

(19)



(11)

EP 3 943 215 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

26.01.2022 Bulletin 2022/04

(51) International Patent Classification (IPC):

B22F 1/00 ^(2022.01) **B22F 1/02** ^(2006.01)
B22F 7/08 ^(2006.01)

(21) Application number: **20778568.4**

(52) Cooperative Patent Classification (CPC):

B22F 1/00; B22F 1/02; B22F 7/08

(22) Date of filing: **19.03.2020**

(86) International application number:

PCT/JP2020/012389

(87) International publication number:

WO 2020/196299 (01.10.2020 Gazette 2020/40)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

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(30) Priority: **22.03.2019 JP 2019055538**

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(54) **METAL PASTE, BONDING METHOD AND METHOD FOR PRODUCING BONDED BODY**

(57) A metal paste for low temperature bonding at temperatures 600°C or lower, the metal paste comprising: a metal particle with an average particle size of 1 to 100 μm; a metal nanoparticle with an average particle

size of 1 to 500 nm; a stress relieving material; and a dispersion medium to disperse the metal particle, metal nanoparticle, and the stress relieving material.

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Description

[Technical Field]

5 **[0001]** The present invention is related to metal pastes, bonding methods and methods of manufacturing bonded bodies.

[Background Art]

10 **[0002]** In the past, lead solder has been widely used for bonding metals, semiconductors, etc. However, from the viewpoint of environmental regulations, etc., there is a need for a bonding material that does not contain lead and that is inexpensive. In addition, with recent technological advances in the field of power semiconductors, power devices with high energy efficiency are expected to be realized so that reliable semiconductor devices can be used at higher temperatures.

15 **[0003]** Several studies have considered the use of copper particles as an inexpensive bonding material in semiconductor device bonding methods. For example, patent document 1 discloses a bonding method in which copper particles with a micro-order particle size are used as a bonding material, and the surface of the copper particles is oxidized by in situ synthesis to form nanostructured particles, which are then heated under a reducing atmosphere. Patent document 2 discloses a method of pressureless bonding using a copper paste containing nanoparticles and micro- or submicron-sized particles whose dispersibility has been improved by coating the surface with organic molecules. Patent document 20 3 discloses a method of forming a sintered layer of a first metallic particle paste and a second metallic particle paste on the respective bonding surfaces of a semiconductor device and a substrate using metallic nanoparticles and metallic submicron particles, and interposing a sintered layer of a third metallic particle paste between the formed sintered layers to improve the reliability of bonding.

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[Citation List]

[Patent Literature 1]

30 **[0004]**

[PTL 1] Japanese Patent Application Laid-Open No. 2017-074598

[PTL 2] Japanese Patent Application Laid-Open No. 2014-167145

[PTL 3] Japanese Patent Application Laid-Open No. 2012-009703

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[Summary OF INVENTION]

[Technical Problem]

40 **[0005]** However, the bonding layer using metal nanoparticles, described in patent document 1 and patent document 2, is harder and less ductile than the bulk of the same metal as the metal nanoparticles. Therefore, thermal stress is generated between the two materials to be bonded, and the bonding strength is not sufficient.

[0006] In addition, the method described in patent document 3 has the problem of complicated operation due to the large number and complexity of processes required.

45 **[0007]** The present invention has been proposed in view of the above, and as an object thereof, in one aspect, to provide a metal paste capable of realizing high bonding strength and high connection reliability under a high temperature environment by low temperature bonding with simple operation, a bonding method using the metal paste, and a method for manufacturing a bonded body using the metal paste.

50 [Solution to Problem]

[0008] A metal paste for low temperature bonding at temperatures 600°C or lower, the metal paste comprising: a metal particle with an average particle size of 1 to 100 μm; a metal nanoparticle with an average particle size of 1 to 500 nm; a stress relieving material; and a dispersion medium to disperse the metal particle, metal nanoparticle, and the stress relieving material.

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[Advantageous Effects of Invention]

5 [0009] According to an embodiment of the present invention, in one aspect, it is possible to provide a metal paste capable of achieving high bonding strength and high connection reliability in a high temperature environment by low temperature bonding with simple operation, a bonding method using the metal paste, and a method for manufacturing a bonded body using the metal paste.

[Description of Embodiments]

10 [0010] The following is a detailed description of the metal paste and the bonding method using the metal paste.

(Metal paste)

[0011] First, a detailed explanation of the metal pastes according to this embodiment will be given.

15 [0012] The metal paste in this embodiment is a metal paste for low temperature bonding at temperatures 600°C or lower, the metal paste comprising:

- 20 a metal particle with an average particle size of 1 to 100 μm;
- a metal nanoparticle with an average particle size of 1 to 500 nm;
- a stress relieving material; and
- a dispersion medium to disperse the metal particle, metal nanoparticle, and the stress relieving material.

[0013] In this embodiment, the average particle size means the cumulative medium diameter (D50) on a volume basis, which is determined from the particle size distribution measured by the laser diffraction scattering method.

25 [0014] Each of the components is described in detail below.

(Metal particles)

30 [0015] The metal particles in this embodiment are the base particles of the metal paste, and the metal species is not particularly limited as long as the average particle diameter is between 1 and 100 μm.

[0016] Generally, copper particles or silver particles are used as the base particles, however, when copper particles are used, migration is less likely to occur than when silver particles are used, thus preventing short circuits with wiring on the substrate. On the other hand, when silver particles are used, they are less easily oxidized than when copper particles are used, and have the advantage of being easily sintered without a reducing atmosphere such as air atmosphere. Metal particles such as copper particles and silver particles can be used as they are from commercially available metal powders.

[0017] In addition, the metal particles according to this embodiment may have nanostructures on their surface. By using metal particles with a nanostructure on the surface, the quantum size effect of the surface nanostructure can improve the bonding strength when bonding with the metal paste of this embodiment.

40 [0018] The method of forming nanostructures on the surface of metal particles includes, for example, the method of forming a (sub)oxide layer on the surface. For example, copper particles with copper oxide on the surface can be obtained by heating copper particles with an average particle diameter of 1 to 100 μm under an oxidizing atmosphere.

[0019] The oxidizing atmosphere in the production of copper particles with a (sub)oxidized copper layer on the surface is an oxygen concentrated atmosphere in which copper can be oxidized, for example, in air. The heating temperature can be 200 to 500°C, for example. The heating time can be determined according to the heating temperature, etc. For example, it can be 5 to 300 minutes.

50 [0020] Within the aforementioned range of average particle size, from the viewpoint of enhancing the dispersibility of the particles and facilitating the formation of nanostructures as described below, the particle size of the metal particles might be preferably 2 μm or larger, 3 μm or larger is more preferable, 3.5 μm or larger is even more preferable, and 4 μm or larger is especially preferable. From the viewpoint of enhancing the fusion between particles and reducing voids during bonding, the particle diameter of the metal particles is preferably 60 μm or less, 50 μm or less is more preferable, 40 μm or less is even more preferable, and 30 μm or less is particularly preferable.

[0021] The shape of the metal particles in this embodiment is not particularly limited, and may be, for example, spherical, in bulk, needle-like, flake-like, etc. Among these, it is preferable to use spherical or flake-like metal particles because nanostructures are easily formed on the surface and the volume of voids between the particles when they are fused together can be reduced. The term "spherical" herein refers not only to a perfectly spherical shape, but also to an abbreviated spherical state with an aspect ratio of 3 or less. Also, "flake shape" herein includes flat shapes such as plate shape, scale shape, etc.

[0022] The content of the metal particles is preferably 20 to 95 mass parts per 100 mass parts of metal paste, more preferably 30 to 90 mass parts, even more preferably 35 to 85 mass parts, and especially preferably 40 to 80 mass parts. If the content of the metal particles is within the above range, high bonding strength and connection reliability due to fusion of the metal particles can be achieved when the metal paste of this embodiment is sintered.

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(Metal nanoparticles)

[0023] The metal paste according to this embodiment contains metal nanoparticles with an average particle diameter of 1 nm to 500 nm. By including metal nanoparticles with an average particle diameter of 1 nm to 500 nm, the bonding strength can be improved through the effect of promoting metal diffusion by increasing the contact area during bonding. In this embodiment, metal nanoparticles include not only single metal particles of the above average particle size, but also particles of metal oxides, metal complex compounds, and metal salts that have been within the above average particle size range by heat treatment or reduction treatment. In this document, unless otherwise mentioned, "metal particles" refers to metal particles with an average particle diameter of 1 to 100 μm as explained above, and "metal nanoparticles" refers to metal particles with an average particle diameter of 1 nm to 500 nm.

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[0024] The metal nanoparticles according to this embodiment are fine as long as the average particle size is between 1 nm and 500 nm, but it is preferable that the average particle size is less than 100 nm. When the average particle diameter is 100 nm or less, the above effect of promoting metal diffusion can be more pronounced.

[0025] The metal species of the metal nanoparticles are not particularly limited, and include, for example, noble metal nanoparticles such as gold nanoparticles, silver nanoparticles, and copper nanoparticles, as well as other transition metal nanoparticles, semi-metal nanoparticles, etc. Among these, it is preferable to include one or more particles selected from the group of gold nanoparticles, silver nanoparticles, and copper nanoparticles, and it is more preferable to include one or more of gold nanoparticles and silver nanoparticles. The above metal nanoparticles may be used as they are commercially available.

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[0026] Furthermore, it may be desirable for the metal nanoparticles to be a different metal species than the metal particles described above. When the metal particles are not compatible with the material to be bonded, the use of metal nanoparticles with a metal species that is compatible with the material to be bonded can develop a more pronounced metal diffusion effect during bonding.

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[0027] The shape of the metal nanoparticles is not particularly limited and may be, for example, spherical, in bulk, needle-like, flake-like, etc. Among these, it is preferable that the shape of the metal nanoparticles is spherical or flake-like, because the volume of the voids between the particles when they are fused together can be reduced.

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[0028] The content of the metal nanoparticles is preferably 0.01 to 60 mass parts per 100 mass parts of metal paste, more preferably 0.1 to 30 mass parts, even more preferably 0.1 to 10 mass parts, and especially preferably 0.1 to 1 mass parts. If the content of the metal nanoparticles is within the above range, when the metal paste according to the present embodiment is dried and sintered, it is easy to effectively segregate the metal nanoparticles to the interface where the difference in thermal expansion coefficient is large among the bonding structure of the bonding part, and the metal nanoparticles are efficiently filled in the voids between the fused metal particles. In addition, the sintered layer, which is formed from a thick layer of submicron to nanoscale particles resulting from the segregation of small particles including metal nanoparticles, contains many grain boundaries suitable for atomic diffusion, which promotes atomic diffusion between the sintered layer and the material to be bonded during the bonding process to form a dense bonding layer. As a result, a strong bond can be achieved between the materials to be bonded by increasing the bonding area, and stress relaxation derived from the difference in thermal expansion coefficient can be easily achieved through the dense bonding layer, thereby ensuring long-term connection reliability.

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(Stress relieving material)

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[0029] The metal paste in this embodiment contains a stress-relieving material to mitigate peeling at the joint due to crack extension (crack arrestor effect). In this embodiment, a stress-relaxing material refers to a material that does not melt or soften at a temperature of 600°C or lower, more preferably 400°C or lower, and does not fuse with metal particles and/or metal nanoparticles via metal diffusion at the above temperature. Such a stress-relieving material serves to stop the extension of the crack, and thus can alleviate the delamination at the joint caused by the extension of the crack.

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[0030] The specific examples of stress-relieving materials include inorganic materials that are difficult to sinter, such as tungsten, alumina, aluminum nitride, and glass, among which tungsten, alumina, and aluminum nitride are preferred as stress-relieving materials. When glass is used as a stress relieving material, it is desirable to use glass with a softening point of 400°C or higher, more preferably with a softening point of 500°C or higher, and even more preferably with a softening point of 600°C or higher. The above stress-relieving materials are considered to be less susceptible to changes such as melting or diffusion at temperatures 600°C or lower. Furthermore, at temperatures 500°C or lower, and especially 400°C or lower, the effect of mitigating delamination at the joint is more reliable. One type of stress relieving material

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may be used alone, or two or more may be used in combination.

[0031] The average particle diameter of the stress relieving material is preferably between 0.01 and 100 μm , more preferably between 0.1 and 50 μm , and even more preferably between 1 and 10 μm . It is preferable to set the average particle size of the stress relieving material within the above range, as it makes it easier for the crack propagation inhibition effect to occur.

[0032] The content of the stress relieving material should be 0.01 to 10 mass parts per 100 mass parts of metal paste, 0.05 to 5 mass parts is more preferable, 0.1 to 4 mass parts is even more preferable, and 0.1 to 2 mass parts is particularly preferable. If the content of the stress relieving material is within the above range, the inhibitory effect on crack extension is easily achieved.

(Dispersion medium)

[0033] The metal paste of this embodiment contains dispersion medium (solvent) for dispersing solid particles such as metal particles and metal nanoparticles described above. The dispersion medium is not particularly limited as long as it can disperse the solid particles, but the boiling point of the dispersion medium should be around 150-400°C. The dispersion medium may be a mixture of two or more solvents.

[0034] Specific examples of dispersion mediums include chain hydrocarbons, aromatic hydrocarbons, alicyclic hydrocarbons, chain alcohols, aromatic alcohols, alicyclic alcohols, polyhydric alcohols such as glycols and triols, ethers, glycol ethers, amines, amides, aldehydes, and ketones, etc.

[0035] Among these, glycols or glycol ethers are preferably used from the viewpoint of superior dispersibility of solid particles. The glycols include alkylene glycols such as ethylene glycol and propylene glycol, and polyalkylene glycols (mainly those with a molecular weight of 1000 or less) such as polyethylene glycol and polypropylene glycol. Glycol ethers include polyalkylene glycol alkyl ethers such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, tripropylene glycol monomethyl ether, tripropylene glycol monoethyl ether, and Tripropylene glycol monoethyl ether, and their ester derivatives (e.g., diethylene glycol monobutyl ether acetate).

[0036] The content of dispersion medium is usually about 5 to 100 mass parts per 100 mass parts of solid particles, and is preferably about 7 to 70 mass parts. If the content of the dispersion medium is within the above range, the metal particles and metal nanoparticles can be properly dispersed and the viscosity of the metal paste can be adjusted to an appropriate range.

(Other components)

[0037] The metal paste may contain additives such as antioxidants, surfactants, antifoaming agent, and ion trapping agents.

[0038] Furthermore, as described below, the bonding method using the metal paste according to this embodiment includes a process of heating and sintering the metal paste. For the purpose of promoting the fusion of metal particles in this sintering process, the metal paste according to this embodiment may contain a reducing agent. The reducing agent may include sulfide, thiosulfate, oxalic acid, formic acid, ascorbic acid, aldehyde, hydrazine and its derivatives, hydroxylamine and its derivatives, dithiothreitol, phosphite, hydrophosphite, phosphite and its derivatives, lithium aluminum hydride diisobutylaluminum hydride, sodium borohydride, and others.

[0039] In addition, the metal paste according to this embodiment may also contain resin components such as polyester resins, polyurethane resins such as blocked isocyanates, epoxy resins, acrylic resins, polyacrylamide resins, polyether resins, melamine resins, terpene resins, etc. These resin components can act as binders for the solid particles. Since the metal paste of this embodiment arranges metal particles that are capable of low-temperature fusion at the interface between the surface of the metal particles and the material to be bonded, it is possible to achieve high bonding performance even when the resin component is not included. However, if particularly high conductivity is required for the bonding part, it is preferable for the metal paste to be virtually free of resin components. When the metal paste of this embodiment contains a resin component, it is preferable that the resin content is 10 mass parts or less per 100 mass parts of solid particles, 5 mass parts or less is more preferable, 3 mass parts or less is even more preferable, and 1 mass part or less is particularly preferable.

(Preparation method of metal paste)

[0040] The metal paste according to this embodiment can be prepared by mixing the solid particles, dispersion medium, and other components described above. The entire amount of solid particles may be dispersed in the dispersion medium at once, or a portion of the solid particles may be dispersed, and then the remaining portion may be added to the dispersion medium. With regard to the metal particles and metal nanoparticles, the metal particles may be added, for example, after the dispersion of the metal particles, or the dispersion of the metal particles and the dispersion of the

metal nanoparticles may be mixed.

[0041] After mixing each component, an agitation process may be performed. The agglomerates may be removed by classification operation before and after the mixing of each component.

[0042] For the agitation process, agitation and kneading equipments such as Ishikawa-type agitators, Silverson agitators, cavitation agitators, spinning and orbiting (planetary) agitators, ultrathin high speed rotating dispersers, ultrasonic dispersers, grinding machines, biaxial kneaders, bead mills, ball mills, three-roll mills, homogenizers, planetary mixers, ultrahigh pressure type dispersers, thin-layer shear disperser, wet-type ultrafine particleizer, supersonic jet mill may be used.

[0043] The classification operation can be performed using filtration, natural sedimentation, or centrifugation. Filters for filtration include water comb, metal mesh, metal filter, and nylon mesh.

(Bonding method)

[0044] The following is a detailed description of the bonding method for this embodiment using the metal paste described above.

[0045] In this embodiment, the materials of the first member and the second member, which are the materials to be bonded, are not particularly limited, and various metal, semiconductor, ceramic or resin materials can be used. Specific examples of the first member include a semiconductor substrate such as a silicon substrate; a metal substrate such as a copper substrate, a lead frame, a metal plate-attached ceramic substrate (e.g., DBC), a substrate for mounting semiconductor devices such as an LED package, a power supply member such as a copper ribbon, a metal block, a terminal, etc., a heat sink, a water cooling plate, etc. Specific examples of the second member include power modules consisting of diodes, rectifiers, thyristors, MOS gate drivers, power switches, power MOSFETs, IGBTs, Schottky diodes, fast recovery diodes, etc., transmitters, amplifiers, sensors, analog integrated circuits, semiconductor lasers, LED modules, etc.

[0046] In this embodiment, the materials of the first member and the second member, which are the materials to be bonded, are not particularly limited, and various metal, semiconductor, ceramic or resin materials can be used. Specific examples of the first member include a semiconductor substrate such as a silicon substrate; a metal substrate such as a copper substrate, a lead frame, a metal plate-attached ceramic substrate (e.g., DBC), a substrate for mounting semiconductor devices such as an LED package, a power supply member such as a copper ribbon, a metal block, a terminal, etc., a heat sink, a water cooling plate, etc. Specific examples of the second member include power modules consisting of diodes, rectifiers, thyristors, MOS gate drivers, power switches, power MOSFETs, IGBTs, Schottky diodes, fast recovery diodes, etc., transmitters, amplifiers, sensors, analog integrated circuits, semiconductor lasers, LED modules, etc.

[0047] The first member and the second member may include a metal on the surface in contact with the metal paste of this embodiment. The metal may include copper, nickel, silver, gold, palladium, platinum, lead, tin, cobalt, manganese, aluminum, beryllium, titanium, chromium, iron, molybdenum, and alloys thereof.

[0048] As a method of providing the metal paste of this embodiment between the first member and the second member, for example, screen printing, transfer printing, offset printing, letterpress printing, intaglio printing, gravure printing, stencil printing, soft lithography, jet printing, dispensing, comma coat, slit coat, die coat, gravure coat, bar coat, play coat, spin coat, electrodeposition coating, etc. are applied to the first member, and then placing the second member by a method using a chip mounter or flip chip bonder, or manually using various jigs can be mentioned.

[0049] The thickness of the metal paste according to this embodiment is usually about 1 to 1000 μm .

[0050] In the bonding method according to this embodiment, the laminate prepared by the above method is heated to sinter the metal paste, thereby bonding the first and second members.

[0051] In the process of heating, the metal nanoparticles in the metal paste are trapped at the interface where the evaporation rate of the dispersion medium is fast (gas-liquid interface), i.e., they segregate at the interface between the second member and the metal paste, forming a concentrated layer of metal nanoparticles. In other words, the metal particles and metal nanoparticles are layer-separated and self-stacked. In addition, heating during evaporation causes the concentrated layer of metal nanoparticles to form a sintered layer containing many grain boundaries suitable for atomic diffusion. It is known that atomic diffusion makes a significant contribution to bonding properties at grain boundaries.

[0052] In addition, the sintered layer, which contains many grain boundaries suitable for atomic diffusion due to the dense layer of metal nanoparticles, promotes atomic diffusion between the sintered layer and the material to be bonded during the bonding process to form a dense bonding layer. As a result, a strong bond between the materials to be bonded is achieved by increasing the bonding area. In addition, the voids in the sintered layer of the metal paste alleviate thermal stress strain, which is one of the factors that cause cracks to develop, reducing the reliability of the connection, thus suppressing the peeling of the bonding part caused by the development of cracks and ensuring the reliability of the connection.

[0053] When copper particles are used as metal particles and nanostructures are formed on the surface of the copper particles, the nanoscale pure copper particles formed may cause a lowering of the melting point due to the quantum size effect. Therefore, although the melting point of copper is usually 1085°C, by using the bonding method of this embodiment, it is possible to fuse and form a metallic bond at a temperature lower than the melting point of copper (for example, about 300°C). In addition, since the nanoscale pure copper particles are fixed on the surface of the copper particles, the problems of agglomeration and uneven distribution seen in bonding when ordinary metal nanoparticles

are used are difficult to occur.

[0054] Furthermore, since the metal paste according to this embodiment contains metal nanoparticles, it is a metal paste that can be bonded at low temperatures of 600°C or lower, preferably 400°C or lower due to the melting point lowering effect brought about by the quantum size effect of the metal nanoparticles, while having micro-order metal particles as base particles.

[0055] The process of heating and sintering the metal paste can be carried out under an oxidizing atmosphere, an oxidation inhibiting atmosphere, or a reducing atmosphere, but from the viewpoint of removing the respective oxide films of the first member, the second member, and the metal in the metal paste, it is preferable to carry out the process under a reducing atmosphere. In this case, the reducing atmosphere includes the presence of a reducing gas such as hydrogen or formic acid. The reducing atmosphere gas can be a mixture of a reducing gas such as hydrogen or formic acid and an inert gas such as nitrogen or a rare gas. If the metal paste itself contains a reducing agent, heating may be performed under an oxidation suppressed atmosphere instead of using a reducing gas. In this case, the reductant is activated by the heating and becomes a reducing atmosphere. An oxidation suppressed atmosphere includes an inert gas atmosphere such as nitrogen or rare gases, or under vacuum, etc.

[0056] From the viewpoint of promoting volatilization of the remaining dispersion medium and fusion of the metal particles while suppressing thermal damage to the first and second members, the maximum temperature reached in heating during sintering is usually 600°C or lower preferably between 150 and 500°C, more preferably between 180 and 450°C, and even more preferably between 200 and 400°C.

[0057] The holding time of the above temperature is preferably 1 minute or more, and 5 minutes or more is more preferable from the viewpoint of sufficiently progressing the volatilization of the dispersion medium and the fusion of the metal particles. The upper limit of the holding time of heating is not limited, but from the viewpoint of yield and process efficiency, 60 minutes or less is preferable.

[0058] In addition, during sintering, heating may be performed while applying pressure as necessary. The applied pressure during heating is usually less than 80 MPa, preferably less than 70 MPa, and more preferably less than 60 MPa, from the viewpoint of promoting fusion of metal particles while suppressing pressure damage to the first and second members.

[0059] In addition, the voids in the cross-section of the bonding layer after sintering the metal paste have the function of alleviating the thermal stress strain that causes delamination at the bonding area due to crack extension. Since the metal paste in this embodiment contains a stress relieving agent, the crack arrestor effect of the stress relieving agent can also be combined to express a more pronounced peeling suppression effect at the bonding area. On the other hand, the presence of voids reduces the bonding area between particles, which can also be a factor in lowering the bonding strength. For this reason, the porosity in the cross-section of the bonding layer is preferably 25% or less, 20% or less is more preferable, and 15% or less is even more preferable.

[0060] In addition, a bonding method using metal paste according to this embodiment, is that, in addition to being able to keep the porosity low, the base particles are micron-sized metal particles, which results in small volume shrinkage during sintering, suppresses distortion within the bonding layer, and also results in a small percentage of grain boundaries within the bonding layer. These are also thought to contribute to the improvement of the bonding strength.

(Example)

[0061] The invention will be described in detail by referring to the examples below, but the invention is not limited to the following examples.

(Example 1)

(Preparation of metal particles)

[0062] Copper oxide particles with nanostructures formed on the surface were obtained by heating copper particles 1400YP (manufactured by Mitsui Mining and Smelting Co., Ltd., average particle size 6.3 μm, flake shape) with stirring under air at 100°C for 10 min, 150°C for 10 min, 200°C for 10 min, 250°C for 10 min, and 300°C for 60 min.

[0063] As metal nanoparticles, 0.76 mass parts (0.23 mass parts as gold nanoparticles) of toluene dispersion solution of gold nanoparticles Au1T/CD (manufactured by ULVAC, Inc., average particle size 7 nm) were prepared, toluene was removed under reduced pressure, and 21.23 mass parts of α-terpineol (manufactured by YASUHARA CHEMICAL CO., LTD., boiling point 213°C) as dispersion medium was mixed with.

[0064] The resulting mixture was planetary stirred for 2 minutes under reduced pressure using an agitator (Mazel Star KK-V300 manufactured by KURABO INDUSTRIES LTD.) at an orbital rotation speed of 1340 rpm and a rotation speed of 737 rpm. After that, 0.77 mass parts of tungsten powder W-2KD (manufactured by JAPAN NEW METALS CO., LTD., average particle diameter 1.49 μm) were added, and planetary stirring was performed in the same manner.

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[0065] To the mixture, 77.77 mass parts of the above copper particles were added, and the resulting mixture was planetary stirred to obtain the copper paste for bonding in Example 1.

(Comparative examples 1 to 3)

[0066] Copper pastes for bonding in comparative Examples 1 through 3 were obtained by the same method as in Example 1, except that the amounts of metal particles, metal nanoparticles, stress relieving material, and dispersion medium were changed to the amounts shown in Table 1.

[0067] The compounding conditions, etc. for the copper paste of example 1 and comparative examples 1 to 3 are shown in Table 1.

[Table 1]

		Example1	Comparative example 1	Comparative example 2	Comparative example 3
Metal particles	Copper oxide particles(mass part)	77.77	77.77	77.77	77.77
Metal nanoparticles	Gold nanoparticles : Au1T/CD (Toluene not included) (mass part)	0.23	0	0	0.23
Stress-relieving materials	Tungsten powder : W-2KD (mass part)	0.77	0	0.77	0
Dispersant	α -Terpineol (mass part)	21.23	22.23	21.46	22.00
Bonding strength (MPa)		0 cycle	40.0	40.0	40.0
		300 cycles	27.4	11.8	13.6

(Example 2)

[0068] Silver powder Ag-2-1C (manufactured by DOWA ELECTRONICS MATERIALS CO., LTD, average particle size 0.8 μm , spherical) was used as the metal particles.

[0069] As metal nanoparticles, 28.6 mass parts (10 mass parts as silver nanoparticles) of toluene dispersion solution of silver nanoparticles Ag1TH1 (manufactured by ULVAC, Inc., average particle size 8 nm) were prepared, toluene was removed under reduced pressure, and 9.12 mass parts of α -terpineol (manufactured by YASUHARA CHEMICAL CO., LTD., boiling point 213°C) as dispersion medium was mixed with.

[0070] The resulting mixture was planetary stirred for 2 minutes under reduced pressure using an agitator (Mazel Star KK-V300 manufactured by KURABO INDUSTRIES LTD.) at an orbital rotation speed of 1340 rpm and a rotation speed of 737 rpm. After that, 0.88 mass parts of tungsten powder W-2KD (manufactured by JAPAN NEW METALS CO., LTD., average particle diameter 1.49 μm) were added, and planetary stirring was performed in the same manner.

[0071] To the mixture, 80.0 mass parts of the above silver particles were added, and the resulting mixture was planetary stirred to obtain the silver paste for bonding in Example 2.

(Examples 3 to 9, comparative examples 4 to 8)

[0072] Silver pastes for bonding in examples 3 through 9 and comparative examples 4 through 8 were obtained by the same method as in Example 2, except that types and amounts of metal particles, metal nanoparticles, stress relieving material, and dispersion medium were changed to the amounts shown in Table 2.

(Example 10)

[0073] Copper powder 1400Y (manufactured by Mitsui Mining and Smelting Co., Ltd., average particle size 5.2 μm , spherical) was used as the metal particles.

[0074] As metal nanoparticles, 2.91 mass parts (0.88 mass parts as gold nanoparticles) of toluene dispersion solution of gold nanoparticles Au1T/CD (manufactured by ULVAC, Inc., average particle size 7 nm) were prepared, toluene was removed under reduced pressure, and 10.24 mass parts of α -terpineol (manufactured by YASUHARA CHEMICAL CO., LTD., boiling point 213°C) as dispersion medium was mixed with.

[0075] The resulting mixture was planetary stirred for 2 minutes under reduced pressure using an agitator (Mazel Star KK-V300 manufactured by KURABO INDUSTRIES LTD.) at an orbital rotation speed of 1340 rpm and a rotation speed of 737 rpm. After that, 0.88 mass parts of tungsten powder W-2KD (manufactured by JAPAN NEW METALS CO., LTD., average particle diameter 1.49 μm) were added, and planetary stirring was performed in the same manner.

[0076] 88.00 mass part of the above copper particles were added to the mixture, and the resulting mixture was planetary stirred to obtain the copper paste for bonding of Example 10.

(Examples 11 to 17, comparative examples 9 to 13)

[0077] Copper pastes for bonding in examples 11 through 17 and comparative examples 9 through 13 were obtained by the same method as in Example 10, except that types and amounts of metal particles, metal nanoparticles, stress relieving material, and dispersion medium were changed to the amounts shown in Table 3.

[0078] The compounding conditions, etc. for the copper paste of examples 2 through 17 and comparative examples 4 to 13 are shown in table 2 and table 3.

[Table 2]

		Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Composition (mass %)	Metal particles	80	80	80	80	80	80	80	80	50	80	88	88	88
	Metal nanoparticles	10	10	10	10	10	10	10	10		10			
	Tungsten powder	0.88	2.64									0.88		
	Aluminum nitride powder			0.88	2.64								0.88	
	Alumina powder					0.88	2.64							0.88
Evaluation Results	0 cycle	40	40	40	40	40	40	40	40	40	40	40	40	40
	150 cycles	40	38	40	36	30	38	38	34	22	30	27	25	23
	Strength remaining ratio (%)	100.0%	95.0%	100.0%	90.0%	75.0%	95.0%	95.0%	85.0%	55.0%	75.0%	67.5%	62.5%	57.5%
	300 cycles	38	33	36	32	35	32	33	30	18	24	20	21	19
	Strength remaining ratio (%)	95.0%	87.5%	90.0%	80.0%	87.5%	80.0%	80.0%	75.0%	45.0%	60.0%	50.0%	52.5%	47.5%

[Table 3]

		Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12	Comparative Example 13
Composition (mass %)	Metal particles	88	88	88	88	88	88	88	88	50	88	88	88	88
	Metal nanoparticles	0.88	0.88	0.88	0.88	0.88	0.88	0.88	0.88		0.88			
	Tungsten powder	0.88	2.64									0.88		
	Aluminum nitride powder			0.88	2.64								0.88	
	Alumina powder					0.88	2.64							0.88
Evaluation Results	0 cycle	40	40	40	40	40	40	40	40	40	40	40	40	40
	150 cycles	40	40	40	40	40	40	40	37	25	35	32	31	29
	Strength remaining ratio (%)	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	92.5%	62.5%	87.5%	80.0%	82.5%	72.5%
	300 cycles	37	34	36	32	37	32	32	28	15	26	21	20	18
	Strength remaining ratio (%)	92.5%	85.0%	90.0%	80.0%	92.5%	80.0%	80.0%	70.0%	37.5%	65.0%	52.5%	50.0%	45.0%

[0079] The following materials were used in Table 2 and Table 3.

[0080]

Silver powder: Ag-2-1C, manufactured by DOWA ELECTRONICS MATERIALS CO., LTD, average particle size 0.8 μ m, spherical,

Silver nanoparticles: Ag1TH1, manufactured by ULVAC, Inc., average particle size 8nm,

Pure copper powder: 1400Y, manufactured by Mitsui Mining and Smelting Co., Ltd., average particle size 5.2 μ m, spherical,

Gold nanoparticles: Au1T/CD (toluene dispersion of gold nanoparticles), manufactured by ULVAC, Inc., average particle size 7nm,

Tungsten powder: W-2KD, manufactured by JAPAN NEW METALS CO., LTD., average particle size 1.49 μ m,

Aluminum nitride powder: TFZ-N01P, manufactured by TOYO ALUMINIUM K.K., average particle size 1.4 μ m,

Alumina powder: TM-5D, manufactured by TAIMEI CHEMICALS CO., LTD., average particle size 0.27 μ m,

Glass powder: ASF-102X, manufactured by AGC Inc., components: SiO₂ and B₂O₃, average particle size 1.1 μ m,

Solvent: α -terpineol, manufactured by YASUHARA CHEMICAL CO., LTD., Boiling point 213°C, were used.

(Evaluation)

[0081] 0.009 g of copper paste for bonding of each of the examples and comparative examples in Table 1 was applied to the center on a 20 mm x 20 mm copper plate (thickness: 1 mm), and a silver-plated SiC chip with a thickness of 0.35 mm and a size of 5 x 5 mm was placed in contact with the paste. The SiC chip was then lightly pressed under a load of 10g to form the laminate.

[0082] The obtained laminate was placed in the furnace of a reduction bonding device (Ayumi Industry Co., Ltd.: RB-100), and the temperature was raised from room temperature to 100°C in 4 minutes under air, and then held at 100°C for 15 minutes for pre-drying. Then, formic acid vapor was introduced into the furnace and the temperature was raised from 100°C to 300°C in 10 minutes under a formic acid atmosphere. Then, it was heated at 300°C for 60 minutes under no pressure, and further heated at 300°C for 30 minutes under 60 MPa pressure. After that, the furnace was replaced with nitrogen gas and cooled down to 35°C or lower, and then the samples were removed.

[0083] The silver pastes for bonding of each example and each comparative example in Table 2 were applied to the center of a 20 mm x 20 mm copper plate (thickness: 1 mm) using a metal mask (5.5 mm x 5.5 mm, thickness: 110 μm). The resulting paste-coated film was placed in the furnace of a reduction bonding system (Ayumi Industry Co., Ltd.: RB-100), and the temperature was raised from room temperature to 100°C in 4 minutes under air, and then held at 100°C for 10 minutes for pre-drying. Then, a silver-plated SiC chip with a thickness of 0.35 mm and a size of 5 × 5 mm was brought into contact with the pre-dried film. Nitrogen was introduced into the furnace and the temperature was raised from 100 °C to 250 °C in 4 min under nitrogen atmosphere. Then, the furnace was heated at 250°C for 30 min under pressure of 10 MPa. After that, the furnace was cooled down to 35°C or lower, and then the samples were removed.

[0084] 0.009 g of copper paste for bonding of each of the examples and comparative examples in Table 3 was applied to the center on a 20 mm × 20 mm copper plate (thickness: 1 mm), and a silver-plated SiC chip with a thickness of 0.35 mm and a size of 5 × 5 mm was placed in contact with the paste. The SiC chip was then lightly pressed under a load of 10 g to form the laminate. The obtained laminates were placed in the furnace of a reduction bonding system (Ayumi Industries, Co., Ltd.: RB-100), and the temperature was raised from room temperature to 100 °C in 4 min under air, and then held at 100 °C for 15 min for pre-drying. Then, formic acid vapor was introduced into the furnace and the temperature was raised from 100°C to 300°C in 10 minutes under a formic acid atmosphere. Then, it was heated at 300°C for 30 minutes under no pressure, and further heated at 300°C for 30 minutes under 10 MPa of pressure. After that, the furnace was replaced with nitrogen gas and cooled down to 35°C or lower, and then the samples were removed.

(Cold and heat cycle test)

[0085] The obtained samples were put into a temperature cycle testing machine TS-100 (manufactured by Kusumoto Chemicals, Ltd.), and cold-heat cycles of 30 minutes at -40°C and 30 minutes at 125°C were repeated for 300 cycles.

(Measurement of die shear strength)

[0086] Using a universal bond tester (Nordson Advanced Technology 4000 series) equipped with a DS-100 load cell, the die shear strength of the above samples was measured under the conditions of a measurement speed of 1 mm/min and a measurement height of 100 μm in air.

[0087] The results of die shear strength are also shown in Tables 1 through 3. As can be seen from Tables 1 to 3, the metal paste of this embodiment contains metal particles, metal nanoparticles, stress relieving material, and dispersant, so it has high die shear strength after cold and heat cycling, high bonding strength, and high connection reliability under high temperature environment.

Claims

1. A metal paste for low temperature bonding at temperatures 600°C or lower, the metal paste comprising:

- a metal particle with an average particle size of 1 to 100 μm ;
- a metal nanoparticle with an average particle size of 1 to 500 nm;
- a stress relieving material; and
- a dispersion medium to disperse the metal particle, metal nanoparticle, and the stress relieving material.

2. The metal paste according to claim 1, wherein the metal particle and the metal nanoparticles have different metal species from each other.

3. The metal paste according to claim 1, wherein the metal particle is a copper particle.

4. The metal paste according to claim 3, wherein the copper particle have a nanostructure on the surface.

5. The metal paste according to claim 1, wherein the metal nanoparticle include one or more particles selected from the group of a gold nanoparticle, a silver nanoparticle, and a copper nanoparticle.

6. The metal paste according to claim 1, wherein the average particle size of the metal nanoparticle is between 1 and 100 nm.

7. The metal paste according to claim 1, wherein the metal nanoparticles are contained in 0.01 to 60 parts by mass in 100 parts by mass of the metal paste.

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8. The metal paste according to claim 1, wherein the average particle size of the stress relieving material is between 0.01 to 100 μm .

5 9. The metal paste according to claim 1, wherein the stress relieving material is one or more inorganic materials selected from the group of tungsten, alumina, aluminum nitride, and glass.

10. A bonding method comprising:

10 preparing a laminate in which the metal paste according to claim 1 is disposed between a first member and a second member; and heating the laminate to sinter the metal paste, wherein the temperature at which the metal paste is sintered is 600°C or lower.

11. A method for producing a bonded body comprising:

15 preparing a laminate in which the metal paste according to claim 1 is disposed between a first member and a second member; and heating the laminate to sinter the metal paste, whereby the first member and the second member are bonded, wherein the temperature at which the metal paste is sintered is 600°C or lower.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/012389

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. B22F1/00(2006.01) i, B22F1/02(2006.01) i, B22F7/08(2006.01) i
 FI: B22F1/00L, B22F1/00K, B22F1/00P, B22F1/02D, B22F7/08C

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 Int.Cl. B22F1/00, B22F1/02, B22F7/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2006-196245 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.)	1, 3, 5-9
Y	27.07.2006 (2006-07-27), paragraphs [0012]-[0045]	2, 4, 10, 11
Y	WO 2019/054225 A1 (LINTEC CORPORATION) 21.03.2019 (2019-03-21), paragraphs [0024], [0098]	2
Y	JP 2017-074598 A (OSAKA UNIVERSITY) 20.04.2017 (2017-04-20), paragraphs [0002], [0011]-[0013]	4, 10, 11

Further documents are listed in the continuation of Box C. See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
28.05.2020

Date of mailing of the international search report
09.06.2020

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Tokyo 100-8915, Japan

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2020/012389

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JP 2006-196245 A	27.07.2006	(Family: none)
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REFERENCES CITED IN THE DESCRIPTION

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- JP 2014167145 A [0004]
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