-containing alumina particles according to claim 1, wherein the circularity is 0.90 or more.

[Claim 5]

A slurry composition containing gallium-containing alumina particles according to any one of claims 1 to 4.

[Claim 6]

The slurry composition according to claim 5, further containing at least one type or more of an inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, carbon fiber, talc, mica, kaolin, calcium oxide, zinc oxide, barium sulfate, calcium sulfate, and alkali earth basic carbonates (calcium carbonate, magnesium carbonate, etc.)

[Claim 7]

A resin composite composition containing gallium-containing alumina particles according to any one of claims 1 to 4.

[Claim 8]

The resin composite composition according to claim 7, further containing at least one type or more of an inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, carbon fiber, talc, mica, kaolin, calcium oxide, zinc oxide, barium sulfate, calcium sulfate, and alkali earth basic carbonates (calcium carbonate, magnesium carbonate, etc.)