

DESCRIPTION

AMORPHOUS SILICA POWDER, PROCESS FOR ITS PRODUCTION AND ITS USE

5 TECHNICAL FIELD

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

BACKGROUND ART

10 In recent years, from an increasing consciousness about global environmental protection, a sealing material for semiconductors, to be used for sealing semiconductor elements, is required to provide flame retardancy without using a hazardous flame retardant such as a brominated epoxy resin or an antimony compound having a large environmental load and to provide heat resistance to a lead-free solder which contains no lead. A sealing material for semiconductors is constituted
15 mainly by e.g. an epoxy resin, a phenol resin curing agent, a curing accelerator, an inorganic filler, etc. Here, in order to satisfy the required properties as mentioned above, it is common to adopt a method of using one having a structure containing many aromatic rings to have high flame retardancy and heat resistance as the epoxy resin, phenol resin, etc., or a method of highly filling an inorganic filler. However, by such methods, the viscosity of the sealing material for semiconductors
20 tends to increase at the time of sealing.

On the other hand, to meet the requirements for high performance and reduction in size and weight of electronic devices, the internal structure of semiconductors has undergone rapid progress in thinning of elements, reduction in diameter of gold wires, long span modification and high densification of wiring pitches. If such semiconductors are sealed by means of a sealing material
25 for semiconductors, having a high viscosity, deformation of gold wires, breakage of gold wires, inclination of semiconductor elements, or failure in e.g. filling narrow spaces, is likely to increase. Therefore, it is strongly desired that the sealing material for semiconductors has flame retardancy and has a low viscosity at the time of sealing to reduce molding failure.

In order to satisfy such requirements, there has been a method to reduce the viscosity and to
30 improve the moldability by e.g. a method of improving an epoxy resin or a phenol resin-curing agent to be used for the sealing material for semiconductors (Patent Documents 1 and 2). Further, for improvement of a curing accelerator, a so-called latency method has been adopted to protect a reactive substrate by using a component to suppress the curing property for the purpose of raising the cure-initiation temperature of the epoxy resin (Patent Documents 3 and 4).

35 For improvement of the inorganic filler, a method of adjusting the particle size distribution has, for example, been adopted so that the viscosity of the sealing material will not increase even when highly filled (Patent Documents 5 and 6). However, such methods are inadequate in the effect to lower the viscosity or in the effect to improve the moldability, and there has been no sealing material for semiconductors whereby an inorganic filler can be highly filled, the viscosity at the time of sealing
40 can be lowered, and the moldability is further improved.

Patent Document 1: JP-A-2007-231159

Patent Document 2: JP-A-2007-262385

Patent Document 3: JP-A-2006-225630

Patent Document 4: JP-A-2002-284859

45 Patent Document 5: JP-A-2005-239892

Patent Document 6: WO/2007/132771

DISCLOSURE OF THE INVENTION

OBJECT TO BE ACCOMPLISHED BY THE INVENTION

It is an object of the present invention to provide a sealing material for semiconductors, which has a low viscosity at the time of sealing and has the moldability further improved even if an inorganic filler is highly filled and to provide an amorphous silica powder suitable for its preparation, and a process for its production.

MEANS TO ACCOMPLISH THE OBJECT

The present invention provides an amorphous silica powder characterized in that after having pyridine adsorbed on the amorphous silica powder, the ratio of L/B is at most 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C, and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C.

Further, in the present invention, after having pyridine adsorbed on the amorphous silica powder, the proportion of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C in the total amount A of pyridine desorbed under heating at from 150°C to lower than 550°C, i.e. $(B/A) \times 100\%$, is preferably at least 20%.

The amorphous silica powder of the present invention preferably has a specific surface area of from 0.5 to 45 m²/g, an average particle size of from 0.1 to 60 μm and an average sphericity of at least 0.80.

Further, the present invention provides an inorganic powder containing the amorphous silica powder of the present invention.

In the present invention, the above inorganic powder is preferably an amorphous silica powder other than the present invention and/or an alumina powder.

Further, the present invention provides a process for producing the amorphous silica powder, characterized in that a mixture comprising a raw material silica powder and an Al source material is sprayed into a flame formed by a burner to produce an amorphous silica powder, and then, the produced powder is held in an atmosphere having a relative humidity of from 60 to 90% at a temperature of from 60 to 150°C for from 15 to 30 minutes.

Further, the present invention provides a resin composition containing the amorphous silica powder of the present invention in a resin. The resin is preferably an epoxy resin.

Further, the present invention provides a sealing material for semiconductors, employing such a resin composition.

EFFECTS OF THE INVENTION

According to the present invention, a resin composition excellent in fluidity, viscosity properties and moldability, and a sealing material for semiconductors, employing such a resin composition, are provided. Further, an amorphous silica powder suitable for preparation of such a resin composition, is provided.

BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will be described in detail.

The amorphous silica powder of the present invention is an amorphous silica powder characterized in that when pyridine is adsorbed thereon and then desorbed under heating, the ratio of L/B is at most 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C, and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C.

In the structure of silica, if Al is substituted at the position of Si, for example, in the case of -O-Si-O-Al-O-Si-O-, such a point will be a Lewis acid point (electron pair acceptor) as a solid acid point

due to a difference between the coordination number of Si and the coordination number of Al. Further, if H₂O (water) is bonded to this Lewis acid point, such a point will be a Brønsted acid point (proton donor). Pyridine as a basic substance will be bonded to such acid points on the surface of the amorphous silica powder, and strongly bonded pyridine will be desorbed at a higher temperature when heated. In the case of an amorphous silica powder, the structure is random as compared with a crystalline substance, whereby the acid strength (desorption temperature) will have a distribution. However, it is generally considered that pyridine desorbed at a heating temperature of from 150 to 250°C is one bonded to Brønsted acid points, and pyridine desorbed at a heating temperature of from 450°C to 550°C is one bonded to Lewis acid points.

"After having pyridine adsorbed on the amorphous silica powder, the ratio of L/B is at most 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C, and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C" means that the amount of Brønsted acid points is larger by at least 1.25 times than the amount of Lewis acid points. When such an amorphous silica is used, it becomes possible to prepare a sealing material excellent in fluidity, viscosity properties and moldability for the after-mentioned reason. Inversely, in a case where the ratio of L/B exceeds 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C, such means that the amount of Brønsted acid points is less than 1.25 times as compared with the amount of Lewis acid points, whereby it becomes difficult to prepare a sealing material excellent in fluidity, viscosity properties and moldability.

The reason for development of the effects by the present invention may be explained as follows. That is, in a sealing material for semiconductors, an epoxy resin, a phenol resin curing agent and a curing promoter are used as the main components in addition to the amorphous silica powder. When the sealing material for semiconductors is heated at a temperature of from about 150°C to 200°C being a usual thermosetting temperature (molding temperature), protons of the phenol resin curing agent will be withdrawn by the curing promoter, whereby an anion polymerization chain reaction between the epoxy resin and the phenol resin curing agent will proceed, and the sealing material will be thermally cured. When the amorphous silica powder of the present invention is used, protons will be discharged from the Brønsted acid points by heating. Such protons will be bonded to anionic polymer terminals, whereby the polymerization chain reaction will temporarily be stopped, thus resulting in such a phenomenon that thermal curing of the sealing material is delayed. That is, by the amorphous silica powder of the present invention, thermal curing of the sealing material can be made to be latency, whereby it becomes possible to prepare a sealing material excellent in fluidity and viscosity properties at the time of molding. Such latency effects are remarkably developed only when the ratio of L/B is at most 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C. Heretofore, there has been no instance reported wherein latency is imparted to an amorphous silica powder by such a mechanism.

On the other hand, if the ratio of L/B exceeds 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C, it is not only difficult to develop the above-mentioned latency phenomenon of the sealing material due to discharge of protons from Brønsted acid points of the amorphous silica powder, but also oxygen in the epoxy resin or the phenol resin tends to be coordination-bonded to Lewis acid points, whereby, inversely, the fluidity of the amorphous silica powder tends to be inhibited, and the fluidity and viscosity properties of the sealing material are likely to be deteriorated, such being undesirable. The ratio of L/B is preferably at most 0.7, more preferably at most 0.6.

The temperature and amount for desorption of pyridine from the amorphous silica powder can

be measured by the following procedure.

(1) Preparation of pyridine solution: 7.91 g of pyridine for spectrometry is taken into a 500 ml measuring flask and adjusted to the constant volume with n-heptane for spectrometry. Then, 1 ml of this pyridine solution is taken into a 200 ml measuring flask and adjusted to the constant volume with n-heptane.

(2) Adsorption of pyridine on amorphous silica powder: 4.00 g of an amorphous silica powder preliminarily dried under heating at 200°C for 2 hours in the atmosphere, followed by cooling in a desiccator together with a magnesium perchlorate, is accurately weighed and put into a 25 ml measuring flask. To this measuring flask, 20 ml of the above pyridine solution is put and mixed by shaking for 3 minutes. This measuring flask is immersed in a constant temperature tank set at 25°C for 2 hours to have pyridine adsorbed on the amorphous silica powder.

(3) Cleaning of amorphous silica powder: In order to clean off pyridine physically adsorbed on the amorphous silica powder, the measuring flask taken out from the constant temperature tank is shaken and then left to stand for 10 minutes to let the amorphous silica powder precipitate. The supernatant of the pyridine solution is discarded, and about 20 ml of n-heptane for spectrometry is added, and then the measuring flask is shaken and left to stand still for 10 minutes. The supernatant is put into a measuring cell of an ultraviolet-visible spectrophotometer, and the adsorbance in a wavelength region of from 190 to 340 nm is measured to confirm the absorption of pyridine at 251 nm. This cleaning operation with n-heptane is repeated until the pyridine absorption is no longer confirmed in the supernatant of n-heptane. When the absorption of pyridine is no longer confirmed, the supernatant is discarded, and the amorphous silica powder is dried at room temperature while blowing a dried nitrogen gas from the top of the measuring flask at a flow rate of 100 ml for 10 minutes.

(4) Measurement of desorption temperature and desorbed amount of pyridine: 10 mg of the dried amorphous silica powder is accurately weighed and put into a sample cup for a double shot pyrolyzer, and while heating it by a pyrolysis apparatus, the mass spectrum of pyridine is monitored, whereby the desorption temperature and the desorbed amount of pyridine are measured. The desorbed amount ratio of pyridine can be calculated from the area ratio of the obtained profile.

Here, as an example of the ultraviolet-visible spectrophotometer to be used for determining the presence or absence of physically adsorbed pyridine, "Ultraviolet-visible Spectrophotometer, Model UV-1800", tradename, manufactured by Shimadzu Corporation may be mentioned. For the measurement, a cell made of quartz glass and having a thickness of 10 mm was used.

As examples of the reagents to be used for preparation of the pyridine solution, pyridine (spectrometry grade) and n-heptane (spectrometry grade), manufactured by Wako Pure Chemical Industries, Ltd., may be mentioned.

Further, as examples of the apparatus to be used for the measurement of the desorption temperature and the desorbed amount of pyridine adsorbed on the amorphous silica powder, the pyrolysis apparatus "Double Shot Pyrolyzer Model PY-2020D", tradename, manufactured by FRONTIER LAB, and a GC/MS measuring apparatus "GC/MSD Model 6890/5973" tradename, manufactured by Agilent may be mentioned.

Measuring conditions by the pyrolytic furnace are such that temperature raising rate: the temperature is raised to from 50 to 700°C at a rate of 25°C/min, ITF temperature: the temperature is raised to from 150 to 300°C, and measuring mode: EGA TEMP PROG. Measuring conditions by GC/MS are such that column: UADTM-2.5N (without liquid phase) 0.15 mm in diameter × 2.5 m, oven temperature: 300°C, inlet temperature: 280°C, measuring mode: SIM, spirit ratio: 30 against 1, and monitor ions: m/z=52 and 79. Here, the sum of the amounts of monitor ions 52 and 79 is taken as the amount of pyridine desorbed.

Since the amount of pyridine desorbed is very small, it is difficult to accurately quantify the

absolute amount. However, on the basis of the abundance (existence ratio) measured by the above measuring methods, it becomes possible to accurately obtain the ratio of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C to the amount L of pyridine desorbed under heating at from 450°C to lower than 550°C, or the ratio of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C to the total amount A of pyridine desorbed under heating at from 150°C to lower than 550°C. When pyridine is not adsorbed or desorbed, the abundance becomes 0, and the larger the adsorbed or desorbed amount, the larger the abundance. In order to obtain the effects to improve the fluidity, viscosity properties and moldability as in the present invention, it is necessary that the maximum value of the abundance i.e. the amount of pyridine desorbed under heating at from 150°C to lower than 250°C is at least 100, preferably at least 200. If the maximum value of the abundance is less than 100, the effects of the present invention tend to be hardly obtainable even if the ratio of L/B satisfies the prescribed value.

Here, the abundance is a numerical value univocally obtainable by the above methods.

The effects to improve the fluidity, viscosity characteristics and moldability according to the present invention are promoted when the amorphous silica powder is under the following condition. That is, the proportion of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C in the total amount A of pyridine desorbed under heating at from 150°C to lower than 550°C, i.e. $(B/A) \times 100\%$, is at least 20%. As mentioned above, a usual thermosetting temperature (molding temperature) of the sealing material for semiconductors is usually from about 150°C to 200°C, and not only the amount of pyridine desorbed under heating at from 250°C to lower than 550°C hardly contributes to latency of the sealing material for semiconductors due to proton discharge, but also and the amount L of pyridine desorbed under heating at from 450°C to lower than 550°C rather tends to inhibit fluidity of the amorphous silica powder, whereby the fluidity and viscosity properties of the sealing material tend to deteriorate, such being undesirable. Therefore, the proportion of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C in the total amount A of pyridine desorbed under heating at from 150°C to lower than 550°C, $(B/A) \times 100\%$, is preferably at least 20%. When this proportion is at least 25%, more preferably at least 30%, improvement in the fluidity and viscosity properties at the time of molding will be particularly distinct.

Further, the effects to improve the fluidity, viscosity properties and moldability according to the present invention will be further promoted when the amorphous silica powder is under such conditions that the specific surface area is from 0.5 to 45 m²/g, the average particle size is from 0.1 to 60 μm, and the average sphericity is at least 0.80.

If the specific surface area of the amorphous silica powder is less than 0.5 m²/g, the contact area of the amorphous silica powder surface with the epoxy resin and the phenol resin curing agent tends to be too small, whereby the effect for latency due to the proton discharge tends to be hardly obtainable. On the other hand, if the specific surface area exceeds 45 m²/g, such means that the amorphous silica powder contains a large amount of small particles, or the surface of particles partially or entirely has irregularities, whereby the viscosity of the sealing material increases at the time of packaging of semiconductors by means of the sealing material for semiconductors, and the molding properties will be impaired. A preferred range of the specific surface area is from 0.6 to 20 m²/g, and a further preferred range is from 0.7 to 10 m²/g.

Further, it is also undesirable that the average particle size of the amorphous silica powder is less than 0.1 μm, whereby the viscosity of the sealing material tends to be increased at the time of packaging semiconductors by means of the sealing material for semiconductors, whereby the moldability tends to be impaired, such being undesirable. Inversely, if the average particle size exceeds 60 μm, there will be a problem such that semiconductor chips are likely to be thereby scratched, or there will be a problem that a uniform package free from irregularities can hardly be

obtainable. A preferred range of the average particle size is from 2 to 55 μm , and a further preferred range is from 3 to 50 μm . Further, the maximum particle size is preferably at most 196 μm , more preferably at most 128 μm .

Further, the average sphericity of the amorphous silica powder of the present invention is preferably at least 0.80, more preferably at least 0.85.

The average particle size of the amorphous 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 the amorphous 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 192 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 amorphous 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 "Macrosorb Model HM-1208", tradename, manufactured by Mountech Co., Ltd.

The amorphous silica powder of the present invention is able to exhibit its effects even when mixed to another inorganic powder. The content of the amorphous silica powder of the present invention in such an inorganic powder is preferably at least 2 mass%, more preferably at least 5 mass%. The type of the inorganic powder is preferably an amorphous silica powder other than the present invention and/or an alumina powder. These powders 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, an amorphous silica powder is selected for use, and in order to impart thermal conductivity, an alumina powder is selected for use. Here, the amorphous silica powder is preferably such that the value of the amorphous ratio as measured by the after-mentioned method is at least 95%, more preferably at least 97%.

The amorphous silica powder of the present invention is such that the amorphous ratio measured by the following method is preferably at least 95%, particularly preferably at least 97%. 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-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 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 obtainable, 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 amorphous 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 of the present invention 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 $sphericity=A/B=A \times 4\pi / (PM)^2$. sphericities of optional 200 particles thus obtained, were determined, and their average value was taken as the average sphericity.

Another method for determining the sphericity is such that the sphericity is obtained from circularities of individual particles quantitatively and automatically measured by a particle image analyzing device (e.g. "Model FPIA-3000" tradename, manufactured by Sysmex) by calculation based on the formula: $Sphericity=(circularity)^2$.

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

The process of the present invention is a process for producing the amorphous silica powder characterized in that a mixture comprising a raw material silica powder and an Al source material is sprayed into a flame formed by a burner to produce an amorphous silica powder, and then, the produced powder is held in an atmosphere having a relative humidity of from 60 to 90% at a temperature of from 60 to 150°C for from 15 to 30 minutes. The mixture comprising a raw material silica powder and an Al source material is sprayed into a flame formed by a burner to carry out melting (conversion to amorphous state) and spheroidizing of the raw material silica powder and substantially simultaneously to fuse the Al source material to the surface of the silica powder thereby to let a $-O-Si-O-Al-O-Si-O-$ structure form, and then, the produced powder is held in an atmosphere having a relative humidity of from 60 to 90% at a temperature of from 60 to 150°C for from 15 to 30 minutes to carry out adjustment of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C and the amount L of pyridine desorbed under heating at from 450°C to lower than 550°C. It is thereby possible to produce for the first time the amorphous silica powder having the characteristics of the present invention.

As an apparatus to spray the mixture comprising a raw material silica powder and an Al source material into the flame thereby to melt, fuse, spheroidize and collect it, one having a collecting device connected to the furnace body equipped with the burners may be used. 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 amorphous silica 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 order to hold the amorphous silica powder in an atmosphere having a relative humidity of from 60 to 90% at a temperature of from 60 to 150°C for from 15 to 30 minutes, for example, a line to supply steam may be installed on the above collecting device, and the steam temperature and the steam supply rate may be adjusted to attain the desired temperature and relative humidity. To adjust the holding time, the opening/closing time of the discharge valve to discharge the amorphous silica powder out of the system from the above collecting device, may be adjusted to attain the desired time.

Immediately after the mixture comprising a raw material silica powder and an Al source material is sprayed into the flame formed by a burner, the type of acid points having a $-O-Si-O-Al-O-Si-O-$ structure is mostly a Lewis acid due to the influence of the high temperature flame, and only a part thereof is changed to a Brønsted acid having bonded H_2O contained in the combustion gas of the flammable gas used to form the flame, whereby the ratio of the desorbed amounts of adsorbed pyridine, i.e. L/B, exceeds 0.8. Therefore, with an amorphous silica powder not treated by the process of the present invention, there will be no improvement in the fluidity and viscosity properties at the time of molding, by the latency effects.

If the humidity during the holding is less than 60% or if the holding time is less than 15 minutes, the change of a Lewis acid to a Brønsted acid tends to be inadequate, and it tends to be difficult to control the pyridine desorption ratio L/B to be at most 0.8. On the other hand, if the humidity exceeds 90%, or the holding time exceeds 30 minutes, the amorphous silica powder tends to be agglomerated, and moldability of the sealing material for semiconductors tends to be low, such being undesirable.

The humidity is more preferably from 65 to 85%, and the humidifying time is preferably within a range of from 20 to 25 minutes. Accordingly, if the humidifying temperature is lower than 60°C, H₂O tends to be hardly bonded, and the change of a Lewis acid to a Brønsted acid tends to be inadequate, whereby it is difficult to control the pyridine desorption ratio L/B to be at most 0.8. On the other hand, if the holding temperature exceeds 150°C, the temperature is too high to bond H₂O, and it is difficult to bring L/B to be at most 0.8. Only when the obtained powder is held within a temperature range of from 60 to 150°C, it becomes possible to adjust the ratio of L/B to be at most 0.8. The holding temperature is more preferably within a range of from 70 to 120°C, further preferably from 75 to 100°C.

As a raw material silica powder, it is possible to use a powder of a naturally produced silica-containing mineral such as high purity silica stone, high purity silica sand, quartz or rock crystal, or a high purity silica powder produced by a synthetic method such as precipitated silica or silica gel. However, when the cost or availability is taken into consideration, silica stone powder is most preferred. With respect to the silica stone powder, ones having various particle sizes, pulverized by a pulverizer such as a vibration mill or a ball mill are commercially available, and a suitable particle size may be selected so that a desired particle size of the amorphous silica powder can be obtained.

In the present invention, the Al source material is preferably an aluminum oxide powder. The Al source material may, for example, be aluminum oxide, aluminum hydroxide, aluminum nitrate, aluminum chloride or an aluminum organic compound. Among them, aluminum oxide is most preferred, since it is close to the melting point of the raw material silica powder, whereby when sprayed from the burner, it tends to readily fuse on the surface of the raw material silica powder, and its impurity content is low.

Further, 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 agglomerate, and the composition when fused on the silica powder tends to be non-uniform, and likewise, if the average particle size exceeds 10 μm, the composition when fused on the silica powder tends to be non-uniform. A preferred range of the average particle size is from 0.03 to 8 μm, and more preferred is from 0.05 to 5 μm.

Further, the content of Al₂O₃ in the amorphous silica powder of the present invention is preferably from 0.1 to 20 mass%. If the content of Al₂O₃ is less than 0.1 mass%, increase of acid points tends to be inadequate. On the other hand, if it exceeds 10 mass%, the thermal expansion of the amorphous silica powder tends to be so large that it is likely to adversely affect the functions of the sealing material for semiconductors. A preferred content of Al₂O₃ is from 0.15 to 18 mass%, and more preferred is from 0.2 to 15 mass%.

The Al₂O₃ content (as calculated as an oxide) in the amorphous silica powder of the present invention can be measured by means of an atomic adsorption analysis as follows. That is, 1 g of the amorphous silica powder is accurately weighed on a platinum dish, and special grade reagent hydrofluoric acid and special grade 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 amorphous 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 measuring, as the frame, an acetylene/nitrous oxide frame is used, and the absorbance at a wavelength of 309.9 nm is measured for quantitative determination.

In the present invention, when pyridine is adsorbed on the amorphous silica powder and desorbed under heating, the amount of pyridine desorbed and the desorption temperature can be adjusted by the size or amount of the Al source material fused on the surface of the raw material silica powder, the condition for holding in humidity, the specific surface area, the average particle size, etc.

The specific surface area and average particle size of the amorphous silica powder can be adjusted by the particle size constitution of the raw material silica powder, the flame temperature, etc. Further, the average sphericity and the amorphous ratio can be adjusted by the amount of the raw material silica powder supplied to the flame, the flame temperature, etc. Further, it is possible that various amorphous silica powders different in e.g. the size or amount of the Al source material fused, the condition for holding in humidity, the specific surface area, the average particle size, etc. are preliminarily prepared, and two or more of them are suitably mixed to prepare an amorphous silica powder having further specified the amount of pyridine desorbed at the time of adsorption and desorption of pyridine, the desorption temperature, the specific surface area, the average particle size, etc.

The resin composition of the present invention is a resin composition containing the amorphous silica powder or the inorganic powder of the present invention. The content of the amorphous 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 having at least two epoxy groups in one molecule is preferred as a resin for a sealing material 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 a halogen atom such as bromine introduced to impart flame retardancy, may be mentioned. Among them, from the viewpoint of the moisture resistance or the solder reflow resistance, an orthocresol novolac type epoxy resin, a bishydroxybiphenyl type epoxy resin or a naphthalene-skeleton epoxy resin is, for example, 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 may, for example, be a novolac resin obtainable by reacting one or more selected from the group consisting of phenol, cresol, xyleneol, resorcinol, chlorophenol, t-butylphenol, nonylphenol, isopropylphenol and octylphenol with formaldehyde, paraformaldehyde or paraxylene in the 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 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.

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 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 epoxy silicone or an alkoxy silicone may, for example, be mentioned.

As a silane coupling agent, an epoxysilane such as γ -glycidoxypolytrimethoxysilane or β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane; an aminosilane such as aminopropyltriethoxysilane, ureidopropyltriethoxysilane or N-phenylaminopropyltrimethoxysilane; a hydrophobic silane compound such as phenyltrimethoxysilane, methyltrimethoxysilane or octadecyltrimethoxysilane or a 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 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 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 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 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 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 restricted to such specific Examples.

EXAMPLES 1 to 10 and COMPARATIVE EXAMPLES 1 to 8

Crystalline silica powder (SiO_2 content: 99.9 mass%) manufactured by Kinsei Matec, alumina

powder manufactured by Nippon Light Metal Co., Ltd. and aluminum hydroxide powder were used as raw materials for preparation of the amorphous silica powder of the present invention. The respective powders were pulverized and classified to adjust the particle sizes thereby to prepare various raw material silica powders and Al source materials, different in the average particle size.

They were melted, fused and spheroidized in the flame, followed by holding-in-humidity treatment to produce various amorphous silica powders shown in Tables 1 and 2 by means of an apparatus disclosed in JP-A-11-57451 and an apparatus having a boiler to generate steam and a line to supply steam, installed to its collecting devices and adapted so that the steam temperature and the steam supply rate can be adjusted to a desired temperature and relative humidity. Further, such powders were suitably blended to produce amorphous silica powders and inorganic powders as shown in Tables 3 and 4.

Here, the amount of pyridine desorbed and the desorption temperature at the time of desorption of pyridine adsorbed on the amorphous silica powder, were adjusted by changing the size or amount of the Al source material fused on the surface of the raw material silica powder, the holding-in-humidity condition, the specific surface area, the average particle size, etc.

The specific surface area and average particle size of the amorphous silica powder was adjusted by the particle size constitution of the raw material silica powder, the flame temperature, etc., and the average sphericity and amorphous ratio of the amorphous silica powder were adjusted by the amount of the raw material silica powder supplied to the flame, the flame temperature, etc. Here, for the formation of the flame, LPG and oxygen gas were used, and oxygen gas was used as a carrier gas to transport the raw material powder to the burner. The maximum temperature of this flame was within a range of from about 2,000°C to 2,300°C.

The adsorption of pyridine on the amorphous silica powder, and the measurements of the amount of pyridine desorbed from the amorphous silica powder and the desorption temperature, were carried out by the methods described in the above paragraph (0014).

The amorphous ratio of the obtained amorphous silica powder was at least 99.5% in each case. With respect to these powders, the specific surface area, the average particle size, the average sphericity, the temperature for desorption of pyridine and the desorbed amount were measured, and the ratio of L/B where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C, and the proportion of the amount of pyridine desorbed under heating at from 150°C to lower than 250°C in the total amount A of pyridine desorbed under heating at from 150°C to lower than 550°C, i.e. $(B/A) \times 100\%$, were calculated. The results are shown in Tables 3 and 4.

The properties of the obtained amorphous silica powders and inorganic powders as a filler for the sealing material for semiconductors were evaluated, that is, to 87.8 parts (parts by mass, the same applies hereinafter) of each powder, 5.9 parts of a biphenyl type epoxy resin (YX-4000H, manufactured by Japan Epoxy Resin), 5.1 parts of a phenol aralkyl resin (XLC-LL, manufactured by Mitsui Chemicals Inc.), 0.2 part of triphenylphosphine, 0.6 part of an epoxy silane coupling agent, 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: 50 to 120 rpm, discharge amount: 2.5 kg/hr, and temperature of the kneaded product: 99 to 100°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 viscosity properties (Curelastometer torque), the moldability (wire deformation ratio) and the fluidity (spiral flow) were evaluated as follows. The results are shown in Tables 3 and 4.

(1) Viscosity properties (Curelastometer torque)

The viscosity properties of the sealing material for semiconductors, obtained as described

above, was measured as follows. Using a Curelastometer (e.g. "Curelastometer Model 3P-S" tradename, manufactured by JSR Trading Co., Ltd.), the sealing material for semiconductors was heated at 110°C, and the torque upon expiration of 30 seconds was taken as a viscosity index. The smaller the value, the better the viscosity properties.

5 (2) Moldability (wire deformation ratio)

The moldability of the sealing material for semiconductors, obtained as described above, was measured as follows. On a BGA (Ball Grid Array) substrate, two sheets of simulated semiconductor element with a size of 8 mm × 8 mm × 0.3 mm were overlaid via a die attach film and connected by a gold wire. Then, using each sealing material for semiconductors, molding into a package size of 10 38 mm × 38 mm × 1.0 mm was carried out by means of a transfer molding machine, followed by curing at 175°C for 8 hours to obtain a BGA type semiconductor. The gold wire portion of the semiconductor was observed by a soft X-ray transmission device to measure the gold wire deformation ratio. For the gold wire deformation ratio, the shortest distance X of wire before sealing and the maximum displacement Y of wire after sealing were measured, and the gold wire 15 deformation ratio was obtained as $(Y/X) \times 100$ (%). This value is an average value of 12 gold wire deformation ratios. Here, the diameter of the gold wire was 30 μm, and the average length was 5 mm. The transfer molding conditions were such that the mold temperature was 175°C, the molding pressure was 7.4 MPa, and the pressure-holding time was 90 seconds. The smaller the value, the smaller the wire deformation and the better the moldability.

20 (3) Fluidity (spiral flow)

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 each sealing material for semiconductors was measured. The transfer molding conditions were such that the mold temperature was 175°C, the molding pressure was 7.4 MPa and 25 the pressure holding time was 120 seconds. The larger the spiral flow value, the better the fluidity.

TABLE 1

Items	Type of amorphous silica powder							
	a	b	c	d	e	f	g	h
Average particle size of raw material silica powder (μm)	26	26	11	52	26	59	0.2	4
Type of Al source material	Al_2O_3	$\text{Al}(\text{OH})_3$	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3
Average particle size of Al source material (μm)	0.5	0.5	0.5	5	0.5	10	0.03	0.5
Amount of Al source material added (mass%)	0.5	1.0	0.5	0.2	2	0.5	8	15
Al_2O_3 content in amorphous silica powder (mass%)	0.5	0.6	0.5	0.2	2.0	0.5	8.0	15
Conditions for melting and spheroidizing	LPG flow rate (m^3/hr)	16	16	24	16	24	14	14
	Oxygen flow rate (m^3/hr)	96	96	144	96	144	84	84
	Sprayed amount of mixture comprising raw material silica powder and Al source material (kg/hr)	40	40	40	50	50	30	30
	Atmosphere temperature in cyclone collecting box ($^{\circ}\text{C}$)	80	80	60	150	80	80	80
Humidifying conditions*	Atmosphere humidity in cyclone collecting box (%RH)	80	80	80	80	80	60	90
	Holding time in cyclone collecting box (min)	20	20	20	20	30	20	20

* A steam-supply line was installed on the collecting box of the collecting apparatus cyclone, and the collected amorphous silica powder was subjected to humidity treatment.

TABLE 2

Items	Type of amorphous silica powder										
	i	j	k	l	m	n	o	p			
Average particle size of raw material silica powder (μm)	26	26	26	26	26	26	26	26			
Type of Al source material		Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	Al_2O_3			
Average particle size of Al source material (μm)	Nil	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
Amount of Al source material added (mass%)		0.5	1.0	0.5	1.0	0.5	1.0	0.5			
Al_2O_3 content in amorphous silica powder (mass%)	0	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
LPG flow rate (m^3/hr)	16	16	16	16	16	16	16	16			
Oxygen flow rate (m^3/hr)	96	96	96	96	96	96	96	96			
Sprayed amount of mixture comprising raw material silica powder and Al source material (kg/hr)	40	40	40	40	40	40	40	40			
Conditions for melting and spheroidizing											
Atmosphere temperature in cyclone collecting box ($^{\circ}\text{C}$)		50	160	80	80	80	80	80			
Atmosphere humidity in cyclone collecting box (%RH)	Nil	80	80	50	95	80	80	80			
Holding time in cyclone collecting box (min)		20	20	20	20	10	40	40			

* A steam-supply line was installed on the collecting box of the collecting apparatus cyclone, and the collected amorphous silica powder was subjected to humidity treatment.

TABLE 3

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
a	100	-	-	-	-	-	-	-	-	-
b	-	100	-	-	-	-	-	-	-	40
c	-	-	100	-	-	-	-	-	-	-
d	-	-	-	100	-	-	-	-	-	-
e	-	-	-	-	100	-	-	-	-	-
f	-	-	-	-	-	100	-	-	-	-
g	-	-	-	-	-	-	100	-	4	-
h	-	-	-	-	-	-	-	100	-	-
i	-	-	-	-	-	-	-	-	96	-
*	-	-	-	-	-	-	-	-	-	60
Peak value of abundance in desorption of pyridine at from 150 to 250°C	570	540	390	360	410	440	5860	1450	250	230
Pyridine desorption ratio L/B (-)	0.4	0.5	0.8	0.8	0.7	0.6	0.8	0.6	0.8	0.5
Pyridine desorption proportion B/Ax100 (%)	26	25	21	20	24	25	17	25	18	24
Specific surface area (m ² /g)	1.5	1.5	2.0	0.8	1.5	0.5	43	9	3.1	1.3
Average particle size (µm)	28	28	13	54	28	60	0.4	6	27	23
Maximum particle size (µm)	128	128	96	196	128	196	8	32	128	128
Average sphericity (-)	0.92	0.89	0.90	0.81	0.91	0.79	0.99	0.99	0.92	0.90
Amorphous ratio (%)	99.9	99.8	99.8	99.6	99.9	99.5	100	100	99.8	-
Curelastometer torque (N·m)	3.4	3.3	3.8	3.9	3.7	4.0	4.2	4.1	4.5	3.8
Wire deformation ratio (%)	0	0	0	1	0	1	1	0	1	1
Spiral flow (cm)	148	145	135	126	137	121	116	128	135	133

* Commercial spherical alumina powder: Average particle size: 18 µm, specific surface area: 1.1 m²/g, and pyridine desorption peak: nil.

TABLE 4

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8
Proportion of the amorphous silica powder blended (mass%)	i	-	-	-	-	-	-	-
	j	100	-	-	-	-	-	-
	k	-	100	-	-	-	-	-
	l	-	-	100	-	-	-	-
	m	-	-	-	100	-	-	-
	n	-	-	-	-	100	-	-
	o	-	-	-	-	-	100	-
	p	-	-	-	-	-	-	100
Peak value of abundance in desorption of pyridine at from 150 to 250°C	0	250	70	80	320	130	370	40
Pyridine desorption ratio L/B (-)	Nil	1.1	1.8	2.5	0.9	3.1	0.9	4.8
Pyridine desorption proportion B/A×100 (%)	Nil	9	9	8	21	4	22	5
Specific surface area (m ² /g)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Average particle size (μm)	28	28	28	28	28	28	28	28
Maximum particle size (μm)	128	128	128	128	128	128	128	128
Average sphericity (-)	0.90	0.91	0.91	0.92	0.92	0.92	0.91	0.91
Amorphous ratio (%)	99.8	99.9	99.9	99.9	99.8	99.8	99.9	99.9
Curelastometer torque (N·m)	6.4	5.2	5.8	5.3	6.9	5.8	6.8	5.3
Wire deformation ratio (%)	7	5	4	3	3	4	3	8
Spiral flow (cm)	105	112	108	112	72	106	89	113

As is evident from comparison between Examples and Comparative Examples, according to the amorphous silica powder of the present invention, it is possible to prepare a resin composition, particularly a sealing material for semiconductors, which is superior in fluidity, viscosity properties and moldability to Comparative Examples.

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INDUSTRIAL APPLICABILITY

The amorphous 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., and as a filler for e.g. a laminated plate for mounting
10 semiconductors. Further, the resin composition of the present invention is useful not only for a sealing material for semiconductors but also for prepregs for printed boards obtained by impregnating and curing it in glass woven fabric, glass nonwoven fabric or other organic material, or various engineering plastics.

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The entire disclosure of Japanese Patent Application No. 2008-129122 filed on May 16, 2008 including specification, claims and summary is incorporated herein by reference in its entirety.

CLAIMS

1. An amorphous silica powder characterized in that after having pyridine adsorbed on the amorphous silica powder, the ratio of L/B is at most 0.8, where L is the amount of pyridine desorbed under heating at from 450°C to lower than 550°C, and B is the amount of pyridine desorbed under heating at from 150°C to lower than 250°C.
2. The amorphous silica powder according to Claim 1, wherein after having pyridine adsorbed on the amorphous silica powder, the proportion of the amount B of pyridine desorbed under heating at from 150°C to lower than 250°C in the total amount A of pyridine desorbed under heating at from 150°C to lower than 550°C, i.e. $(B/A) \times 100\%$, is at least 20%.
3. The amorphous silica powder according to Claim 1, which has a specific surface area of from 0.5 to 45 m²/g, an average particle size of from 0.1 to 60 μm and an average sphericity of at least 0.80.
4. The amorphous silica powder according to Claim 2, which has a specific surface area of from 0.5 to 45 m²/g, an average particle size of from 0.1 to 60 μm and an average sphericity of at least 0.80.
5. An inorganic powder containing the amorphous silica powder as defined in any one of Claims 1 to 4.
6. The inorganic powder according to Claim 5, wherein the inorganic powder contains an amorphous silica powder other than the present invention and/or an alumina powder.
7. A process for producing the amorphous silica powder as defined in any one of Claims 1 to 4, characterized in that a mixture comprising a raw material silica powder and an Al source material is sprayed into a flame formed by a burner to produce an amorphous silica powder, and then, the produced powder is held in an atmosphere having a relative humidity of from 60 to 90% at a temperature of from 60 to 150°C for from 15 to 30 minutes.
8. A resin composition containing the amorphous silica powder as defined in any one of Claims 1 to 4, or inorganic powder containing said amorphous silica powder.
9. The resin composition according to Claim 8, wherein the resin in the resin composition is an epoxy resin.
10. A sealing material for semiconductors, employing the resin composition as defined in Claim 8.