DESCRIPTION

Title of the Invention: BONDING COMPOSITION AND BONDED STRUCTURE

TECHNICAL FIELD

[0001]

The present invention relates to a bonding composition and a bonded structure.

BACKGROUND ART

[0002]

In recent years, semiconductor elements, called power devices, have been increasingly used in power conversion and control apparatuses such as inverters. Such a semiconductor element is mounted (bonded) on a substrate, such as a circuit board or a ceramic substrate, or on a wiring body, such as a lead frame. Meanwhile, solder has conventionally been widely used for mounting semiconductor elements. In addition, with the recent increase in environmental awareness, there has been a demand for the use of lead-free solder that does not contain lead.

[0003]

However, power devices generate a large amount of heat during operation because they control large currents. Lead-free solder has low heat resistance, which has posed the problem of being insufficient for mounting power devices.

[0004]

Accordingly, it has been proposed to use, in place of solder, a paste-like bonding composition containing metal powder such as copper powder. During bonding (mounting), the bonding composition is applied to a surface of one body to be bonded (substrate or the like) to form a coating film. Subsequently, another body to be bonded (power device or the like) is placed on the coating film to form a stacked body. When the stacked body is subjected to heat treatment, the metal powder contained in the bonding composition is sintered to form a bonding portion, thereby obtaining a bonded structure in which the bodies to be bonded are bonded to each other.

[0005]

Patent Documents 1 and 2 are examples of documents that disclose such bonding compositions. Patent Document 1 discloses a bonding copper paste that contains metal particles and a dispersion medium, the metal particles including submicron copper particles and micron copper particles (claim 1 of Patent Document 1). This bonding copper paste is used to bond a first body and a second body to each other, examples of the first and second bodies including semiconductor elements (paragraphs [0072] to [0085] of Patent Document 1). Patent Document 2 discloses a bonding copper paste that contains copper particles, a solvent, and an additive made of a phosphate ester (claim 1 of Patent Document 2).

[0006]

Patent Document 1: Japanese Unexamined Patent Application, Publication No. 2022-180400

Patent Document 2: Japanese Unexamined Patent Application, Publication No. 2022-128185

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0007]

In this context, although bonding compositions containing metal powder such as copper powder (hereinafter sometimes referred to simply as "compositions") have conventionally been proposed, there remains room for improvement in such conventional compositions.

[0008]

As described above, during bonding, the paste-like bonding composition is applied to the surface of the body to be bonded, such as a substrate. The application is performed by a technique such as printing. At this time, the solvent contained in the bonding composition may wet and spread over the body to be bonded (substrate) and reach an area other than a printed region. Such a phenomenon in which the solvent wets and spreads is referred to as a bleed-out phenomenon.

[0009]

For example, a case where a substrate 2 serving as a body to be bonded and a semiconductor element 6 are bonded together will be described with reference to FIGS. 1 and 2. A bonding composition 4 is applied onto the substrate 2, and the

semiconductor element 6 is placed thereon. FIG. 1 is a top view illustrating a state in which the semiconductor element 6 is placed, and FIG. 2 is a side view thereof. At this time, the solvent may be separated from the applied bonding composition 4 and wet and spread over an upper surface of the substrate 2. This is the bleed-out phenomenon. In this case, a region (bleed-out region) 8 in which the solvent wets and spreads is formed beyond a region (paste region) in which the bonding composition 4 has been applied. The bleed-out region 8 is a region in which the solvent wets and spreads and is a region other than the paste region.

[0010]

The bleed-out phenomenon occurs to a certain extent. However, when bleed-out occurs markedly, the metal powder (copper powder or the like) contained in the bonding composition may flow out together with the solvent and adhere to an insulating portion on the body to be bonded (substrate), which may cause a problem such as an insulation failure. Therefore, in order to prevent such a problem, it is important to suppress the bleed-out phenomenon.

[0011]

Further, it is desired to enhance the shear strength (bonding strength) of the bonding portion between the bodies to be bonded so as to ensure the reliability of the bonded structure. However, in the prior art, it has been difficult to achieve both suppression of bleed-out and improvement in shear strength.

[0012]

In view of these problems, the present inventors conducted intensive studies. As a result, they found that, in a bonding composition containing copper powder and a solvent, replacing a portion of the solvent with a high-surface-tension solvent having predetermined physical properties makes it possible to suppress bleed-out and obtain a bonded structure having a bonding portion with high shear strength.

[0013]

The present invention has been completed based on the above findings, and an object thereof is to provide a bonding composition exhibiting a bleed-out suppression effect and capable of providing a bonded structure having a bonding portion with high shear strength.

Means for Solving the Problems

[0014]

The present invention encompasses the following aspects (1) to (7). In the present specification, the expression "to" used to define a numerical range includes the numerical values at both ends of the range. That is, "X to Y" is synonymous with "X or more and Y or less".

[0015]

(1) A bonding composition including copper powder and a solvent,

wherein the solvent includes:

a first solvent having a boiling point of 150°C or higher and 300°C or lower and a surface tension of 30 mN/m or

more; and

a second solvent having a surface tension of less than 30 mN/m,

wherein a content of the first solvent relative to the copper powder is 0.1% by mass or more and 20% by mass or less, and

wherein a content of the second solvent relative to the copper powder is 1.5% by mass or more and 20% by mass or less.

[0016]

(2) The bonding composition according to (1) above, wherein the surface tension of the first solvent is 30 mN/m or more and 65 mN/m or less, and the surface tension of the second solvent is 20 mN/m or more and less than 30 mN/m.

[0017]

(3) The bonding composition according to (1) or (2) above, wherein the first solvent is one or more selected from the group consisting of alcohol-based solvents, glycol-based solvents, ketone-based solvents, and ester-based solvents.

[0018]

(4) The bonding composition according to any one of (1) to (3) above, wherein the second solvent is a liquid carboxylic acid.

[0019]

(5) The bonding composition according to any one of (1) to (4) above, wherein a content of the copper powder in the bonding composition is 80% by mass or more and 96% by mass or less.

[0020]

(6) The bonding composition according to any one of (1) to (5) above, wherein the bonding composition has a paste viscosity of 10 Pa·s or more and 800 Pa·s or less.

[0021]

(7) A bonded structure including:

a first body to be bonded;

a second body to be bonded; and

a sintered body of the bonding composition according to any one of (1) to (6) above, the sintered body bonding the first body to be bonded and the second body to be bonded.

Effects of the Invention

[0022]

According to the present invention, a bonding composition is provided that exhibits a bleed-out suppression effect and is capable of providing a bonded structure having a bonding portion with high shear strength.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

FIG. 1 is a diagram (top view) for explaining a bleed-out phenomenon.

FIG. 2 is a diagram (side view) for explaining the bleed-out phenomenon.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0024]

Specific embodiments of the present invention (hereinafter referred to as the “present embodiment”) will be described. The present invention is not limited to the following embodiments, and various modifications can be made thereto without departing from the gist of the present invention.

[0025]

<<1. Bonding Composition>>

A bonding composition of the present embodiment contains copper powder and a solvent. The solvent includes a first solvent having a boiling point of 150°C or higher and 300°C or lower and a surface tension of 30 mN/m or more, and a second solvent having a surface tension of less than 30 mN/m. The content of the first solvent relative to the copper powder is 0.1% by mass or more and 20% by mass or less. The content of the second solvent relative to the copper powder is 1.5% by mass or more and 20% by mass or less. Details of the respective components will be described below.

[0026]

<Copper Powder>

The copper powder is a powder containing copper as a main component and serves as a constituent material of a bonding portion obtained by firing the bonding composition. That is, a sintered body of the copper powder contained in the composition constitutes the bonding portion. In the present specification, a powder refers to an aggregate of a large number of particles. It may also be said that a large number of particles constitute a powder.

[0027]

The copper powder may contain elemental copper, with the balance being unavoidable impurities. The unavoidable impurities may include, for example, oxides unavoidably formed on the surfaces of copper particles constituting the copper powder. Normally, the content of elements other than elemental copper in the copper powder is 5% by mass or less. Alternatively, the copper powder may contain copper in a proportion of 50% by mass or more, with the balance containing other elements. Examples of such copper powder include copper alloy powder. From the viewpoint of enhancing electrical conductivity, the copper content in the copper powder is preferably 80% by mass or more, more preferably 90% by mass or more, and still more preferably 95% by mass or more. The content of each element in the copper powder can be measured by, for example, ICP emission spectrometry or an inert gas fusion-nondispersive infrared absorption method.

[0028]

The shape of the copper particles constituting the copper powder is not particularly limited. For example, the copper particles may have various shapes, such as a spherical shape, a flaky (scale-like) shape, a polyhedral shape, a dendritic (tree-like) shape, and a columnar shape. However, from the viewpoint of increasing the packing density of the particles and obtaining a bonding portion with high shear strength, the copper particles are preferably spherical. Whether the copper particles are spherical or not can be determined from a

circularity coefficient of the particles. Specifically, the copper powder is observed using a scanning electron microscope (SEM), the areas S and perimeters L of randomly selected copper particles are measured, and the circularity coefficient, $4\pi S/L^2$, is determined therefrom. The circularity coefficients of a plurality of copper particles are determined, and an average value thereof is calculated. When the arithmetic mean value of the circularity coefficients is 0.85 or more, the copper particles are defined as being spherical.

[0029]

The content of the copper powder in the bonding composition is preferably 80% by mass or more and 96% by mass or less. By setting the content of the copper powder to an appropriately high level, the electrical conductivity and shear strength of the bonding portion can be further enhanced. In addition, by lowering the content of the copper powder to an appropriate level, aggregation of the copper particles in the composition is suppressed, resulting in an improvement in the applicability of the composition. The content of the copper powder refers to the total amount of the copper powder contained in the bonding composition.

That is, when the copper powder contains a first copper powder and a second copper powder as described below, the content of the copper powder refers to the total amount of the first copper powder and the second copper powder.

[0030]

The average particle diameter (D_{50}) of the copper powder is preferably 0.03 μm or more, and more preferably 0.05 μm or more. By setting the particle diameter of the copper powder to an appropriately large value, aggregation of the particles in the composition can be prevented, thereby improving the particle dispersibility. Meanwhile, the average particle diameter (D_{50}) of the copper powder is preferably 20 μm or less, and more preferably 10 μm or less. By setting the particle diameter of the copper powder to an appropriately small value, the sinterability of the copper powder can be improved.

[0031]

The average particle diameter (D_{50}) of the copper powder can be determined as follows. First, 2-propanol is added to the bonding composition in an amount 10 times (by mass) that of the bonding composition, and after the mixture is sufficiently stirred, a washing operation in which only the supernatant liquid is removed while the solids (cake) are left is repeated. The resulting cake is allowed to stand at room temperature and sufficiently dried, and the resulting dried product (copper powder) is observed by SEM. In the SEM observation, an SEM image at a magnification of 1,000X to 100,000X is obtained. In this SEM image, 50 or more particles whose outlines are observed are randomly selected, and their particle diameters (Heywood diameters) are measured. The volume of each particle, assuming that the particle is a true sphere, is calculated from the Heywood diameter, and a volume-

based particle size distribution is determined from the obtained data. Next, in the obtained particle size distribution, the particle diameter at which the volume (cumulative volume) accumulated from the smaller particle diameter side reaches 50% by volume (the cumulative 50% volume diameter) is calculated, and this is defined as the average particle diameter (D_{50}).

[0032]

More preferably, the copper powder contains a first copper powder having a cumulative 50% volume diameter (D_{50}) of 0.11 μm or more and less than 1 μm in a particle-size region of less than 1 μm in a particle size distribution measured by SEM observation, and a second copper powder having a cumulative 50% volume diameter (D_{50}) of 1 μm or more and 10 μm or less in a particle-size region of 1 μm or more in the particle size distribution.

[0033]

The D_{50} of the first copper powder is preferably 0.11 μm or more from the viewpoint of preventing aggregation of particles in the bonding composition and achieving favorable particle dispersibility. The D_{50} of the first copper powder is preferably 0.9 μm or less, more preferably 0.8 μm or less, and still more preferably 0.6 μm or less from the viewpoint of sufficiently ensuring the sinterability of the copper powder. The D_{50} of the second copper powder is preferably 1 μm or more from the viewpoint of improving the shear strength of a bonding portion obtained by sintering the copper powder. The

D_{50} of the second copper powder is preferably 10 μm or less, more preferably 8 μm or less, and still more preferably 6 μm or less from the viewpoint of improving the applicability of the composition.

[0034]

The D_{50} of each of the first copper powder and the second copper powder can be determined as follows. First, the particle size distribution of the entire copper powder is determined by the method described above. Subsequently, the obtained particle size distribution is divided into the region in which the particle diameter is less than 1 μm (first copper powder region) and the region in which the particle diameter is 1 μm or more (second copper powder region). For particle diameter measurement, the particle diameters of 50 or more particles are measured in each of the first copper powder region and the second copper powder region. The cumulative 50% volume diameter (D_{50}) is measured from the particle size distribution in the first copper powder region and defined as the particle diameter of the first copper powder. Similarly, the cumulative 50% volume diameter (D_{50}) is measured from the particle size distribution in the second copper powder region and defined as the particle diameter of the second copper powder.

[0035]

The proportion of the first copper powder relative to the total mass of the first copper powder and the second copper powder in the bonding composition is preferably 10% by mass or

more and 95% by mass or less, more preferably 15% by mass or more and 90% by mass or less, and still more preferably 20% by mass or more and 80% by mass or less. The proportion of the second copper powder relative to the total mass of the first copper powder and the second copper powder is preferably 5% by mass or more and 90% by mass or less, more preferably 10% by mass or more and 85% by mass or less, and still more preferably 20% by mass or more and 80% by mass or less. By setting the proportions within the above respective ranges, the packing density of the particles can be increased, thereby sufficiently enhancing the shear strength of the bonding portion. The masses of the first copper powder and the second copper powder can be calculated as follows. Specifically, the dried product (copper powder) prepared as described above is divided, based on SEM observation, into the region of less than 1 μm and the region of 1 μm or more in the particle size distribution. The mass of the copper powder in the former region is regarded as the mass of the first copper powder, whereas the mass of the copper powder in the latter region is regarded as the mass of the second copper powder. More specifically, the average particle diameter of the copper powder is calculated in each of the region of less than 1 μm and the region of 1 μm or more in the particle size distribution. Subsequently, the volume of the copper powder in each region is calculated from the corresponding average particle diameter, and the mass of the copper powder in each region is calculated by multiplying the volume by the density.

[0036]

The copper powder may be one that has not been subjected to surface treatment (untreated copper powder). Alternatively, the copper powder may be one that has been subjected to surface treatment to an extent that does not impair the effects of the present embodiment (surface-treated copper powder). Examples of the surface-treated copper powder include copper powder having, on the surfaces thereof, a surface treatment layer formed of a fatty acid, a copper salt of a fatty acid, an aliphatic amine, a silane coupling agent, a titanate coupling agent, an aluminate coupling agent, or the like.

[0037]

<Solvent>

The solvent functions to impart an appropriate viscosity and consequently favorable applicability to the bonding composition. The solvent also has the effect of ensuring favorable electrical conductivity and shear strength of the bonding portion obtained by firing the composition, by allowing the copper particles to be uniformly dispersed in the composition.

[0038]

In the present embodiment, a mixed solvent of a first solvent and a second solvent is used as the solvent. Of these, the first solvent is a component having a relatively high surface tension of 30 mN/m or more. The use of the first solvent having a high surface tension makes it possible to

suppress bleed-out. This is presumably because an increase in the surface tension of the entire solvent (mixed solvent of the first solvent and the second solvent) reduces wettability with respect to the body to be bonded, and as a result, suppresses wetting and spreading of the solvent when the bonding composition is applied onto the body to be bonded. In contrast, when the surface tension of the first solvent is less than 30 mN/m, wetting and spreading of the solvent progresses, resulting in an insufficient bleed-out suppression effect. From the viewpoint of the dispersibility of the bonding composition, the surface tension of the first solvent is preferably 30.2 mN/m or more and 65 mN/m or less, and more preferably 30.4 mN/m or more and 50 mN/m or less. The surface tension is measured by a method described in Examples below or a method equivalent thereto.

[0039]

The content of the first solvent in the bonding composition relative to the copper powder is 0.1% by mass or more and 20% by mass or less. Here, the content of the first solvent is the mass ratio of the first solvent to the copper powder. When the content thereof is less than 0.1% by mass, the effect provided by the first solvent, that is, the bleed-out suppression effect, becomes insufficient. When the content thereof exceeds 20% by mass, the total amount of the solvent becomes excessively large. As a result, the paste viscosity of the bonding composition becomes excessively low, which may cause the bleed-out phenomenon. In addition, the shear

strength of a bonding portion obtained by firing the bonding composition may be reduced. From the viewpoint of achieving both improvement in shear strength and suppression of bleed-out at higher levels, the content of the first solvent relative to the copper powder is preferably 0.1% by mass or more and 15% by mass or less, and more preferably 0.1% by mass or more and 10% by mass or less.

[0040]

The boiling point of the first solvent is 150°C or higher and 300°C or lower. When the boiling point exceeds 300°C, volatilization and removal of the first solvent during firing of the bonding composition become insufficient. If volatilization and removal are insufficient, organic matter may remain in the resulting bonding portion, thereby reducing the shear strength and electrical conductivity. When the boiling point is lower than 150°C, the composition may undergo sudden boiling during firing, causing formation of pores in the bonding portion. This may reduce the electrical conductivity and shear strength of the bonding portion. From the viewpoint of further enhancing the electrical conductivity and shear strength of the bonding portion, the boiling point of the first solvent is preferably 150°C or higher and 290°C or lower, and more preferably 150°C or higher and 280°C or lower.

[0041]

The second solvent is a component having a relatively low surface tension of less than 30 mN/m. Such a second solvent

acts to improve wettability for the copper powder, thereby improving the dispersibility of the copper powder. Consequently, the second solvent has the effect of improving the shear strength of the bonding portion in the bonded structure. Meanwhile, the first solvent having a high surface tension provides a bleed-out suppression effect; however, only the first solvent cannot provide the bonding portion with the desired shear strength. Accordingly, by using the second solvent having a low surface tension in combination with the first solvent as in the present invention, the shear strength can be improved while maintaining suppression of bleed-out. When the surface tension of the second solvent is 30 mN/m or more, the effect of improving the shear strength becomes insufficient. From the viewpoint of suppressing bleed-out, the surface tension of the second solvent is preferably 20 mN/m or more and 29.5 mN/m or less, and more preferably 22 mN/m or more and 29 mN/m or less.

[0042]

The content of the second solvent in the bonding composition relative to the copper powder is 1.5% by mass or more and 20% by mass or less. Here, the content of the second solvent is the mass ratio of the second solvent to the copper powder. When the content is less than 1.5% by mass, the effect provided by the second solvent becomes insufficient, resulting in an insufficient effect of improving the shear strength. When the content exceeds 20% by mass, the total amount of the solvent becomes excessively large. As a result, the paste

viscosity of the bonding composition becomes excessively low, which may cause the bleed-out phenomenon. In addition, the shear strength of a bonding portion obtained by firing the bonding composition may be reduced. From the viewpoint of improving the shear strength, the content of the second solvent relative to the copper powder is preferably 2% by mass or more. From the viewpoint of achieving both improvement in shear strength and suppression of bleed-out at higher levels, the content of the second solvent relative to the copper powder is preferably 15% by mass or less, and more preferably 10% by mass or less.

[0043]

The boiling point of the second solvent is not limited. However, the boiling point is preferably 150°C or higher and 300°C or lower. By setting the boiling point to 300°C or lower, organic matter is prevented from remaining in the bonding portion, thereby making it easier to prevent reductions in electrical conductivity and shear strength. By setting the boiling point to 150°C or higher, it likewise becomes easier to prevent reductions in the electrical conductivity and shear strength of the bonding portion. From the viewpoint of further enhancing the electrical conductivity and shear strength of the bonding portion, the boiling point is preferably 150°C or higher and 290°C or lower, and more preferably 150°C or higher and 280°C or lower.

[0044]

Preferably, the surface tension of the first solvent is 30

mN/m or more and 65 mN/m or less, and the surface tension of the second solvent is 20 mN/m or more and less than 30 mN/m. This achieves both improvement in shear strength and suppression of bleed-out at higher levels.

[0045]

The types of the first solvent and the second solvent are not limited, provided that the requirements described above are satisfied. Examples thereof include alcohols, ketones, esters, ethers, hydrocarbons, and organic acids. Specific examples thereof include alcohols such as propylene glycol, ethylene glycol, hexylene glycol, diethylene glycol, 1,3-butanediol, 1,4-butanediol, dipropylene glycol, tripropylene glycol, and dihydroterpineol; ethers such as ethylene carbitol and butyl carbitol; and organic acids such as carboxylic acids. However, the first solvent and the second solvent are preferably mutually compatible solvents. Whether the solvents are compatible or not can be determined by examining whether phase separation occurs or not when a mixed solvent of the first solvent and the second solvent is allowed to stand.

[0046]

The first solvent is preferably one or more selected from the group consisting of alcohol-based solvents, glycol-based solvents, ketone-based solvents, and ester-based solvents. Although not limited thereto, examples of the first solvent include one or more selected from the group consisting of cyclohexanol, ethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol,

glycerin, acetonylacetone, acetophenone, monoacetin, triacetin, diethylene glycol, triethylene glycol, methyl triglycol, γ-butyrolactone, dipropylene glycol, terpineol, dihydroterpineol, octylene glycol, benzyl alcohol, ethoxyethoxyethanol, butoxyethoxyethanol, tripropylene glycol, isophorone, and butyl carbitol acetate. The first solvent may consist of only one type of solvent or may be a mixed solvent of multiple types of solvents. When the mixed solvent is used, the respective types of solvents contained in the mixed solvent are preferably mutually compatible. In addition, it is sufficient that the total amount of these solvents in the mixed solvent falls within the desired range for the amount of the first solvent (0.1% by mass or more and 20% by mass or less relative to the copper powder).

[0047]

The second solvent is preferably a liquid carboxylic acid. The liquid carboxylic acid refers to a carboxylic acid that is liquid at 20°C under a pressure of 1 atm. When a carboxylic acid is used as the solvent, the surfaces of the copper particles are etched, thereby activating the copper particles, which consequently results in the formation of copper carboxylate having a sintering-promoting effect. Consequently, the sinterability of the copper powder can be improved, thereby sufficiently enhancing the shear strength of the bonding portion. In addition, the use of the liquid carboxylic acid allows the copper particles to be uniformly dispersed, thereby making it possible to obtain a composition having

favorable applicability.

[0048]

Examples of the liquid carboxylic acid include branched saturated aliphatic monocarboxylic acids having 4 to 18 carbon atoms. The liquid carboxylic acid is preferably one or more selected from saturated secondary aliphatic monocarboxylic acids and saturated tertiary aliphatic monocarboxylic acids that are liquid at 20°C under a pressure of 1 atm. Such a carboxylic acid is preferably one or more selected from the group consisting of 2,2-dimethylbutyric acid, neodecanoic acid, and octylic acid, and more preferably one or more selected from the group consisting of neodecanoic acid and octylic acid. The use of such a carboxylic acid makes it possible to further enhance the shear strength of the bonding portion. The second solvent may consist of only one type of solvent or may be a mixed solvent of multiple types of solvents. When the mixed solvent is used, the respective types of solvents contained in the mixed solvent are preferably mutually compatible. In addition, it is sufficient that the total amount of these solvents in the mixed solvent falls within the desired range for the amount of the second solvent (1.5% by mass or more and 20% by mass or less relative to the copper powder).

[0049]

The total content of the first solvent and the second solvent in the bonding composition is preferably 4% by mass or more and 20% by mass or less, more preferably 4% by mass or

more and 15% by mass or less, and particularly preferably 4% by mass or more and 10% by mass or less.

[0050]

The mixed solvent of the first solvent and the second solvent preferably has a surface tension of 20 mN/m or more and 40 mN/m or less. Here, the mixed solvent is a solvent obtained by mixing the first solvent and the second solvent such that their respective proportions are the same as those in the liquid composition. By setting the surface tension of the mixed solvent within the above range, the bleed-out suppression effect can be exhibited more markedly.

[0051]

In particular, the following combinations of the first solvent and the second solvent are preferred:

• First solvent: terpineol; second solvent: neodecanoic acid

• First solvent: dipropylene glycol; second solvent: neodecanoic acid

• First solvent: octylene glycol; second solvent: neodecanoic acid

• First solvent: diethylene glycol; second solvent: neodecanoic acid

• First solvent: terpineol; second solvent: octylic acid

• First solvent: dipropylene glycol; second solvent: octylic acid

• First solvent: octylene glycol; second solvent: octylic acid

• First solvent: diethylene glycol; second solvent: octylic acid

[0052]

<Other Components>

The bonding composition of the present embodiment may contain other additives in addition to the copper powder, the first solvent, and the second solvent. Examples of other additives include a sintering aid, a binder resin, a reducing agent, a surface tension modifier, an antifoaming agent, and a viscosity modifier. However, the bonding composition may be composed solely of the copper powder, the first solvent, and the second solvent, without containing other additives. Even without other additives, the effects of improving shear strength and suppressing bleed-out can be sufficiently exhibited.

[0053]

<Viscosity>

The paste viscosity of the bonding composition is preferably 10 Pa·s or more and 800 Pa·s or less. By setting the viscosity to an appropriately high level, the bleed-out suppression effect can be exhibited more firmly. In addition, the copper particles can be uniformly dispersed in the composition, and sedimentation thereof can be suppressed. Furthermore, the packing density of the copper particles in a coating film obtained by applying the composition is improved, making it possible to obtain a bonding portion that is excellent in terms of electrical conductivity and shear strength. From the same viewpoints, the paste viscosity of the bonding composition is preferably 30 Pa·s or more, and more

preferably 50 Pa·s or more. By lowering the viscosity to an appropriate level, the applicability of the composition can be improved. In addition, when the copper particles are densely concentrated in the composition, they tend to aggregate more easily. By lowering the viscosity, aggregation of the copper particles can be suppressed, thereby obtaining a bonding portion that is particularly excellent in terms of electrical conductivity and shear strength. From the same viewpoints, the paste viscosity of the bonding composition is preferably 600 Pa·s or less, and more preferably 400 Pa·s or less. The viscosity is measured by a method described in Examples below or a method equivalent thereto.

[0054]

By using the bonding composition of the present embodiment, the bleed-out phenomenon is less likely to occur after application of the composition. Thus, it is possible to suppress the occurrence of problems such as insulation failure caused by bleed-out. In addition, the bonding portion formed using the bonding composition has high shear strength (bonding strength). Therefore, a highly reliable bonded structure can be produced.

[0055]

<<2. Method for Producing Bonding Composition>>

The bonding composition of the present embodiment is produced by mixing the copper powder, the first solvent, the second solvent, and, if necessary, other additives. The copper powder may be one produced by any of various methods, such as

a wet reduction method, an atomization method, or an electrolytic reduction method. For example, when a wet reduction method or an atomization method is used, spherical particles tend to be obtained. When an electrolytic reduction method is used, dendritic or columnar particles tend to be obtained. Flaky particles can be obtained, for example, by applying an external mechanical force to spherical particles to plastically deform the particles. When a copper powder containing a fine first copper powder and a coarse second copper powder is used, the first copper powder and the second copper powder may be separately prepared and then mixed together. The mixing may be performed using a known mixing apparatus such as a roll mill.

[0056]

<<3. Method for Producing Bonded Structure>>

The method for producing a bonded structure of the present embodiment includes: a step of applying the bonding composition described above to a surface of a first body to be bonded to form a coating film, and subsequently placing a second body to be bonded on the coating film to obtain a stacked body (applying and stacking step); and a step of subjecting the obtained stacked body to heat treatment to sinter the copper powder contained in the coating film, thereby obtaining a bonded structure in which the first body to be bonded and the second body to be bonded are bonded together and a bonding portion derived from the bonding composition is formed (heating step).

[0057]

<Applying and Stacking Step>

In the applying and stacking step, the bonding composition is applied to the surface of the first body to be bonded to form the coating film, and the second body to be bonded is subsequently placed on the coating film to obtain the stacked body. The coating film may be formed by a known application method, such as screen printing, dispense printing, gravure printing, reverse coating, or doctor blade coating. The coating film may be provided over the entire surface of the first body to be bonded or may be discontinuously provided on a portion of the surface. From the viewpoint of more reliably ensuring high shear strength, the coating film may be provided not only on the surface of the first body to be bonded but also on a surface of the second body to be bonded.

[0058]

By placing the second body to be bonded on the coating film, the stacked body including the first body to be bonded, the second body to be bonded, and the coating film interposed therebetween is obtained. The first body to be bonded and the second body to be bonded may be formed from the same type of material or from different types of materials. From the viewpoint of obtaining a bonding portion that stably exhibits high shear strength, the coating film portion provided when the first body to be bonded and the second body to be bonded are superposed on each other preferably has a thickness of 1 μm or more and 500 μm or less, and more preferably 5 μm or

more and 300 μm or less.

[0059]

<Heating Step>

In the heating step, the obtained stacked body is subjected to heat treatment to sinter the copper powder contained in the coating film, thereby obtaining the bonded structure in which the first body to be bonded and the second body to be bonded are bonded together and the bonding portion derived from the bonding composition is formed. As necessary, the coating film may be dried at a low temperature before the heat treatment. The bonding portion, which is the sintered body of the copper powder formed by the heat treatment, mechanically bonds the first body to be bonded and the second body to be bonded to each other and electrically and thermally connects these bodies. Thus, the bonded structure having the bonding portion excellent in electrical conductivity, shear strength, and thermal conductivity is obtained.

[0060]

The heat treatment is preferably performed in an atmosphere of a reducing gas such as hydrogen or formic acid, or in an atmosphere of an inert gas such as nitrogen or argon. The heating temperature is preferably lower than 300°C, and more preferably 150°C or higher and lower than 300°C. The heating temperature may be 180°C or higher and lower than 300°C, or may be 200°C or higher and lower than 300°C. Assuming that the heating temperature is within the above range, the heating time (firing time) is preferably 20 minutes

or longer, more preferably 20 minutes or longer and 120 minutes or shorter, and still more preferably 30 minutes or longer and 120 minutes or shorter.

[0061]

The heat treatment is performed without application of pressure or under application of pressure. Treatment without application of pressure refers to treatment performed without applying any pressure other than pressure resulting from the weight of the body to be bonded and atmospheric pressure, whereas treatment with application of pressure refers to treatment performed while applying pressure in addition to pressure resulting from the weight of the body to be bonded and atmospheric pressure. When the treatment under application of pressure is performed, the applied pressure is preferably 0.001 MPa or more, more preferably 0.001 MPa or more and 20 MPa or less, and still more preferably 0.01 MPa or more and 15 MPa or less.

[0062]

<Bonded Structure>

The bonded structure of the present embodiment includes the first body to be bonded, the second body to be bonded, and the sintered body of the bonding composition that bonds the first body to be bonded and the second body to be bonded. Here, the bodies to be bonded (first body to be bonded and second body to be bonded) are objects to be bonded. Examples thereof include conductive bodies such as spacers and heat dissipation plates formed from various conductive metals such

as gold, silver, and copper; metal wires; substrates having metal wires on their surfaces; and semiconductor chips. Specific examples include semiconductor elements such as power modules, transmitters, amplifiers, and LED modules; lead frames; metal-clad ceramic substrates; substrates for mounting semiconductor elements; metal wiring; block bodies; power feeding members; heat dissipation plates; water-cooling plates; and metal clips.

[0063]

A specific example of the bonded structure is a semiconductor device in which a substrate for mounting a semiconductor element is used as the first body to be bonded, a semiconductor chip is used as the second body to be bonded, and both bodies are bonded together by the sintered body of the bonding composition. Other examples include a bonded body in which a substrate for mounting a semiconductor element is used as the first body to be bonded, a heat dissipation plate is used as the second body to be bonded, and both bodies are bonded together by the sintered body of the bonding composition; and a bonded body in which a semiconductor chip electrode is used as the first body to be bonded, a metal clip is used as the second body to be bonded, and both bodies are bonded together by the sintered body of the bonding composition.

[0064]

The bonded structure obtained by the method of the present embodiment includes the bonding portion formed from the

sintered body of the bonding composition. This composition has favorable sinterability of copper powder, and the bonding portion formed from the sintered body thereof has high electrical conductivity and high shear strength. The bonded structure having such characteristics can be suitably used in various electronic circuits, particularly electronic circuits used in high-temperature environments, such as automotive electronic circuits and electronic circuits in which power devices are mounted.

EXAMPLES

[0065]

The present invention will be described in further detail with reference to the following Examples. However, the present invention is not limited to the following Examples.

[0066]

(1) Preparation of Bonding Composition

[Example 1]

As the copper powder, a mixture of a first copper powder (CH-0200L1, Mitsui Mining & Smelting Co., Ltd.) and a second copper powder (CS-20, Mitsui Mining & Smelting Co., Ltd.) at a mass ratio of first copper powder : second copper powder = 3 : 7 was used. The D_{50} values of the first copper powder and the second copper powder were measured by the measurement method described above after the powders had been formulated into the paste-like bonding composition as described below. The D_{50} of the first copper powder was 0.14 μm, and the D_{50} of the second

copper powder was 2.2 μm. Both the first copper powder and the second copper powder were spherical powders.

[0067]

Terpineol was used as the first solvent, and neodecanoic acid (Versatic 10, Hexion Inc.) was used as the second solvent. Neodecanoic acid (Versatic 10) is a branched saturated tertiary aliphatic monocarboxylic acid that is liquid at 20°C under a pressure of 1 atm and has 10 carbon atoms.

[0068]

Two parts by mass of the first solvent (terpineol) and 3 parts by mass of the second solvent (neodecanoic acid) were added to 95 parts by mass of the copper powder. The resulting mixture was preliminarily kneaded with a spatula and then formed into a paste using a planetary centrifugal vacuum mixer (ARE-500, THINKY CORPORATION). During the paste formation, two cycles of treatment were performed, each cycle consisting of a stirring mode (1,000 rpm for 1 minute) and a deaeration mode (2,000 rpm for 30 seconds). Subsequently, the resulting paste was dispersed and mixed using a three-roll mill to prepare a paste-like bonding composition.

[0069]

(2) Production of Bonded Structure

The bonding composition was applied by dispense printing to the center of a chip-mounting portion of a copper lead frame (having a thickness of 2.0 mm) serving as the first body to be bonded. Subsequently, a 3 mm square-sized SiC piece

(having a thickness of 0.2 mm and provided with gold plating on its back surface) was placed as the second body to be bonded, at the center of the bonding composition with the back surface of the piece facing the bonding composition, thereby obtaining a stacked body. The thickness of the bonding composition at this time was 50 μm. In this state, the stacked body was fired at 150°C for 90 minutes in a formic acid atmosphere to produce a bonded structure.

[0070]

[Example 2]

Dipropylene glycol was used as the first solvent instead of terpineol. Except for this change, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0071]

[Example 3]

Octylene glycol was used as the first solvent instead of terpineol. Except for this change, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0072]

[Example 4]

The amount of the first solvent (terpineol) added was changed to 3.5 parts by mass, and the amount of the second solvent (neodecanoic acid) added was changed to 1.5 parts by mass. Except for these changes, a bonding composition and a bonded structure were produced by the same procedures as in

Example 1.

[0073]

[Example 5]

The amount of the copper powder was changed to 93.5 parts by mass, the amount of the first solvent (terpineol) added was changed to 3.5 parts by mass, and the amount of the second solvent (neodecanoic acid) added was changed to 3 parts by mass. Except for these changes, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0074]

[Example 6]

Octylic acid was used as the second solvent instead of neodecanoic acid. Except for this change, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0075]

[Comparative Example 1]

The first solvent (terpineol) was not added. The amount of the second solvent (neodecanoic acid) added was changed to 5 parts by mass. Except for these changes, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0076]

[Comparative Example 2]

Dodecane was used as the first solvent instead of terpineol. Except for this change, a bonding composition and a

bonded structure were produced by the same procedures as in Example 1.

[0077]

[Comparative Example 3]

1-Hexanol was used as the first solvent instead of terpineol. Except for this change, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0078]

[Comparative Example 4]

The amount of the first solvent (terpineol) added was changed to 4 parts by mass, and the amount of the second solvent (neodecanoic acid) added was changed to 1 part by mass. Except for these changes, a bonding composition and a bonded structure were produced by the same procedures as in Example 1.

[0079]

Table 1 below shows the physical property values (surface tensions and boiling points) of the first solvent, the second solvent, and the mixed solvent thereof used in each of Examples 1 to 6 and Comparative Examples 1 to 4, as well as the contents of the first solvent and the second solvent in each composition (mass ratios relative to the copper powder and mass proportions in the composition).

[0080]

(3) Evaluation

Various properties of the bonding compositions and bonded

structures obtained in Examples 1 to 6 and Comparative Examples 1 to 4 were evaluated by the following procedures.

[0081]

<Surface Tension>

The respective surface tensions of the first solvent and the second solvent were each measured by a Pt plate method using a surface tensiometer (K20 Easy Dyne, manufactured by KRUSS GmbH). The measurements were performed in an environment at 25°C. The surface tension of the mixed solvent of the first solvent and the second solvent was also measured by the same method. The respective proportions of the first solvent and the second solvent in the mixed solvent were set to be the same as those in the bonding composition.

[0082]

<Paste Viscosity>

The viscosity of the bonding composition paste was measured. The viscosity measurement was performed under the following conditions, thereby determining the viscosity value at a shear rate of 10 s^{-1}.

[0083]

· Measurement apparatus: MARS III rheometer (manufactured by Thermo Fisher Scientific Inc.)

· Measurement mode: shear-rate-dependence measurement

· Sensor: parallel type (φ20 mm)

· Measurement temperature: 25°C

· Gap: 0.300 mm

· Shear rate: 0.05 to 120.01 s^{-1}

· Measurement time: 2 minutes

[0084]

<Bleed-Out Ratio>

A stacked body was produced in the same manner as in each Example and Comparative Example, except that the copper lead frame was replaced with a 10 mm square-sized AMB substrate for a bleed-out test. The AMB substrate used had a bonded structure including a silicon nitride ceramic substrate having a thickness of 0.32 mm and a copper plate having a thickness of 0.2 mm (oxygen-free copper C1020), the bonded structure having been subjected to rust-preventive treatment using a rust inhibitor containing benzotriazole as a main component. The AMB substrate had an arithmetic mean height Sa of 0.13 μm. The arithmetic mean height Sa was measured over a 2 mm square area using a white-light interferometer (ZeGage (registered trademark) Pro, manufactured by Zygo Corporation).

[0085]

The stacked body was observed from above using an optical microscope, and its optical microscope image was captured. Subsequently, in the obtained optical microscope image (top-view image), the area (bonding composition area) of a region to which the bonding composition had been applied (bonding composition region 4 in FIG. 1) and the area (bleed-out area) of a region over which the solvent had wetted and spread (bleed-out region 8 in FIG. 1) were determined. The ratio of the bleed-out area to the bonding composition area (bleed-out area/bonding composition area × 100) was calculated as the

bleed-out ratio (%).

[0086]

<Shear Strength>

The shear strength of the bonded structure was measured using a bond tester (Condor Sigma, xyztec B.V.). The shear strength was calculated as the ratio (fracture load/bonding area) of the fracture load (unit: N) to the bonding area (unit: mm^2).

[0087]

(4) Evaluation Results

The obtained evaluation results are summarized in Table 1 below.

[0088]

Samples of Examples (Examples 1 to 6), in which the surface tensions and contents of the first solvent and the second solvent satisfied the ranges specified in the present embodiment, had bleed-out ratios of 22.9% or less and shear strengths of the bonding portions of 27 MPa or more. In particular, Examples 1, 2, and 6 had low bleed-out ratios of 16.3% or less and high shear strengths of 50 MPa or more.

[0089]

In contrast, a sample of Comparative Example (Comparative Example 1), which contained no first solvent, had a high bleed-out ratio of 24.2%. Samples of Comparative Examples (Comparative Examples 2 and 3), which contained a first solvent having a low surface tension, had relatively high bleed-out ratios of 23.6% or more. Furthermore, a sample of

Comparative Example (Comparative Example 4), in which the content of the second solvent was excessively small, had a very low shear strength of 8 MPa.

[0090]

From the above results, it is understood that the present embodiment provides a bonding composition that exhibits a bleed-out suppression effect and is capable of providing a bonded structure having a bonding portion with high shear strength.

[0091]

[Table 1]

Table 1 Formulation and properties of the bonding composition

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
First solvent	Type	Terpineol	Dipropylene glycol	Octylene glycol	Terpineol	Terpineol	Terpineol	-	Dodecane	1-Hexanol	Terpineol
	Surface tension [mN/m]	32.3	34.5	30.8	32.3	32.3	32.3	-	25.6	26.4	32.3
	Boiling point [°C]	214	232	244	214	214	214	-	216	157	214
	Content A (Note 1) [mass%]	2.1	2.1	2.1	3.7	3.8	2.1	-	2.1	2.1	4.2
	Content B (Note 2) [mass%]	2	2	2	3.5	3.5	2	-	2	2	4
Second solvent	Type	Neodecanoic acid	Neodecanoic acid	Neodecanoic acid	Neodecanoic acid	Neodecanoic acid	Octylic acid	Neodecanoic acid	Neodecanoic acid	Neodecanoic acid	Neodecanoic acid
	Surface tension [mN/m]	28.5	28.5	28.5	28.5	28.5	27.7	28.5	28.5	28.5	28.5
	Boiling point [°C]	275	275	275	275	275	228	275	275	275	275
	Content A (Note 1) [mass%]	3.2	3.2	3.2	1.6	3.2	3.2	5.3	3.2	3.2	1.1
	Content B (Note 2) [mass%]	3	3	3	1.5	3	3	5	3	3	1
Mixed solvent	Surface tension [mN/m]	29.4	29.2	29.2	30.8	30	29.2	28.5	26.6	27.1	31.3
Bonding composition	Copper powder content [mass%]	95	95	95	95	93.5	95	95	95	95	95
	Paste viscosity [Pa·s] (10/s)	229	485	375	215	115	221	274	86	141	248
	Bleed-out ratio (Note 3) [%]	16.2	8.9	19.2	11.5	22.9	16.3	24.2	44.3	23.6	10.1
	Shear strength [MPa]	68	50	66	27	62	69	65	45	60	8

Note 1) Content A is the amount (by mass) of the solvent relative to the copper powder.
Note 2) Content B is the amount (by mass) of the solvent in the bonding composition.
Note 3) The bleed-out ratio is a value determined as follows: bleed-out area/paste area × 100.

EXPLANATION OF REFERENCE NUMERALS

[0092]

2 body to be bonded

4 bonding composition (bonding composition region)

6 semiconductor element

8 bleed-out (bleed-out region)

CLAIMS

[Claim 1]

A bonding composition comprising copper powder and a solvent,

wherein the solvent comprises:

a first solvent having a boiling point of 150°C or higher and 300°C or lower and a surface tension of 30 mN/m or more; and

a second solvent having a surface tension of less than 30 mN/m,

wherein a content of the first solvent relative to the copper powder is 0.1% by mass or more and 20% by mass or less, and

wherein a content of the second solvent relative to the copper powder is 1.5% by mass or more and 20% by mass or less.

[Claim 2]

The bonding composition according to claim 1, wherein the surface tension of the first solvent is 30 mN/m or more and 65 mN/m or less, and the surface tension of the second solvent is 20 mN/m or more and less than 30 mN/m.

[Claim 3]

The bonding composition according to claim 1 or 2, wherein the first solvent is one or more selected from the group consisting of alcohol-based solvents, glycol-based solvents,

ketone-based solvents, and ester-based solvents.

[Claim 4]

The bonding composition according to claim 1 or 2, wherein the second solvent is a liquid carboxylic acid.

[Claim 5]

The bonding composition according to claim 1 or 2, wherein a content of the copper powder in the bonding composition is 80% by mass or more and 96% by mass or less.

[Claim 6]

The bonding composition according to claim 1 or 2, wherein the bonding composition has a paste viscosity of 10 Pa·s or more and 800 Pa·s or less.

[Claim 7]

A bonded structure comprising:

a first body to be bonded;

a second body to be bonded; and

a sintered body of the bonding composition according to claim 1 or 2, the sintered body bonding the first body to be bonded and the second body to be bonded.