

DESCRIPTION

Siliceous Powder, Process For Production Of The Same, And
Use Thereof

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TECHNICAL FIELD

The present invention relates to a silica powder, a process for its production and its use.

10 BACKGROUND ART

To meet requirements for downsizing, weight saving and high performance of electronic equipment, downsizing, reduction in thickness and high densification of semiconductors are rapidly in progress. Further, with
15 respect to the mounting method for semiconductors, surface mounting suitable for high density mounting on a printed board or the like is predominant. In recent years, for a semiconductor of such a surface mounting type, an ultrathin semiconductor package has been used to lower the mounting
20 height on a printed board, whereby the thickness of the package has become very thin. More recently, a PoP (Package on Package) mounting method to mount another semiconductor on a semiconductor, has been practically used, whereby reduction in thickness of semiconductors has been
25 in progress more than ever.

On the other hand, from an increasing consciousness about environmental problems in recent years, it has been common to use a lead-free solder which does not contain

lead having a large environmental load, for mounting a semiconductor on a circuit board, and the temperature at the time of mounting has become higher by a few tens degrees in centigrade than ever. Namely, a semiconductor package which has become thinner than ever, is mounted as exposed to a temperature higher than ever, whereby a problem of package cracking has become frequented, and a sealing material for semiconductors is required to have the flexural strength, solder cracking resistance, etc. further improved.

In order to satisfy such requirements, it has been attempted to improve the flexural strength or to reduce the stress by such a means to improve e.g. an epoxy resin or phenol resin curing agent to be used for the sealing material for semiconductors (Patent Documents 1 and 2). However, the effects to improve the flexural strength by such means have been inadequate, and there has been no sealing material for semiconductors whereby a package thinner than ever is durable at a mounting temperature with a lead-free solder and the solder cracking resistance can be remarkably improved.

Further, as a method of modifying a ceramic powder, a case may be mentioned wherein for the purpose of improving the high temperature storage property (reliability) of a sealing material for semiconductors, the chemical adsorption of ammonia is controlled, and impurities in the sealing material for semiconductors are

trapped (Patent Document 3).

Patent Document 1: JP-A-2001-233937

Patent Document 2: JP-A-10-279669

Patent Document 3: WO/2007/132771

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SUMMARY

In a first aspect of the present disclosure, there is provided a silica powder characterized in that it has a Freundlich adsorption constant K of pyridine of from
10 1.3 to 5.0, the total of contents (as calculated as oxides) of SiO_2 , Al_2O_3 and B_2O_3 is at least 99.5 mass%, and the total of contents of Al_2O_3 and B_2O_3 is from 0.1 to 20 mass%.

In a second aspect of the present disclosure, there
15 is provided an inorganic powder characterized in that it contains the silica powder as defined herein.

In a third aspect of the present disclosure, there is provided a process for producing the silica powder as defined herein, characterized in that at least two
20 burners are disposed in a furnace body with an angle of from 2 to 10° to the central axis of the furnace body, and from one burner, a raw material silica powder is sprayed and from at least one burner, an aluminum source material and/or a boron source material is sprayed, into
25 a flame.

In a fourth aspect of the present disclosure, there is provided a resin composition characterized in that it

contains the silica powder as defined herein.

In a fifth aspect of the present disclosure, there is provided a sealing material for semiconductors, employing the resin composition as defined herein.

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DISCLOSURE OF THE INVENTION

OBJECT TO BE ACCOMPLISHED BY THE INVENTION

It is an object of the present invention to provide a silica powder useful for preparing e.g. a sealing
10 material for semiconductors having the flexural strength improved and having solder cracking resistance further improved.

MEANS TO ACCOMPLISH THE OBJECT

15 The present inventors have conducted an extensive study to accomplish the above object and have found a silica powder which accomplishes the object. The present invention is based on such a discovery and provides the following.

20 (1) A silica powder characterized in that it has a Freundlich adsorption constant K of pyridine of from 1.3 to 5.0.

(2) The silica powder according to the above (1), wherein the total of contents (as calculated as oxides)
25 of SiO_2 , Al_2O_3 and B_2O_3 is at least 99.5 mass%, and the total of contents of Al_2O_3 and B_2O_3 is from 0.1 to 20 mass%.

(3) The silica powder according to the above (1) or (2), which has a specific surface area of from 0.5 to 5 m²/g and an average particle size of from 1 to 60 μm.

(4) An inorganic powder characterized in that it
5 contains the silica powder as defined in any one of the above (1) to (3).

(5) The inorganic powder according to the above (4), wherein the inorganic powder is a silica powder and/or an alumina powder.

10 (6) A process for producing the silica powder as defined in any one of the above (1) to (3), characterized in that at least two burners are disposed in a furnace body with an angle of from 2 to 10° to the central axis of the furnace body, and from one burner, a raw material silica
15 powder is sprayed and from at least one burner, an aluminum source material and/or a boron source material is sprayed, into a flame.

(7) The process for producing the silica powder according to the above (6), wherein the aluminum source
20 material is an aluminum oxide powder, and the raw material silica powder has an Al₂O₃ content of at most 1 mass%.

(8) The process for producing the silica powder according to the above (7), wherein the aluminum oxide
25 powder has an average particle size of from 0.01 to 10 μm.

(9) A resin composition characterized in that it contains the silica powder as defined in any one of the

above (1) to (3) or the inorganic powder as defined in the above (4) or (5).

(10) The resin composition according to the above (9), wherein the resin in the resin composition is an epoxy resin.

(11) A sealing material for semiconductors, employing the resin composition as defined in the above (9) or (10).

EFFECTS OF THE INVENTION

10 The present invention provides a resin composition, particularly a resin composition as a sealing material for semiconductors, having the flexural strength and solder cracking resistance improved, and a silica powder useful for the preparation of such a resin composition.

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BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will be described in detail.

The silica powder of the present invention is a silica powder which has a Freundlich adsorption constant K of pyridine of from 1.3 to 5.0. Pyridine as a basic substance will be adsorbed to acid points on the surface of the silica powder. Accordingly, the value of the adsorption constant K of this substance being large means
20 that the number of acid points on the surface of the silica powder is large. When acid points of the silica powder are many, bonding points with a basic silane
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coupling agent such as aminosilane or phenylaminosilane will be many. Accordingly, the adhesion between the silica powder surface and a resin component such as an epoxy resin or a phenol resin in a sealing agent for semiconductors will be firmer, whereby the flexural strength will be improved, and moisture tends to hardly penetrate into the interface between the silica powder and the resin component, and thus the solder cracking resistance will also be remarkably improved.

10 If the Freundlich adsorption constant K of pyridine is less than 1.3, bonding points of the silica powder with the silane coupling agent will be less, whereby it becomes impossible to remarkably improve the solder cracking resistance or flexural strength of the sealing material for semiconductors. On the other hand, if the Freundlich adsorption constant K of pyridine exceeds 5.0, the number of acid points on the surface of the silica powder will be too many, whereby the epoxy resin will be cured. Consequently, there will be problem such that at 15 the time of packaging a semiconductor by means of a sealing material for semiconductors, the viscosity of the sealing material increases, and the moldability will be impaired. The value of the Freundlich adsorption constant K of pyridine is preferably from 1.5 to 4.5, particularly preferably from 2.0 to 4.3. These values are unique and distinct as compared with from 0.07 to 0.8 i.e. the value of the Freundlich adsorption constant K of 20

conventional silica powder.

The Freundlich adsorption constant K of pyridine can be measured by the following procedure.

(1) Preparation of pyridine standard solutions: 0.1
5 mol of pyridine for spectrometry is taken into a 500 ml measuring flask and adjusted to the constant volume with n-heptane for spectrometry. Then, 0.25 ml, 0.50 ml and 1.00 ml of such a pyridine solution are, respectively, taken into 200 ml measuring flasks and adjusted to the
10 constant volume with n-heptane to prepare pyridine standard solutions of 0.25 mmol/l, 0.50 mmol/l and 1.00 mmol/l.

(2) Adsorption on silica powder: 4.00 g each of silica powder preliminarily dried under heating at 200°C
15 for 2 hours, followed by cooling in a desiccator, is accurately weighed and put into three 25 ml measuring flasks. Into the respective measuring flasks, 20 ml of the pyridine standard solutions of 0.25 mmol/l, 0.50 mmol/l and 1.00 mmol/l are put and mixed by shaking for 3
20 minutes. These measuring flasks are immersed in a constant temperature tank set at 25°C for 2 hours to have pyridine adsorbed on the silica powder.

(3) Measurement of adsorbed amount of pyridine: From the above measuring flasks having the pyridine standard
25 solutions and silica powders mixed therein, the supernatants were respectively taken and put into measuring cells of an ultraviolet-visible

spectrophotometer and the concentration of residual pyridine remaining without being adsorbed is quantified by the absorbance.

(4) Calculation of Freundlich adsorption constant K of pyridine: The Freundlich adsorption constant K of pyridine is calculated by the Freundlich adsorption formula of $\log A = \log K + (1/n) \log C$. Namely, when a graph is drawn so that Y axis represents $\log A$ and X axis represents $(1/n) \log C$, $\log K$ is obtained from Y-intercept, whereby K can be calculated. Here, A is the amount ($\mu\text{mol/g}$) of pyridine adsorbed on 1 g of silica powder, C is the concentration ($\mu\text{mol/ml}$) of residual pyridine in the supernatant, and K and n are constants.

Here, as an example of the ultraviolet-visible spectrophotometer to be used for the measurement, "Ultraviolet-visible Spectrophotometer, Model UV-1800", tradename, manufactured by Shimadzu Corporation may be mentioned. As examples of the reagents to be used for preparation of the pyridine standard solutions, pyridine (spectrometry grade) and n-heptane (spectrometry grade), manufactured by Wako Pure Chemical Industries, Ltd., may be mentioned. Further, the wavelength for measurement of the absorbance was 251 nm, and only n-heptane was measured, and background correction was carried out. For the preparation of a calibration curve, the pyridine standard solutions of 0.00 mmol/l, 0.25 mmol/l, 0.50 mmol/l and 1.00 mmol/l were used.

Further, a characteristic of the silica powder of the present invention is that the total of contents (as calculated as oxides) of SiO_2 , Al_2O_3 and B_2O_3 is at least 99.5 mass%, and the total of contents of Al_2O_3 and B_2O_3 is from 0.1 to 20 mass%. If the total of contents of SiO_2 , Al_2O_3 and B_2O_3 is less than 99.5 mass%, i.e. if the content other than SiO_2 , Al_2O_3 and B_2O_3 exceeds 0.5 mass%, when the powder is formed into a sealing material for semiconductors, unnecessary substances will increase as impurities, such being undesirable. For example, Na_2O , Fe_2O_3 , etc., are likely to be partially ionized and elute to present damages to semiconductor chips or wirings. MgO , K_2O , CaO , etc. are likely to increase the thermal expansion coefficient of silica powder and thus present an adverse effect to the solder cracking resistance.

The total of contents of SiO_2 , Al_2O_3 and B_2O_3 is preferably at least 99.6 mass%, more preferably at least 99.7 mass%.

Further, the total of contents of Al_2O_3 and B_2O_3 in the silica powder is preferably from 0.1 to 20 mass%. When Al and B are present in the silica powder, the positions of Al and B will be strong acid points. By such acid points, bonding points of the silica powder surface with the basic silane coupling agent will increase, whereby the flexural strength and the solder cracking resistance will be improved. If the total of contents of Al_2O_3 and B_2O_3 is less than 0.1 mass%, the

increase of acid points tends to be inadequate. On the other hand, if it exceeds 20 mass%, the thermal expansion coefficient of the silica powder tends to be too large, which is likely to adversely affect the solder cracking resistance. The total of contents of Al_2O_3 and B_2O_3 is more preferably from 0.2 to 18 mass%, further preferably from 0.3 to 15 mass%.

The SiO_2 content (as calculated as an oxide) in the silica powder of the present invention can be measured by a mass reduction method, the Al_2O_3 content (as calculated as an oxide) can be measured by an atomic adsorption analysis, and the B_2O_3 content (as calculated as an oxide) can be measured by an ICP emission spectrometry, as follows.

(1) Measurement of SiO_2 content: 2.5 g of silica powder is accurately weighed on a platinum dish, and special grade reagent hydrofluoric acid, special grade reagent sulfuric acid and pure water are added in amounts of 20 ml, 1 ml and 1 ml, respectively. Such a platinum dish is left to stand still for 15 minutes on a sand bath heated at 300°C to let the powder dissolve and be dried. Then, into a muffle furnace heated at $1,000^\circ\text{C}$, the platinum dish is put and heated for 10 minutes to let fluosilicic acid evaporate. In a desiccator, the platinum dish is left to cool to room temperature, and then, the mass of the platinum dish is accurately weighed, whereupon the content of SiO_2 in the silica powder is

calculated from the mass reduction.

(2) Measurement of Al_2O_3 content: 1 g of silica powder is accurately weighed on a platinum dish, and special reagent hydrofluoric acid and special reagent perchloric acid are added in amounts of 20 ml and 1 ml, respectively. Such a platinum dish is left to stand still for 15 minutes on a sand bath heated at 300°C and then cooled to room temperature, and the content is transferred to a 25 ml measuring flask and adjusted to the constant volume with pure water. The Al amount in this solution is quantified by a calibration method by means of an atomic absorption photometer. The Al amount is calculated into Al_2O_3 to obtain the content in the silica powder. As an example of the atomic absorption photometer, "Atomic Absorption Photometer Model AA-969", tradename, manufactured by Nippon Jarrel-Ash may be mentioned. As an example of the standard solution to be used for preparing the calibration curve, Al standard solution for atomic absorption (concentration: 1,000 ppm) manufactured by Kanto Chemical Co., Ltd. may be mentioned. Further, at the time of the measurement, as the frame, an acetylene/nitrous oxide frame was used, and the absorbance at a wavelength of 309.3 nm was measured for quantitative determination.

(3) Measurement of B_2O_3 content: 1 g of silica powder is accurately weighed on a platinum dish, and special grade hydrofluoric acid, special grade nitric

acid and a 1% aqueous solution of special grade mannitol are added in amounts of 20 ml, 1 ml and 1 ml, respectively, and the platinum dish was left to stand still for 15 minutes on a sand bath heated at 300°C to let the powder dissolve and be dried. Then, to the dried product on the platinum dish, special reagent grade nitric acid and pure water are added in an amount of 1 ml each for redissolution, and then, the solution is transferred to a 25 ml measuring flask and adjusted to the constant volume with pure water. The B amount in this solution is quantified by a calibration curve method by means of an ICP emission spectrophotometer. Such a B amount is calculated into B_2O_3 to obtain the content in the silica powder. As an example of the ICP emission spectrophotometer, "Model SPS-1700R", tradename, manufactured by Seiko Instruments Inc. may be mentioned, and the emission intensity at a wavelength of 249.8 nm is measured. As an example of a standard solution to be used for preparing the calibration curve, B-standard solution for atomic absorption (concentration: 1,000 ppm) manufactured by Kanto Chemical Co., Ltd. may be mentioned.

The effect for improving the flexural strength and the solder cracking resistance by the resin composition of the present invention will be further increased when the specific surface area of the silica powder is within a range of from 0.5 to 5 m^2/g , and the average particle size is within a range of from 1 to 60 μm . If the

specific surface area is less than $0.5 \text{ m}^2/\text{g}$, the bonding area of the silica powder surface with the silane coupling agent tends to be too small, whereby the flexural strength or the solder cracking resistance tends to be hardly improved. On the other hand, if the specific surface area exceeds $5 \text{ m}^2/\text{g}$, such means that the silica powder contains a large amount of fine particles, or a part or whole of the particle surface has irregularities, whereby at the time of packaging a semiconductor by means of a sealing agent for semiconductors, the viscosity of the sealing material increases to impair the moldability. The range of the specific surface area is preferably from 0.6 to $4.8 \text{ m}^2/\text{g}$, more preferably from 0.7 to $4.7 \text{ m}^2/\text{g}$.

Further, if the average particle size of the silica powder is less than $1 \text{ }\mu\text{m}$, likewise, at the time of packaging a semiconductor by means of a sealing material for semiconductors, the viscosity of the sealing material increases to impair the moldability, such being undesirable. On the other hand, if the average particle size exceeds $60 \text{ }\mu\text{m}$, since the thickness of the semiconductor package is very thin, there will be a problem that a semiconductor chip will thereby be damaged by scratching, or it tends to be difficult to obtain a uniform package free from irregularities. The range of the average particle size is preferably from 2 to $55 \text{ }\mu\text{m}$, more preferably within a range of from 3 to $50 \text{ }\mu\text{m}$.

Further, the maximum particle size is preferably at most 196 μm , more preferably at most 128 μm .

The average particle size of the silica powder of the present invention is measured based on the particle size measurement by a laser diffraction scattering method. As the measuring machine to be used, for example, "Cirrus Granulometer Model 920", tradename, manufactured by CIRRUS, is used, and silica powder is dispersed in water and further subjected to dispersion treatment by an ultrasonic homogenizer at an output of 200 W for 1 minute, followed by measurement. Here, the measurement of the particle size distribution is carried out by particle size channels of 0.3, 1, 1.5, 2, 3, 4, 6, 8, 12, 16, 24, 32, 48, 64, 96, 128 and 196 μm . In the measured particle size distribution, the particle size where the cumulative mass becomes 50%, is the average particle size, and the particle size where the cumulative mass becomes 100%, is the maximum particle size.

The specific surface area of the silica powder of the present invention is measured based on the specific surface area measurement by a BET method. The specific surface area measuring apparatus may, for example, be "Macsorb Model HM-1208", tradename, manufactured by Mountech Co., Ltd.

The silica powder of the present invention is able to exhibit its effects even when mixed to another inorganic powder. The content of the silica powder of

the present invention in such an inorganic powder is preferably at least 0.5 mass%, more preferably at least 2 mass%. The type of the inorganic powder is preferably a silica powder and/or an alumina powder. These powders
5 may be used alone or in combination as a mixture of two of them. In order to lower the thermal expansion coefficient of the sealing material for semiconductors or to reduce the abrasion of a mold, a silica powder is selected for use, and in order to impart thermal
10 conductivity, an alumina powder is selected for use. Here, the silica powder is preferably such that the value of the amorphous ratio as measured by the after-mentioned method is at least 95%.

The silica powder of the present invention is such
15 that the amorphous ratio measured by the following method is preferably at least 95%, particularly preferably at least 98%. The amorphous ratio is obtained from the intensity ratio of specific diffraction peaks by carrying out an X-ray diffraction analysis by means of a powder X-
20 ray diffraction apparatus (such as "Model Mini Flex", tradename, manufactured by RIGAKU K.K.) within such a range that 2θ of $\text{CuK}\alpha$ -line is within a range of from 26° to 27.5° . In the case of the silica powder, crystalline silica has the main peak at 26.7° , while amorphous silica
25 has no peak. When amorphous silica and crystalline silica are present in a mixed state, a peak height at 26.7° corresponding to the proportion of the crystalline

silica is obtained, and from the ratio of the X-ray intensity of a sample to the X-ray intensity of the crystalline silica standard sample, the mixed ratio of the crystalline silica (X-ray diffraction intensity of the sample/X-ray diffraction intensity of crystalline silica) is calculated, and the amorphous ratio is obtained by the formula, amorphous ratio (%) = (1-mixed ratio of crystalline silica) $\times$ 100.

The average sphericity of each of the silica powder of the present invention, the inorganic powder and the alumina powder is preferably at least 0.80, particularly preferably at least 0.85. It is thereby possible to lower the viscosity of the resin composition and to improve the moldability. For the average sphericity, a particle image photographed by e.g. a stereoscopic microscope (such as "Model SMZ-10", tradename, manufactured by Nikon Corporation) is taken into an image analyzer (such as "MacView", tradename, manufactured by Mountech Co., Ltd.), and from the photograph, the projected area (A) and the periphery length (PM) of a particle are measured. When the area of a perfect circle corresponding to the peripheral length (PM) is represented by (B), the sphericity of the particle is represented by A/B. Accordingly, when a perfect circle having the same peripheral length as the peripheral length (PM) of a sample is assumed, $PM=2\pi r$ and $B=\pi r^2$, and thus, $B=\pi \times (PM/2\pi)^2$. The sphericity of an individual

particle will be $\text{sphericity} = A/B = A \times 4\pi / (PM)^2$. Sphericities of optional 200 particles thus obtained, were determined, and the average value was taken as the average sphericity.

Now, the process for producing the silica powder of the present invention will be described.

The process of the present invention is a process for producing the silica powder, characterized in that at least two burners are disposed in a furnace body with an angle of from 2 to 10° to the central axis of the furnace body, and from one burner, a raw material silica powder is sprayed and from at least one burner, an aluminum source material and/or a boron source material is sprayed, into a flame. If the raw material silica powder, and the aluminum source material and/or the boron source material, are sprayed from the same one burner, the sprayed materials necessarily spread in a conical shape, whereby the proportion of the aluminum source material and/or the boron source material fused on the surface of the raw material silica powder tends to be small, and it becomes impossible to produce the silica powder of the present invention wherein the total of contents of Al_2O_3 and B_2O_3 is from 0.1 to 20 mass%. Further, even in a case where the raw material silica powder, and the aluminum source material and/or the boron source material, are preliminarily mixed, they will be spread in a conical shape at the time of spraying and will be dispersed and separated, whereby the composition will be non-uniform.

At least two burners are disposed in a furnace body with an angle of from 2 to 10° to the central axis of the furnace body, to form a focal point, and from one burner, a raw material silica powder is sprayed and from at least
5 one burner, an aluminum source material and/or a boron source material is sprayed, into a flame, whereby the silica powder of the present invention can be produced very efficiently. By using a plurality of burners to spray the aluminum source material and/or the boron
10 source material, it is possible to further increase the uniformity of the composition of the silica powder of the present invention. A preferred number of burners is two burners to spray the aluminum source material and/or the boron source material per one burner to spray the raw
15 material silica powder. Here, the disposed angle of burners is required to be from 2 to 10° to the central axis of the furnace body. If the disposed angle of burners is less than 2°, the focal point will be out of the flame, and the proportion of the aluminum source
20 material and/or the boron source material to be fused on the surface of the raw material silica powder tends to be small. On the other hand, if the disposed angle of burners exceeds 10°, the focal point will be formed before the aluminum source material and/or the boron
25 source material is fused on the surface of the raw material silica powder, such being undesirable. The disposed angle of burners is more preferably within a

range of from 3 to 8°.

In the present invention, the aluminum source material is preferably an aluminum oxide powder. The aluminum source material may, for example, be aluminum oxide, aluminum hydroxide, aluminum sulfate, aluminum chloride or an aluminum organic compound. However, aluminum oxide is most preferred, since it is close to the melting point of the raw material silica powder, so that it is readily fused on the surface of the raw material silica powder when sprayed from a burner, and the impurity content is also small. Here, the average particle size of the aluminum oxide powder is preferably from 0.01 to 10 μm . If the average particle size is less than 0.01 μm , the powder tends to be agglomerated, and the composition when fused with the silica powder tends to be non-uniform, and likewise, if it exceeds 10 μm , the composition when fused with the silica powder tends to be non-uniform. The range of the average particle size is preferably from 0.03 to 8 μm , more preferably from 0.05 to 5 μm .

In the present invention, the Al_2O_3 content in the raw material silica powder is preferably at most 1 mass%. Among Al and B in the silica powder, only one located on the surface of the powder will form a strong acid point and is capable of bonding to a basic silane coupling agent. Thus, Al_2O_3 present in the interior of the raw material silica powder will present an adverse effect to

increase the thermal expansion coefficient of the silica powder. Accordingly, the Al_2O_3 content in the raw material silica powder is more preferably at most 0.8 mass%, further preferably at most 0.5 mass%.

5 The raw material silica powder may contain Fe_2O_3 , Na_2O , MgO , CaO , B_2O_3 , etc. in addition to the above-mentioned Al_2O_3 . However, the SiO_2 content in the raw material silica powder is preferably at least 97 mass%, more preferably at least 98 mass%.

10 As an apparatus to spray the raw material silica powder and the aluminum source material and/or the boron source material to the flame thereby to fuse them and collect them, one having a collecting device connected to the furnace body equipped with the burners may be used.

15 The furnace body may be an open or closed type or a vertical or horizontal type. The collecting device is provided with at least one of a gravity settling chamber, a cyclone, a bag filter, an electrical dust collector, etc., and is capable of collecting the produced silica

20 powder by adjusting the collecting conditions. Examples of such a collecting device are disclosed, for example, in JP-A-11-57451 and JP-A-11-71107.

 In the present invention, the Freundlich adsorption constant K of pyridine, of the silica powder, may be

25 increased or reduced by adjusting the sizes of the aluminum source material and/or the boron source material to be fused on the surface of the raw material silica

powder, the Al_2O_3 content and the B_2O_3 content in the silica powder, the specific surface area and the average particle size of the silica powder, etc. The Al_2O_3 content and the B_2O_3 content in the silica powder may
5 respectively be increased or reduced by adjusting the ratio of the spray amounts of the raw material silica powder and the aluminum source material and/or the boron source material to the burner flame. The specific surface area, the average particle size, etc. of the
10 silica powder may be adjusted by e.g. the particle size constitution of the raw material silica powder or the flame temperature. Further, the average sphericity and amorphous ratio may be adjusted by e.g. the amount of the raw material silica powder supplied to the flame or the
15 flame temperature. Further, various silica powders different in the specific surface area, the average particle size, the Al_2O_3 content, the B_2O_3 content, etc., may be preliminarily produced, and two or more of them may suitably be mixed to produce a silica powder having
20 the Freundlich adsorption constant K , Al_2O_3 content, B_2O_3 content, specific surface area, average particle size, etc. further specified.

The resin composition of the present invention is a resin composition containing the silica powder or the
25 inorganic powder of the present invention. The content of the silica powder or the inorganic powder in the resin composition is from 10 to 95 mass%, more preferably from

30 to 90 mass%.

The resin may, for example, be an epoxy resin, a silicone resin, a phenol resin, a melamine resin, a urea resin, an unsaturated polyester, a fluororesin, a polyamide such as polyimide, polyamideimide or polyetherimide, a polyester such as polybutylene terephthalate or polyethylene terephthalate, a polyphenylene sulfide, an organic polyester, a polysulfone, a liquid crystal polymer, a polyether sulfone, a polycarbonate, a maleimide-modified resin, an ABS resin, an AAS (acrylonitrile/acryl rubber/styrene) resin, an AES (acrylonitrile/ethylene/propylene/diene rubber/styrene) resin or the like. Among them, an epoxy resin, a silicone resin or a phenol resin is, for example, preferred.

Among them, an epoxy resin having at least two epoxy groups in one molecule is preferred as a sealing agent for semiconductors. For example, a phenol novolac type epoxy resin; an orthocresol novolac type epoxy resin; one having a novolac resin of a phenol and an aldehyde epoxidized; a glycidyl ether such as bisphenol A, bisphenol F or bisphenol S; a glycidyl ester acid epoxy resin obtained by a reaction of a polybasic acid such as phthalic acid or dimer acid with epochlorohydrin; a linear aliphatic epoxy resin; an alicyclic epoxy resin; a heterocyclic epoxy resin; an alkyl-modified polyfunctional epoxy resin; a β -naphthol novolac type

epoxy resin; a 1,6-dihydroxynaphthalene type epoxy resin;
a 2,7-dihydroxynaphthalene type epoxy resin; a
bishydroxybiphenyl type epoxy resin; and an epoxy resin
having an halogen atom such as bromine introduced to
5 impart flame retardancy, may be mentioned. Among them,
from the viewpoint of the moisture resistance or the
solder reflow resistance, a orthocresol novolac type
epoxy resin, a bishydroxybiphenyl type epoxy resin or a
naphthalene-skeleton epoxy resin is, for example,
10 preferred.

The epoxy resin to be used in the present invention
is one containing a curing agent for an epoxy resin, or a
curing agent for an epoxy resin and a curing accelerator
for an epoxy resin. The curing agent for an epoxy resin
15 may, for example, be a novolac resin obtainable by
reacting one or more selected from the group consisting
of phenol, cresol, xylenol, resorcinol, chlorophenol, t-
butylphenol, nonylphenol, isopropylphenol and octylphenol
with formaldehyde, paraformaldehyde or paraxylene in the
20 presence of an oxidation catalyst; a
polyparahydroxystyrene resin; a bisphenol compound such
as bisphenol A or bisphenol S; a tri-functional phenol
such as pyrogallol or phloroglucinol; an acid anhydride
such as maleic anhydride, phthalic anhydride or
25 pyromellitic anhydride; or an organic amine such as
metaphenylenediamine, diaminodiphenylmethane or
diaminodiphenylsulfone.

In order to accelerate the reaction of the epoxy resin with the curing agent, a curing accelerator such as triphenylphosphine, benzyldimethylamine or 2-methylimidazole, may be used.

5 To the resin composition of the present invention, the following components may further be incorporated, as the case requires.

As a stress-lowering agent, a rubber-like substance such as a silicone rubber, a polysulfide rubber, an
10 acrylic rubber, a butadiene rubber, a styrene block copolymer or a saturated elastomer; a thermoplastic resin; a resin-like substance such as a silicone resin; or a resin having a part of or whole of an epoxy resin or phenol resin modified with e.g. an amino silicone, an
15 epoxy silicone or an alkoxy silicone may, for example, be mentioned.

As a silane coupling agent, an epoxysilane such as γ -glycidoxypropyltrimethoxysilane or β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane; an aminosilane
20 such as aminopropyltriethoxysilane, ureidopropyltriethoxysilane or N-phenylaminopropyltrimethoxysilane; a hydrophobic silane compound such as phenyltrimethoxysilane, methyltrimethoxysilane or octadecyltrimethoxysilane or a
25 mercaptosilane may, for example, be mentioned.

As a surface treating agent, Zr chelate, a titanate coupling agent or an aluminum coupling agent may, for

example, be mentioned.

As an auxiliary flame retardant, Sb_2O_3 , Sb_2O_4 or Sb_2O_5 may, for example, be mentioned.

As a flame retardant, a halogenated epoxy resin or a
5 phosphorus compound may, for example, be mentioned.

As a coloring agent, carbon black, iron oxide, a dye or a pigment may, for example, be mentioned.

Further, as a mold release agent, a natural wax, a synthetic wax, a metal salt of a linear fatty acid, an
10 acid amide, an ester or a paraffin may, for example, be mentioned.

The composition of the present invention can be produced by blending predetermined amounts of the above respective materials by e.g. a blender or a Henschel
15 mixer, kneading the blended product by e.g. a hot roll, a kneader, a single screw or twin screw extruder, and cooling and grinding the kneaded product.

The sealing material for semiconductors of the present invention is made of the resin composition
20 containing an epoxy resin, which further contains a curing agent for the epoxy resin and a curing accelerator for the epoxy resin. To seal a semiconductor using the sealing material for semiconductors of the present invention, a conventional molding means such as a
25 transfer molding method or a vacuum printing molding method may be employed.

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples, but it should be understood that the present invention is by no means
5 restricted to such specific Examples.

EXAMPLES 1 to 9 and COMPARATIVE EXAMPLES 1 to 7

Various raw material silica powders different in the average particle size and in the Al_2O_3 content, aluminum source materials and boron source materials were prepared,
10 and they were subjected to melting, fusing and spheroidizing treatments in the flame to produce various silica powders shown in Table 1 by means of an apparatus disclosed in JP-A-11-57451 i.e. an apparatus wherein a plurality of burners are disposed in a furnace body so
15 that they are adjustable at an angle of from 0 to 15° to the central axis of the furnace body. Further, such powders were suitably blended to produce silica powders and inorganic powders as shown in Table 2.

Here, adjustment of the Freundlich adsorption
20 constant K of pyridine, of the silica powder, was made by changing e.g. the average particle size of the aluminum source material and/or the boron source material to be fused on the surface of the raw material silica powder, the Al_2O_3 content and the B_2O_3 content in the silica
25 powder, or the specific surface area and the average particle size of the silica powder. Adjustment of the Al_2O_3 content and the B_2O_3 content in the silica powder

was carried out by adjusting the ratio of the raw material silica powder and the aluminum source material and/or the boron source material sprayed to the burners. Adjustment of the specific surface area, the average particle size, etc. of the silica powder was carried out by adjusting e.g. the particle constitution of the raw material silica powder or the flame temperature. Further, adjustment of the average sphericity, amorphous ratio, etc. of the silica powder was carried out by adjusting the amount of the raw material silica powder supplied to the flame or the flame temperature. Here, the maximum temperature of the flame was within a range of from about 2,000°C to 2,300°C.

The amorphous ratio of the silica powder was at least 99.5% in each case.

With respect to these silica powders, the Freundlich adsorption constant K of pyridine, the SiO_2 content, the Al_2O_3 content, the B_2O_3 content, the specific surface area, the average particle size, the average sphericity, etc. were measured and shown in Table 2.

In order to evaluate properties of the obtained silica powders and inorganic powders as a filler for the sealing material for semiconductors, to 86.5 parts (parts by mass, the same applies hereinafter) of each powder, 6.7 parts of a 4,4'-bis(2,3-epoxypropoxy)-3,3',5,5'-tetramethylbiphenyl type epoxy resin, 5.5 parts of a phenol resin, 0.3 part of triphenylphosphine, 0.6 part of

phenylaminosilane, 0.1 part of carbon black and 0.3 part of carnauba wax were added, followed by dry blending by a Henschel mixer. Then, the blended product was heat-kneaded by a parallel matching twin screw extruder (screw diameter D: 25 mm, kneading disk length: 10 Dmm, number of revolution of paddle: 80 to 120 rpm, discharge amount: 2.5 kg/hr, and temperature of the kneaded product: 100 to 101°C). The kneaded product (discharged product) was pressed by a pressing machine and cooled, and then ground to produce a sealing material for semiconductors, and the flexural strength, the solder cracking resistance and the moldability (spiral flow) were evaluated as follows. The results are shown in Table 2.

(1) Flexural strength

The flexural strength of the cured product for the sealing material for semiconductors, obtained as described above, was measured as follows. That is, each of the above sealing materials for semiconductors was molded in a shape of 10 mm in width × 80 mm in length × 4 mm in height by means of a transfer molding machine under molding conditions at 175°C for 120 seconds, followed by post-curing at a temperature of 175°C for 6 hours to prepare five test pieces for evaluation in each case. And, using "Autograph Model AG-5000A", tradename, manufactured by Shimadzu Corporation, the flexural strength was measured in accordance with JIS K7171. Here, the distance between supporting points was 64 mm, the

loading rate was 5 mm/min, and the measuring environment was 25°C under a relative humidity of 50%. The average value of the respective measured values (n=5) was obtained and taken as the flexural strength.

5 The larger the numerical value (MPa), the higher the flexural strength.

(2) Solder cracking resistance

 The solder cracking resistance of the sealing materials for semiconductors obtained as described above
10 was measured as follows. That is, a simulated semiconductor chip of 9.6 mm × 9.6 mm × 0.4 mm was bonded by a silver paste to a lead frame made of copper and having a silver plating with a thickness of 150 nm applied. Then, by using each sealing material for
15 semiconductors, sealing was carried out by means of a transfer molding machine under molding conditions of 175°C for 120 seconds, followed by post-curing at a temperature of 175°C for 6 hours to obtain 60 pin QFP (Quad Flat Package) samples of 15 mm × 19 mm × 1.8 mm for
20 evaluation of solder cracking resistance. Then, in each case, ten such samples for evaluation were treated for 72 hours under environmental conditions at 85°C under a relative humidity of 85% and then heated in a solder reflow apparatus at a temperature of 250°C. Then, each
25 sample for evaluation was cut into a half, and the cut surface was polished, whereupon the size of a formed crack was observed by a microscope. A case where the

size of the crack is 70 μm or more was regarded as "no good", and the number of "no good" among ten samples was obtained. The results are shown in Table 2.

(3) Spiral flow

5 Using a transfer molding machine having a mold for measuring spiral flow attached thereto in accordance with EMMI-I-66 (Epoxy Molding Material Institute; Society of Plastic Industry), the spiral flow value of the sealing material for semiconductors was measured. The transfer
10 molding conditions were such that the mold temperature was 175°C, the molding pressure was 7.4 MPa and the holding time was 120 seconds. The larger the spiral flow value, the better the fluidity.

TABLE 1

Items		Type of silica powder					
		A	B	C	D	E	F
Average particle size of raw material silica powder (μm)		20	20	20	0.8	59	55
Al_2O_3 content of raw material silica powder (mass%)		0.06	0.06	0.06	1.2	0.03	0.08
Type of aluminum source material or boron source material		Aluminum oxide	Boron oxide	Aluminum oxide	Aluminum hydroxide	Aluminum oxide	Aluminum oxide
Average particle size of aluminum source material or boron source material (μm)		0.8	8	4	0.3	0.8	4
Angle for disposition of burners ($^\circ$)		5	5	10	5	5	2
Number of burners for spraying raw material silica powder (number)		1	1	1	1	1	1
Number of burners for spraying aluminum source material and/or boron source material (number)		2	2	2	2	2	2
Conditions for burners	LPG flow rate (m^3/hr)	8	8	8	7	12	12
	Oxygen flow rate (m^3/hr)	56	56	56	49	84	84
	Amount of raw material silica powder sprayed (kg/hr)	40	40	40	20	30	30
	Amount of aluminum source material and/or boron source material (kg/hr)	0.4	1.1	3.5	4.0	2.0	0.3

TABLE 1 (continued)

Items		Type of silica powder					
		G	H	I	J	K	L
Average particle size of raw material silica powder (μm)		1.2	17	20	22	20	20
Al_2O_3 content of raw material silica powder (mass%)		0.8	0.9	0.06	13	0.06	0.06
Type of aluminum source material or boron source material		Aluminum oxide	Aluminum oxide	-	Aluminum oxide	Aluminum hydroxide	Aluminum oxide
Average particle size of aluminum source material or boron source material (μm)		0.3	0.8	-	0.8	16	0.8
Angle for disposition of burners ($^\circ$)		2	5	5	0	0	15
Number of burners for spraying raw material silica powder (number)		1	*3	**1	1	1	1
Number of burners for spraying aluminum source material and/or boron source material (number)		2	0	0	2	2	2
Conditions for burners	LPG flow rate (m^3/hr)	7	8	8	8	8	8
	Oxygen flow rate (m^3/hr)	49	56	56	56	56	56
	Amount of raw material silica powder sprayed (kg/hr)	20	40	40	40	40	40
	Amount of aluminum source material and/or boron source material (kg/hr)	2.5	0.0	0.0	4.1	2.8	5.0

* A powder obtained by preliminarily mixing the raw material silica powder (85 mass%) and aluminum oxide powder (15 mass%), was sprayed.

** Only the raw material silica powder was sprayed.

TABLE 2

Items		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9
Proportion of the silica powder blended (mass%)	A	100	0	0	0	0	0	0	0	0
	B	0	100	0	0	0	0	0	0	0
	C	0	0	100	0	0	0	0	0	10
	D	0	0	0	0	100	0	0	20	0
	E	0	0	0	100	0	0	0	0	0
	F	0	0	0	0	0	100	0	0	0
	G	0	0	0	0	0	0	100	0	0
	H	0	0	0	0	0	0	0	0	0
	I	0	0	0	0	0	0	0	0	0
	J	0	0	0	0	0	0	0	0	0
	K	0	0	0	0	0	0	0	0	0
	L	0	0	0	0	0	0	0	0	0
Proportion of spherical silica powder (*) blended (mass%)		0	0	0	0	0	0	0	80	0
Proportion of spherical alumina powder (**) blended (mass%)		0	0	0	0	0	0	0	0	90
Freundlich adsorption constant K of pyridine (-)		3.9	4.2	3.2	3.8	4.6	2.9	3.5	1.8	1.3
Content of SiO ₂ , Al ₂ O ₃ and B ₂ O ₃ (mass%)		99.8	99.8	99.8	99.9	99.8	99.7	99.9	99.8	99.7
Content of Al ₂ O ₃ and B ₂ O ₃ (mass%)		0.9	2.5	8	6	17	0.7	12	3	91
Specific surface area (m ² /g)		1.9	1.9	1.7	0.4	5.3	0.7	4.7	2.5	1.2
Average particle size (μm)		24	24	24	62	0.9	58	1.4	21	19
Average sphericity (-)		0.96	0.94	0.95	0.91	0.98	0.86	0.95	0.98	0.98
Amorphous ratio (%)		100	100	99.9	100	99.9	98.7	100	99.8	-
Flexural strength (MPa)		177	175	171	161	174	165	169	165	161
Solder cracking resistance (number of "no good" among 10 samples)		0	0	0	1	1	0	0	0	1
Spiral flow (cm)		147	141	149	127	125	137	139	144	143

TABLE 2 (continued)

Items		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Proportion of the silica powder blended (mass%)	A	0	0	0	0	0	0	0
	B	0	0	0	0	0	0	0
	C	0	0	0	0	0	0	0
	D	0	0	0	0	0	0	0
	E	0	0	0	0	0	0	0
	F	0	0	0	0	0	0	0
	G	0	0	0	0	0	0	0
	H	0	0	100	0	0	0	0
	I	0	0	0	100	0	0	0
	J	0	0	0	0	100	0	0
	K	0	0	0	0	0	100	0
	l	0	0	0	0	0	0	100
Proportion of spherical silica powder (*) blended (mass%)		100	0	0	0	0	0	0
Proportion of spherical alumina powder (**) blended (mass%)		0	100	0	0	0	0	0
Freundlich adsorption constant K of pyridine (-)		0.3	0.6	1.1	0.8	6.4	0.9	0.6
Content of SiO ₂ , Al ₂ O ₃ and B ₂ O ₃ (mass%)		99.9	99.8	98.1	99.7	99.7	99.8	99.7
Content of Al ₂ O ₃ and B ₂ O ₃ (mass%)		0.07	99.5	14.4	0.05	22.4	7	11
Specific surface area (m ² /g)		1.7	1.1	1.3	1.9	2.0	1.6	1.7
Average particle size (μm)		25	18	19	24	25	23	24
Average sphericity (-)		0.95	0.93	0.99	0.96	0.98	0.98	0.95
Amorphous ratio (%)		99.8	-	100	100	99.9	99.7	99.8
Flexural strength (MPa)		124	130	125	133	78	136	121
Solder cracking resistance (number of "no good" among 10 samples)		5	9	10	9	2	5	8
Spiral flow (cm)		145	141	136	130	50	128	134

* Commercial product: average particle size: 25 μm, specific surface area: 1.7 m²/g, and Freundlich adsorption constant K: 0.3

** Commercial product: average particle size: 18 μm, specific surface area: 1.1 m²/g, and Freundlich adsorption constant K: 0.6

As is apparent from the comparison between Examples and Comparative Examples, according to the silica powder of the present invention, it is possible to prepare a resin composition, particularly a sealing material for semiconductors, which is excellent in flexural strength and solder cracking resistance, as compared with Comparative Examples.

INDUSTRIAL APPLICABILITY

10 The silica powder of the present invention is useful for a sealing material for semiconductors to be used for e.g. automobiles, portable electronic equipments, personal computers, household electric products, etc., for a laminated plate for mounting semiconductors, and as
15 a filler for e.g. patty, sealing materials, various rubbers, various engineering plastics, etc. Further, the resin composition of the present invention is useful for, in addition to a sealing material for semiconductors, prepregs for printed boards obtained by impregnating and
20 curing it in glass woven fabric, glass nonwoven fabric or other organic material, or various engineering plastics.

 The entire disclosure of Japanese Patent Application No. 2008-018973 filed on January 30, 2008 including
25 specification, claims and summary is incorporated herein by reference in its entirety.

CLAIMS:

1. A silica powder characterized in that it has a Freundlich adsorption constant K of pyridine of from 1.3 to 5.0, the total of contents (as calculated as oxides)
5 of SiO_2 , Al_2O_3 and B_2O_3 is at least 99.5 mass%, and the total of contents of Al_2O_3 and B_2O_3 is from 0.1 to 20 mass%.
2. The silica powder according to Claim 1, which has a specific surface area of from 0.5 to 5 m^2/g and an
10 average particle size of from 1 to 60 μm .
3. An inorganic powder characterized in that it contains the silica powder as defined in Claim 1 or 2.
4. The inorganic powder according to Claim 3, wherein the inorganic powder is a silica powder and/or an alumina
15 powder.
5. A process for producing the silica powder as defined in Claim 1 or 2, characterized in that at least two burners are disposed in a furnace body with an angle of from 2 to 10° to the central axis of the furnace body,
20 and from one burner, a raw material silica powder is sprayed and from at least one burner, an aluminum source material and/or a boron source material is sprayed, into a flame.
6. The process for producing the silica powder
25 according to Claim 5, wherein the aluminum source material is an aluminum oxide powder, and the raw material silica powder has an Al_2O_3

content of at most 1 mass%.

7. The process for producing the silica powder according to Claim 6, wherein the aluminum oxide powder
5 has an average particle size of from 0.01 to 10 μm .

8. A resin composition characterized in that it contains the silica powder as defined in Claim 1 or 2.

9. The resin composition according to Claim 8, wherein the resin in the resin composition is an epoxy resin.

10 10. A sealing material for semiconductors, employing the resin composition as defined in Claim 8.

Siliceous Powder, Process For Production Of The Same, And Use Thereof

Abstract

5 To provide a silica powder useful for preparation of a sealing material for semiconductors, and a process for its production.

 It is a silica powder which has a Freundlich adsorption constant K of pyridine of from 1.3 to 5.0. It is particularly preferred that the total of contents (as calculated as oxides) of SiO_2 , Al_2O_3 and B_2O_3 is at least 99.5 mass%, and the
10 total of contents of Al_2O_3 and B_2O_3 is from 0.1 to 20 mass%. The process for producing the silica powder is such that at least two burners are disposed in a furnace body with an angle of from 2 to 10° to the central axis of the furnace body, and from one burner, a raw material silica powder is sprayed and from at least one burner, an aluminum source material and/or a boron source material is
15 sprayed, into a flame. A resin composition is further provided which contains the above silica powder or inorganic powder.

(No suitable figure)