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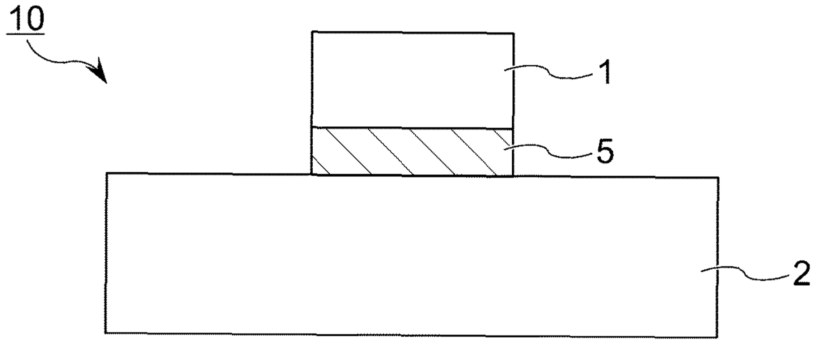
(54) COPPER PASTE, BONDING METHOD, AND METHOD FOR PRODUCING BONDED BODY

(57) This copper paste includes metal particles and a dispersion medium. The metal particles includes first-type particles and second-type particles. The first-type particles are copper particles having nanostructures on the surfaces thereof, and having an average particle diameter of 1 to 100 μm. The second-type particles are copper particles having an average particle diameter of 0.05 to 5 μm. The average particle diameter of the first-type particles is 2 to 550 times the average particle diameter of the second-type particles. For example, a laminate, in which a copper paste (5) is disposed between a first member (1) and a second member (2), is heated in a reducing atmosphere to sinter the copper paste, whereby the first member and the second member can be bonded without pressurizing.

FIG. 2



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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper paste, a bonding method using the copper paste, and a method for producing a bonded body using the copper paste.

BACKGROUND ART

[0002] High-melting-point lead solder has been heretofore widely used for bonding metals and semiconductors, but from the viewpoint of environmental regulations and the like, lead-free bonding materials have been desired. Methods are known in which nanoparticles of metal such as silver are used as a material which enables low-temperature bonding. Nanoparticles are welded at a temperature lower than the melting point thereof due to the nanosize effect, and therefore enable low-temperature pressureless bonding. However, silver nanoparticles are expensive in terms of material cost, and do not provide sufficient bonding strength at present.

[0003] Some studies have been reported in which copper particles are used as a less expensive bonding material. Patent Document 1 discloses a bonding method in which copper particles having a particle diameter of micrometer order are prepared as a bonding material, the surfaces of the copper particles are oxidized through in situ synthesis to form nanoparticles, and heating is then performed in a reducing atmosphere. Patent Document 2 suggests a method in which a copper paste containing covered nanoparticles and microparticles having surfaces covered with organic molecules is used in pressureless bonding to enhance dispersibility.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0004]

Patent Document 1: Japanese Patent Laid-open Publication No. 2017-074598
Patent Document 2: Japanese Patent Laid-open Publication No. 2014-167145

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] The methods of Patent Documents 1 and 2 cannot be said to ensure sufficient bonding strength. In view of the above-mentioned problem, an object of the present invention is to provide a copper paste capable of achieving high bonding strength even in low-temperature bonding.

MEANS FOR SOLVING THE PROBLEMS

[0006] The copper paste of the present invention contains metal particles and a dispersion medium. The metal particles include first-type particles and second-type particles. The first-type particles are copper particles having an average particle diameter of 1 to 100 μm and having nanostructures on the surface. The second-type particles are copper particles having an average particle diameter of 0.05 to 5 μm. The average particle diameter D1 of the first-type particles is preferably 2 to 550 times the average particle diameter D2 of the second-type particles.

[0007] The nanostructures of the first-type particles is formed of, for example, thermally oxidized copper. Examples of the nanostructures include irregular shapes, particulate shapes and fiber shapes.

[0008] By preparing a laminate with the copper paste disposed between members to be bonded, and heating the laminate in a reducing atmosphere, the copper paste can be sintered to bond the members to each other.

EFFECTS OF THE INVENTION

[0009] The copper paste of the present invention can be applied to low-temperature pressureless bonding. By using the copper paste of the present invention, high-strength bonding can be performed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1 shows scanning microscope photographs of copper particles.
FIG. 2 is a sectional view showing an example of a configuration of a laminate used for pressureless bonding.
FIG. 3 shows scanning microscopes of cross-sections of bonding layers in Example 1 and Comparative Example 3.

MODE FOR CARRYING OUT THE INVENTION

[Copper paste]

[0011] The copper paste of the present invention contains metal particles and a dispersion medium. The metal particles include first-type particles and second-type particles. The average particle diameter D1 of the first-type particles is 1 to 100 μm, and the average particle diameter D2 of the second-type particles is 0.05 to 5 μm. The average particle diameter D1 of the first-type particles is larger than the average particle diameter D2 of the second-type particles. The average particle diameter D1 is preferably 2 to 550 times the average particle diameter D2. In the specification of the present application, the average particle diameter is a volume cumulative median diameter (D_{50}) determined from a particle diameter distribution measured by a laser diffraction scattering method.

[0012] The first-type particles have nanostructures on the surfaces thereof. At the time of bonding by heating, the first-type particles having nanostructures on the surfaces thereof are welded together, and gaps between the first-type particles are filled with the second-type particles having a small particle diameter, so that the bonding material has few air gaps, and thus high bonding strength can be achieved.

<Metal particles>

(First-type particles)

[0013] The first-type particles are copper particles having nanostructures on the surfaces thereof and having an average particle diameter of 1 to 100 μm. Examples of the nanostructures on the surfaces of copper particles include nanosized irregularities, nanoparticles and nanofibers. For example, copper particles having a particle diameter of 1 to 100 μm are thermally oxidized to obtain copper particles having a copper oxide (cuprous oxide) nanostructures on the surfaces thereof.

[0014] FIG. 1(A) is a scanning microscope (SEM) photograph of wet copper powder ("1400YM" manufactured by Mitsui Mining and Smelting Co., Ltd., average particle diameter: 4.2 μm) which has not been heat-treated. The surface of the copper powder before heat treatment is smooth, and is not provided with nanostructures.

[0015] FIG. 1(B1) shows a SEM photograph of wet copper powder heated in air at 100°C for 10 minutes, at 150°C for 10 minutes, at 200°C for 10 minutes, at 250°C for 10 minutes and at 300°C for 10 minutes in sequence. FIGS. 1(B2) and 1(B3) show SEM photographs of wet copper powder heat-treated in the same manner as in FIG. 1(B1) except that the heating time at 300°C is changed to 30 minutes and 120 minutes, respectively. FIG. 1(C1) shows a SEM photograph of wet copper powder heated in air at 100°C for 10 minutes, at 150°C for 10 minutes, at 200°C for 10 minutes, at 250°C for 10 minutes, at 300°C for 10 minutes, at 350°C for 10 minutes and at 400°C for 10 minutes in sequence. FIGS. 1(C2) and 1(C3) show SEM photographs of wet copper powder heat-treated in the same manner as in FIG. 1(C1) except that the heating time at 400°C is changed to 30 minutes and 120 minutes, respectively.

[0016] It can be seen that the powder of (B1) has fine irregularities formed on the surfaces of particles, and for the powder of (B2) and (B3), the irregularities on the surfaces grow in a particulate shape as the heating time at 300°C increases. For the powder of (C1) heated at 400°C, finer irregularities are formed as compared to the powder of (B1), and fine fiber-shaped nanostructures are formed. It can be seen that for the powder of (C2) and (C3), the nanofibers grow as the heating time at 400°C increases.

[0017] The melting point of copper is 1085°C, and like nanoparticles, nanostructures such as nanoscale irregularities, particles and fibers which are formed on the surfaces of copper particles undergo lowering of the melting point due to the size effect. Thus, the first-type particles having nanostructures on the surface can be welded at a temperature lower than the melting point of copper (for example, about 300°C) to form a metal bond. That is, the first-type particles can be bonded at a low temperature while having a particle diameter of micrometer order. In addition, since the nanostructures are fixed on the surfaces of the first-type particles, the problems of aggregation and uneven distribution, which are found in metal nanoparticles, are unlikely to occur.

[0018] As described above, by heating copper particles having a particle diameter of micrometer order (hereinafter, sometimes referred to as "copper microparticles"), nanostructures can be formed on the surfaces of the copper particles.

[0019] The shape of the copper microparticles to be used as a raw material for the first-type particles is not particularly limited, and examples thereof include spherical shapes, lump shapes, needle shapes and flake shapes. In particular, the shape of the copper microparticles is preferably a spherical shape or a flake shape because nanostructures are easily formed on the surfaces, and the volume of air gaps between particles (voids) in welding of the particles can be reduced. The "spherical shape" is not limited to perfect spheres, and includes substantially spherical shapes having an aspect ratio of 3 or less. The "flake shape" includes tabular shapes such as plate shapes and scale shapes.

[0020] The particle diameter of the copper microparticle is preferably 1 to 100 μm. Since the particle diameter of the copper particle hardly changes before and after formation of the nanostructures by heating, the particle diameter of the copper microparticle is substantially equal to the particle diameter of the first-type particle. From the viewpoint of enhancing dispersibility and facilitating formation of nanostructures, the particle diameter of the copper microparticle is preferably 2 μm or more, more preferably 3 μm or more, still more preferably 3.5 μm or more, especially preferably 4 μm or more. From the viewpoint of enhancing weldability between particles in bonding, and reducing the amount of voids, the particle diameter of the copper microparticle is preferably 60 μm or less, more preferably 50 μm or less, still more preferably 40 μm or less, especially preferably 30 μm or less. Commercially available copper powder may be directly used as copper microparticles.

[0021] When the particle diameter of the copper microparticle is within the above-described range, the particle diameter of the first-type particle can fall within the range of 1 to 100 μm. The particle diameter of the first-type particles is preferably 2 to 60 μm, more preferably 3 to 50 μm, still more preferably 3.5 to 40 μm, especially preferably 4 to 30 μm.

[0022] By heating the copper microparticles in an oxidizing atmosphere, nanostructures are formed on the surfaces of the particles. The oxidizing atmosphere is an atmosphere having an oxygen concentration enabling oxidation of copper, and may be an air atmosphere (having an oxygen concentration of about 21%). The heating temperature is preferably 200 to 500°C. The heating time may be appropriately determined depending on the heating temperature or the like such that nanostructures are formed on the surfaces of copper microparticles, and the heating time is, for example, about 5 to 300 minutes.

[0023] Although the reason why nanostructures are formed on the surface of copper microparticles by heating is uncertain, this may be relevant to a difference in coefficient of thermal expansion between copper and copper oxide (or cuprous oxide). When copper microparticles are heated in an oxidizing atmosphere, the surfaces of the copper particles are oxidized to form an oxide film. When heating is further performed in this state, oxidation proceeds from the surfaces to the inside of particles, and as the temperature increases, both the copper oxide (cuprous oxide) on the surfaces of the particles and the copper in the core portion of the particles thermally expand. It is considered that since copper has a larger coefficient of thermal expansion than copper oxide, inside copper expands the crystal grain boundaries of the oxide film on the surface as the temperature increases, and copper is deposited on the surface layer along the expanded grain boundaries, and upon the deposition, the copper is exposed to an oxidizing atmosphere to oxidize the copper, so that nanostructures such as nanoparticles or nanofibers are formed.

[0024] As shown in FIG. 1, nanostructures on the surfaces of copper microparticle tend to grow as the heating temperature becomes higher and the heating time becomes longer. In addition, fiber-shaped nanostructures (nanofibers) tend to be formed as the heating temperature increases. When nanofibers are formed on the surfaces of the first-type particles, the weldability of the copper particles tends to be improved. For forming fiber-shaped nanostructures, it is referable that the temperature increase rate is reduced (to, for example, 5°C/min or less), or the temperature is increased stepwise to 350°C or higher, and heating is performed at a temperature of 350°C or higher for 10 minutes or more. It is considered that by gradually increasing the temperature, the deposition rate of the metal from the inside to the surface layers of the particles is reduced, so that deposits easily grow in a fiber shape.

[0025] When irregular or particulate nanostructures are formed on the surfaces of the copper microparticles, the particle diameter of the nanostructure is preferably 500 nm or less, more preferably 200 nm or less. When nanofibers are formed on the surfaces of copper microparticles, the diameter of the fiber is preferably 100 nm or less, more preferably 50 nm or less. The length of the fiber is not particularly limited, and is, for example, 10 μm or less, preferably 5 μm or less. As long as the size of the nanostructure is in the above-described range, good bondability can be secured at a low temperature (for example, about 200 to 500°C). The size of the nanostructure is measured on the basis of a SEM image of particles.

(Second-type particles)

[0026] The second-type particles are copper particles having an average particle diameter of 0.05 to 5 μm. The second-type particles may have nanostructures on the surfaces thereof, or no may have no nanostructures on the surface thereof. The second-type particles have a function of reducing the volume of air gaps by filling gaps between particles at the time when the first-type particles are welded. Thus, particles having an average particle diameter smaller than that of the first-type particles are used as the second-type particles.

[0027] For effectively filling gaps between the welded first-type particles, the ratio (D1/D2) of the average particle diameter D1 of the first-type particles to the average particle diameter D2 of the second-type particles is preferably 2 or more, more preferably 2.5 or more, still more preferably 3 or more. On the other hand, from the viewpoint of reducing the ratio of grain boundaries during bonding to secure bonding strength, the ratio D1/D2 is preferably 550 or less, more preferably 300 or less, still more preferably 100 or less, especially preferably 50 or less.

[0028] From the viewpoint of securing dispersibility to suppress aggregation and reducing the number of grain boundaries during bonding, the average particle diameter of the second-type particles is preferably 0.07 μm or more, more preferably 0.1 μm or more, still more preferably 0.2 μm or more.

[0029] It is preferable that the second-type particles have weldability in the temperature range of 400°C or lower. When the second-type particles do not have nanostructures on the surfaces thereof, the average particle diameter D2 is preferably 4 μm or less, more preferably 3 μm or less, still more preferably 2 μm or less, for lowering the melting point with the aid of the size effect. When the second-type particles have nanostructures on the surfaces thereof like the first-type particles, welding can be performed at a low temperature owing to the nanostructures, so that the average particle diameter D2 of the second-type particles may be 5 μm or less, and the ratio D1/D2 may be within the above-described range.

[0030] The shape of the second-type particles is not particularly limited, and examples thereof include spherical shapes, lump shapes, needle shapes and flake shapes. In particular, the shape of the second-type particles is preferably a spherical shape or a flake shape because the volume of air gaps between particles in welding of the particles can be reduced. As described above, the second-type particles may have nanostructures formed on the surfaces thereof.

[0031] The shape of the second-type particle may be identical to or different from the shape of the first-type particle. For example, both the first-type particle and the second-type particle may have a spherical shape, both the second-type particle and the second-type particle may have a flake shape, the first-type particle may have a flake shape while the second-type particle has a spherical shape, or the first-type particle may have a spherical shape while the second-type particle has a flake shape.

[0032] As the second-type particles, commercially available copper powder having an average particle diameter of 0.05 to 5 μm may be used as it is. In addition, it is also possible to use particles in which nanostructures are formed on the surfaces by thermally oxidizing commercially available copper powder.

(Other metal particles)

[0033] The copper paste may contain metal particles other than the first-type particles and the second-type particles. Examples of the metal particles other than copper particles include copper nanoparticles, and particles of nickel, silver, gold, palladium, platinum and the like. The average particle diameter of the metal particles other than copper particles is preferably about 0.01 to 50 μm. The amount of the metal particles other than copper particles is preferably 20 parts by mass or less, more preferably 10 parts by mass or less, still more preferably 5 parts by mass or less, based on 100 parts by mass of all metal particles. In other words, the content of copper particles (including copper particles having nanostructures of an oxide on the surfaces thereof) based on 100 parts by mass of all metal particles is preferably 80 parts by mass or more, more preferably 90 parts by mass or more, still more preferably 95 parts by mass or more. When the amount of copper particles is within the above-described range, it becomes easy to secure bonding strength.

(Contents of first-type particles and second-type particles)

[0034] As described above, the second-type particles have a function of filling gaps between welded first-type particles. The contents of the first-type particles and the second-type particles in the metal particles may be set depending on the ratio (D1/D2) of the particle diameters of the first-type particles to the second-type particles or the like so that the second-type particles have the above-described function.

[0035] The content of the first-type particles is preferably 20 to 95 parts by mass, more preferably 30 to 90 parts by mass, still more preferably 35 to 85 parts by mass, especially preferably 40 to 80 parts by mass, based on 100 parts by mass of all metal particles. When the content of the first-type particles is within the above-described range, high bonding strength and connection reliability can be achieved by welding of the first-type particles at the time of sintering a copper paste for pressureless bonding.

[0036] The content of the second-type particles is preferably 5 to 80 parts by mass, more preferably 10 to 70 parts by mass, still more preferably 15 to 65 parts by mass, especially preferably 20 to 60 parts by mass, based on 100 parts by mass of all metal particles. When the content of the second-type particles is within the above-described range, air gaps between the welded first-type particles is easily filled with the second-type particles efficiently at the time of sintering a copper paste for pressureless bonding. Thus, the porosity decreases, so that bonding strength can be improved. In addition, nanostructures on the surfaces of the first-type particles are also welded to the second-type particles, leading to an increase in bonding area. Thus, bonding strength tends to increase as compared to a case where only the first-type particles are present.

[0037] For promoting welding of the first-type particles, and efficiently filling gaps between the first-type particles with the second-type particles, the amount of the second-type particles is preferably 0.05 to 5 times, more preferably 0.1 to 2 times, still more preferably 0.2 to 1.5 times, especially preferably 0.25 to 1.3 times the amount of the first-type particles.

<Dispersion medium>

[0038] The copper paste contains a dispersion medium (solvent) for dispersing the metal particles. The dispersion medium is not particularly limited as long as it enables metal particles to be dispersed therein, and can be volatilized during sintering of the paste, and various aqueous solvents and organic solvents can be used. The boiling point of the dispersion medium is preferably about 150 to 400°C. A plurality of solvents having different boiling points may be mixed, and used as a dispersion medium.

[0039] Specific examples of the dispersion medium include chain hydrocarbons, aromatic hydrocarbons, cycloaliphatic hydrocarbons, chain alcohols, aromatic alcohols, cycloaliphatic alcohols, polyhydric alcohols such as glycols and triols, ethers, glycol ethers, amines, amides, aldehydes and ketones.

[0040] Of these, glycols or glycol ethers are preferably used as the dispersion medium because of they are excellent in dispersibility of copper particles. Examples of the glycols include alkylene glycols such as ethylene glycol and propylene glycol, and polyalkylene glycols such as polyethylene glycol and polypropylene glycol (mainly those having a molecular weight of 1000 or less). Examples of the 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 monobutyl ether, and ester derivatives thereof (for example, diethylene glycol monobutyl ether acetate).

[0041] The amount of the dispersion medium is about 5 to 100 parts by mass, preferably about 7 to 70 parts by mass, based on 100 parts by mass of metal particles. When the content of the dispersion medium is within the above-described range, metal particles can be appropriately dispersed, and the viscosity of the copper paste can be adjusted within an appropriate range.

<Additives>

[0042] The copper paste may contain various additives as necessary. Examples of the additives include antioxidants, surfactants, antifoaming agents and ion trap agents.

[0043] As described below, the copper paste of the present invention promotes welding of copper particles when heated in a reducing atmosphere. The copper paste may contain a reducing agent for the purpose of, for example, promoting welding of copper. Examples of the reducing agent include sulfide, thiosulfate, oxalic acid, formic acid, ascorbic acid, aldehyde, hydrazine and derivatives thereof, hydroxylamine and derivatives thereof, dithiothreitol, phosphite, hydrophosphite, phosphorus acid and derivatives thereof, lithium aluminum hydride, diisobutylaluminum hydride and sodium borohydride.

[0044] The copper paste contains a resin component such as a polyester-based resin, a polyurethane-based resin such as blocked isocyanate, an epoxy-based resin, an acryl-based resin, a polyacrylamide-based resin, a polyether-based resin, a melamine-based resin or a terpene-based resin. Such a resin component can act as a binder for metal particles. The copper paste of the present invention is capable of achieving high bondability even when the copper paste is free of a resin component because gaps between the first-type particles can be filled with the second-type particles having a particle diameter smaller than that of the first-type particles. In particular, when high electrical conductivity is required for the bonded part, it is preferable that the copper paste is substantially free of a resin component. The content of the resin in the copper paste is preferably 10 parts by mass or less, more preferably 5 parts by mass or less, still more preferably 3 parts by mass or less, especially preferably 1 part by mass or less, based on 100 parts by mass of metal particles.

<Preparation of copper paste>

[0045] A copper paste can be prepared by mixing the metal particles and optional additives with a dispersion medium. All metal particles may be dispersed in the dispersion medium at a time, or some of the metal particles may be dispersed, followed by adding the other metal particles. In addition, the first-type particles may be added after the second-type particles are dispersed, or a dispersion liquid of the first-type particles may be mixed with a dispersion liquid of the second-type particles.

[0046] Stirring treatment may be performed after the components are mixed. In addition, aggregates may be removed by a classification operation before and after the components are mixed.

[0047] For stirring treatment, a stirring/kneading apparatus such as an Ishikawa stirrer, a Silverson stirrer, a cavitation stirrer, a rotation/revolution type (planetary) stirrer, an ultrathin film high-speed rotary disperser, an ultrasonic disperser, a Raikai machine, a twin-screw kneader, a bead mill, a ball mill, a three-roll mill, a homogenizer, a planetary mixer, an ultra-high pressure disperser, a thin-layer shear disperser, a wet ultrafine atomizer or an ultrasonic jet mill may be used.

[0048] The classification operation can be carried out by filtration, spontaneous sedimentation or centrifugation. Examples of the filter for filtration include water combs, metal meshes, metal filters, and nylon meshes.

[Bonding with copper paste]

[0049] The copper paste can be used as an electrically conductive paste for forming various wirings and electrically conductive films, a bonding material for bonding a plurality of members, or the like. In particular, the copper paste is capable of achieving high bondability when sintered in a reducing atmosphere, and is suitably used as a paste for pressureless bonding.

[0050] In pressureless bonding, a laminate is prepared in which a copper paste is disposed between a first member and a second member, and the laminate is heated in a reducing atmosphere while the copper paste and the second member are disposed in a direction along which the self-weight of the first member acts, or a pressure of 0.01 MPa or less is applied. When the copper paste is sintered by heating in a reducing atmosphere, welding of metal particles proceeds, so that the first member and the second member are bonded to each other.

(Preparation of laminate)

[0051] FIG. 2 is a sectional view showing an example of a configuration of a laminate 10 with a copper paste 5 disposed between a first member 1 and a second member 2. Such a laminate can be prepared by, for example, providing the copper paste 5 in a predetermined region of the second member 2, and disposing the first member 1 thereon.

[0052] The first member 1 and the second member 2 are not particularly limited, and various metal materials, semiconductor materials, ceramic materials or resin materials can be used. Specific examples of the second member include semiconductor substrate such as silicon substrates, metal substrates such as copper substrates, lead frames, metal plate-attached ceramic substrates (e.g. DBCs), a semiconductor element mounting substrates such as LED packages, copper ribbons, power feeding members such as copper ribbons, metal blocks and terminals, heatsinks, and water cooling plates. Specific examples of the first member include power modules including diodes, rectifiers, thyristors, MOS gate drivers, power switches, power MOSFETs, IGBTs, Schottky diodes and fast recovery diodes, transmitters, amplifiers, sensors, analog integrated circuits, semiconductor lasers and LED modules. The first member and the second member are not limited to those described above. Moreover, a material described above as an example of the first member may be used as the second member, or a material described above as an example of the second member may be used as the first member.

[0053] The first member 1 and the second member 2 may include a metal on a surface that contacts the copper paste 5 (bonding material). Examples of the metal include copper, nickel, silver, gold, palladium, platinum, lead, tin, cobalt, manganese, aluminum, beryllium, titanium, chromium, iron, molybdenum and alloys thereof.

[0054] As a method for providing the copper paste 5 as a bonding material on the second member 2, any of various coating methods may be employed such as screen printing, transfer printing, offset printing, letterpress printing, intaglio printing, gravure printing, stencil printing, soft lithography, jet printing, a method using a dispenser, comma coating, slit coating, die coating, gravure coating, bar coating, play coating, spin coating and electrodeposition coating.

[0055] The thickness of the copper paste 5 (thickness after drying the dispersion medium, i.e. thickness of the bonding layer) is, for example, about 1 to 1000 μm. The thickness of the bonding layer can be 10 μm or more, 30 μm or more, 50 μm or more, 70 μm or more, or 100 μm or more. The coating thickness can be 700 μm or less, 500 μm or less, 400 μm or less, 300 μm or less, or 200 μm or less.

[0056] The copper paste for pressureless bonding, which is disposed on the second member, may be appropriately dried for the purpose of, for example, suppressing flow and generation of voids during sintering. The gas atmosphere during drying may be an air atmosphere, an oxygen-free atmosphere or a reducing atmosphere. The drying may be performed at normal temperature and normal pressure, or may be accelerated by heating or decompression.

[0057] The disposition of the first member 1 on the paste 5 provided on the second member 2 may be performed using a chip mounter, a flip chip bonder, etc., or performed manually using various jigs.

(Sintering)

[0058] The copper paste is sintered by heating the laminate. By heating in a reducing atmosphere, the nanostructures of copper oxide (cuprous oxide) formed on the surface of the first-type particles is reduced to generate copper nanostructures, and the size effect of nanostructures causes welding to proceed at a low temperature. When the second-type particles have an oxide film or nanostructures of copper oxide (cuprous oxide) on the surfaces thereof, the surfaces of the second-type particles are reduced in a reducing atmosphere, so that welding is promoted.

[0059] Examples of the reducing atmosphere include atmospheres in which a reducing gas such as hydrogen or formic acid is present. The reducing atmosphere gas may be a mixed gas of a reducing gas such as hydrogen or formic acid and an inert gas such as nitrogen or a rare gas. When the paste contains a reducing agent, heating may be performed in an oxidation suppressing atmosphere instead of using a reducing gas. In this case, the reducing agent is volatilized by heating to produce a reducing atmosphere. Examples of the oxidation suppressing atmosphere include atmospheres of an inert gas such as nitrogen or a rare gas, and atmospheres under vacuum.

[0060] The maximum temperature during heating is preferably 200 to 500°C, more preferably 230 to 450°C, still more preferably 250 to 400°C from the viewpoint of promoting volatilization of the dispersion medium and welding of metal particles while suppressing thermal damage to the first member and the second member.

[0061] The holding time at a temperature in the above-described range is preferably 1 minute or more, more preferably 5 minutes or more, from the viewpoint of ensuring that volatilization of the dispersion medium and welding of metal particles sufficiently proceed. The upper limit of the holding time for heating is not particularly limited, and is preferably 60 minutes or less from the viewpoint of a yield, process efficiency and the like.

[0062] The die shear strength of a bonded body obtained by bonding the first member and the second member with copper paste sintered body (bonding material) interposed therebetween is preferably 20 MPa or more, more preferably 23 MPa or more, still more preferably 25 MPa or more. Use of the copper paste enables high shear strength to be achieved by pressureless bonding at a low temperature which is equal to or lower than the melting point of copper.

[0063] The reason why such high bonding strength can be achieved is supposed to be that welding can be performed at a low temperature because the first-type particles having a relatively large particle diameter have nanostructures on the surfaces thereof, and a densified bonding layer with few air gaps is formed because the second-type particles having a relatively small particle diameter enter air gaps between the first-type particles to form fine structures, and sintering between the particles proceeds. The porosity on the cross-section of the bonding layer after sintering of the copper paste is preferably 25% or less, more preferably 20% or less, still more preferably 15% or less. The porosity can be calculated from the SEM observation image of the bonded cross-section (see FIG. 3).

[0064] There are few air gaps, and due to use of microparticles, volume shrinkage during sintering is small, so that strain in the bonding layer is suppressed. This may also contribute to improvement of bonding strength. In addition, it is considered that since the second-type particles can be welded at a low temperature, and have such a particle diameter that aggregation hardly occurs, welding of the second-type particles to the nanostructures on the surfaces of the first-type particles and welding of the second-type particles proceed, leading to further enhancement of bonding strength. Further, since the ratio (D1/D2) of the average particle diameter D1 of the first-type particles to the average particle diameter D2 of the second-type particles is within a specific range, the ratio of grain boundaries in the bonding layer is small. This may also contribute to enhancement of bonding strength.

[0065] The bonding method of the present invention can be applied to production of various electronic components and semiconductor devices. In other words, the bonded body obtained by bonding a plurality of components by sintering the copper paste of the present invention can be an electronic component, a semiconductor device, or the like. The bonded body of the present invention has high die shear strength at the bonded part, and is excellent in connection reliability. In addition, the bonding material is mainly composed of copper, and the porosity is low because air gaps between the first-type particles are filled with the second-type particles. Therefore, it is also possible to achieve a high thermal conductivity and electrical conductivity.

EXAMPLES

[0066] Hereinafter, the present invention will be described in detail by ways of examples, which should not be construed as limiting the present invention.

[Preparation of copper particles]

[0067] The following commercially available copper powders A to I were prepared.

A: "Tn-Cu100" (spherical-shaped copper powder with an average particle diameter of 0.1 μm) manufactured by TAIYO NIPPON SANSO CORPORATION
B: "1050YP" (flake-shaped copper powder with an average particle diameter of 0.9 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.
C: "MAC03K" (spherical-shaped copper powder with an average particle diameter of 3.0 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.
D: "MAC03KP" (flake-shaped copper powder with an average particle diameter of 4.0 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.
E: "1400YM' (spherical-shaped copper powder with an average particle diameter of 4.2 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.

F: "1400YP" (flake-shaped copper powder with an average particle diameter of 5.2 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.
G: "MA-CF" (flake-shaped copper powder with an average particle diameter of 21.1 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.
H: "Cu6500" (spherical-shaped copper powder with an average particle diameter of 50 μm) manufactured by Culox Technologies, Inc
I: "MACNS" (spherical-shaped copper powder with an average particle diameter of 64 μm) manufactured by Mitsui Mining and Smelting Co., Ltd.

[Preparation of copper particles having nanofiber structures on surfaces]

[0068] The particles E were heated at 100°C for 10 minutes, at 150°C for 10 minutes, at 200°C for 10 minutes, at 250°C for 10 minutes, at 300°C for 10 minutes, at 350°C for 10 minutes and at 400°C for 30 minutes while being stirred in air. Observation of the particles R by SEM after heating showed that there was almost no aggregate, and fiber-shaped nanostructures were formed on the surfaces of the particles as shown in FIG. 1(C2).

[0069] The particles C, D, F, G, H and I were heated under the same conditions as in the preparation of the particles R to prepare particles P, Q, S, T, U and V having fiber-shaped nanostructures on the surfaces thereof.

[Example 1]

[0070] 50 parts by mass of the particles R as the first-type particles, 50 parts by mass of the particles B as the second-type particles, and 30 parts by mass of tripropylene glycol monomethyl ether (MFTG; boiling point: 242.4°C.) as a dispersion medium were mixed. Under reduced pressure, the mixture was subjected to planetary stirring at a revolution speed of 1340 rpm and a rotation speed of 737 rpm for 2 minutes with a stirrer ("Mazerustar KK-V300" manufactured by KURABO INDUSTRIES LTD.) to obtain a copper paste for pressureless bonding.

[Examples 2 and 9 and Comparative Examples 1 to 6]

[0071] The blending amounts of the metal particles and the solvent were changed as shown in Table 1 (the values of the blending amounts in Table 1 each represent the number of parts by mass). Except for the above, the same procedure as in Example 1 was carried out to obtain copper pastes.

[Evaluation]

(Preparation of sample for die shear strength test)

[0072] 0.009 g of the copper paste was applied to the center of a 20 mm × 20 mm copper plate (thickness: 1 mm), a Cu chip with a thickness of 1 mm and a size of 5 × 5 mm was brought into contact with the copper paste, and the Cu chip was lightly pressed under a load of 10 g to form a laminate.

[0073] This laminate was placed in a furnace of a reduction bonding apparatus ("RB-100" manufactured by Ayumi Industry Co., Ltd.), the temperature was raised from room temperature to 130°C in 4 minutes, and the laminate was then held at 130°C for 5 minutes to perform preliminary drying. Thereafter, the temperature was raised from 130°C to 300°C in 10 minutes. For the samples of Examples 1 to 9, Comparative Examples 1 to 3 and Comparative Example 6, the temperature was raised from room temperature to 300°C in an air atmosphere. For the samples of Comparative Examples 4 and 5, the temperature was raised from room temperature to 300°C in a nitrogen atmosphere. After the temperature was raised to 300°C, formic acid vapor was introduced into the furnace to produce a formic acid atmosphere, and the laminate was heated at 300°C for 30 minutes. The inside of the furnace was washed with nitrogen gas and cooled to 35°C or lower, and the sample was then taken out.

(Measurement of die shear strength)

[0074] Using a universal bond tester equipped with a DS-100 load cell (4000 Series manufactured by Nordson Advanced Technology LLC), the die shear strength of the sample was measured under the conditions of a measurement speed of 1 mm/min and a measurement height of 200 μm in air.

[0075] Table 1 shows the compositions of the copper pastes of Examples and Comparative Examples, the ratio of the average particle diameters (D1/D2) of the metal particles in the copper paste, and the die shear strength of the bonded sample. In Table 1, the content of the first-type particles having a relatively large particle diameter is underlined. For the samples of Example 1 and Comparative Example 3, cross-section was observed by SEM, and the porosity was calculated from the SEM photographs of FIGS. 3(A) and 3(B).

Table 1

			Average particle diameter (µm)	Shape	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Copper particles	Non-oxidized	A	0.1	spherical						60	10								60
		B	0.9	flake	50	50	50										50	50	
		C	3.0	spherical											100				
		D	4.0	flake				50	50										
		E	4.2	spherical										100			50		
		F	5.2	flake														50	
	oxidized	P	3.0	spherical			50												
		Q	4.0	flake							90								
		R	4.2	spherical	50							39				100			
		S	5.2	flake		50							39						
		T	21	flake								61	61						
		U	50	spherical				50		40									
		V	64	spherical					50										40
Dispersion medium			MFTG		30	30	20	11	11	18	25	52	52	18	14	30	18	18	18
D1 / D2					4.7	5.8	3.3	12.5	12.5	500	40	5.0	4.1	-	-	-	4.7	5.8	600
Die shear strength (MPa)					33.6	25.3	29.2	20.3	20.4	20.0	29.1	23.1	26.6	18.1	16.0	12.5	5.7	6.6	5.0

[0076] In Comparative Example 1 and Comparative Example 2 where only copper particles having no nanostructures were used, the die shear strength of the bonded sample was less than 20 MPa. In Comparative Example 3 where only the copper microparticles having nanostructures on the surfaces thereof, the shear strength was lower than that in each of Comparative Examples 1 and 2. The porosity of the bonded cross-section in Comparative Example 3 determined from FIG. 3(B) was 30.4%.

[0077] In each of Examples 1 to 9 where in addition to microparticles having nanostructures on the surfaces thereof (first-type particles), copper particles having a particle diameter smaller than that of the first-type particles (second-type particles) were used as metal particles, the die shear strength was as large as 20 MPa or more. In Example 1, the porosity on the bonded cross-section as determined in FIG. 3(A) was 11.5%, and it was confirmed that the porosity was considerably lower than that in Comparative Example 3 because air gaps between micrometer order-sized particles were filled with fine particles. These results revealed that by using copper microparticles with nanostructures formed on the surfaces thereof through oxidation by heating and copper particles having a relatively small particle diameter, air gaps between the copper microparticles are filled with particles having a relatively small particle diameter, and bonding between the metal particles was strengthened to enhance bonding strength.

[0078] In Examples 8 and 9 where copper microparticles having nanostructures on the surfaces thereof were used as the second-type particles having a relatively small particle diameter, high bonding strength was exhibited as in other examples. On the other hand, in Comparative Examples 4 and 5, two types of copper particles having different particle diameters were used as in Comparatives 1 and 2, but the die shear strength was lower than that in each of Comparative Examples 1 to 3. These results indicates that in Examples, the bonding strength increased because the nanostructures formed on the surfaces of copper particles had a function of promoting welding of microparticles, whereas in Comparative Examples 4 and 5 where microparticles having no nanostructures were used, the bonding strength decreased because microparticles were not welded together.

[0079] In Comparative Example 6 where the particles V having nanostructures on the surfaces thereof and having an average particle diameter of 64 μm and the particles A having an average particle diameter of 0.1 μm were used, the bonding strength was insufficient although microparticles having nanostructures on the surfaces thereof and copper particles having a small particle diameter were used. It is considered that in Comparative Example 6, the bonding strength decreased because the ratio of the particle diameters of two types of particles (D1/D2) was large and the ratio of grain boundaries was high. These results reveal that high bondability can be achieved by setting the ratio (D1/D2) of the average particle diameter of the first-type particles to the average particle diameter of the second-type particles within a specific range.

Claims

1. A copper paste comprising: metal particles including first-type particles and second-type particles having an average particle diameter smaller than an average particle diameter of the first-type particles; and dispersion medium, wherein the first-type particles are copper particles having the average particle diameter of 1 to 100 μm and having nanostructures on the surface thereof,
   the second-type particles are copper particles having the average particle diameter of 0.05 to 5 μm,
   the average particle diameter of the first-type particles is 2 to 550 times the average particle diameter of the second-type particles.

2. The copper paste according to claim 1, wherein the nanostructures of the first-type particles is formed of thermally oxidized copper.

3. The copper paste according to claim 1 or 2, wherein the first-type particles have fiber-shaped nanostructure on the surfaces of the particles.

4. The copper paste according to any one of claims 1 to 3, wherein the average particle diameter of the first-type particles is 3 to 50 μm, and the average particle diameter of the second-type particles is 0.1 to 5 μm.

5. The copper paste according to any one of claims 1 to 4, wherein an amount of the dispersion medium is 5 to 100 parts by mass based on 100 parts by mass of the metal particles.

6. Abonding method comprising:

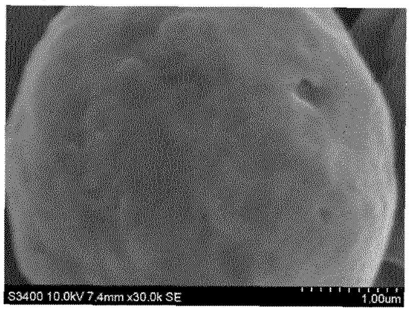
   preparing a laminate in which the copper paste according to any one of claims 1 to 5 is disposed between a first member and a second member; and heating the laminate in a reducing atmosphere to sinter the copper paste.

7. A method for producing a bonded body comprising:

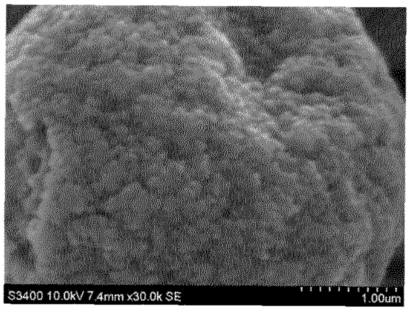
preparing a laminate in which the copper paste according to any one of claims 1 to 5 is disposed between a first member and a second member; and
heating the laminate in a reducing atmosphere to sinter the copper paste, whereby the first member and the second member are bonded.

FIG. 1

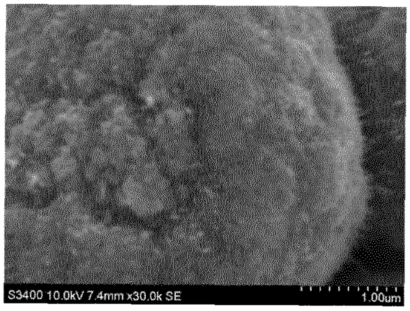
(A) No heat-treatment



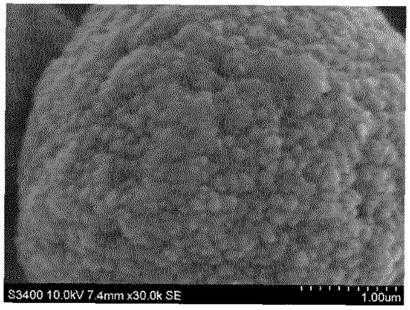
(B1) 300°C for10 minutes



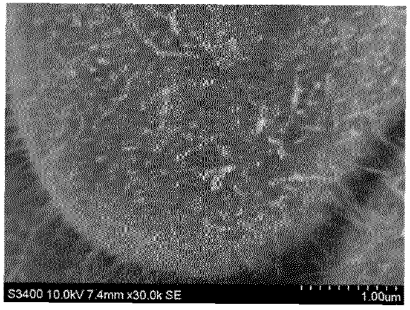
(C1) 400°C for 10 minutes



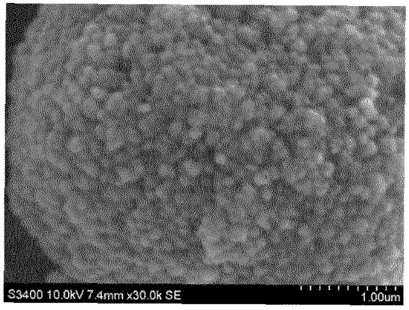
(B2) 300°C for 30 minutes



(C2) 400°C for 30 minutes



(B3) 300°C for 120 minutes



(C3) 400°C for 120 minutes

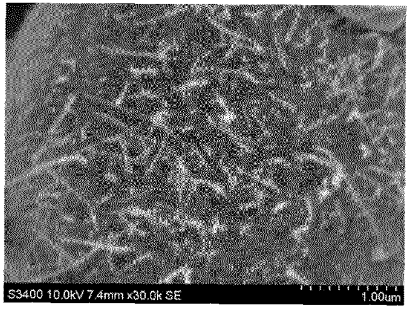


FIG. 2

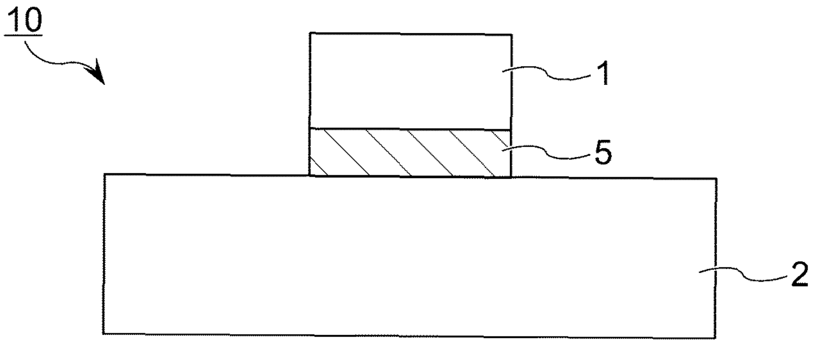
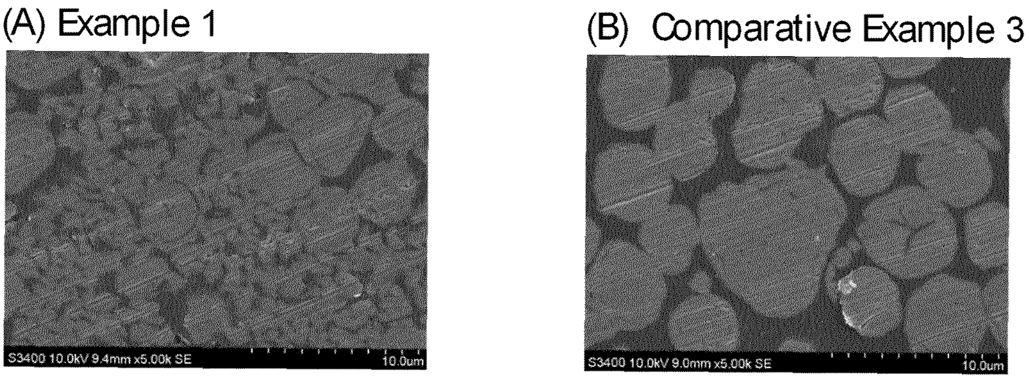


FIG. 3


(A) Example 1

(B) Comparative Example 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/011213

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. B22F1/00(2006.01)i, H01B1/00(2006.01)i, H01B1/22(2006.01)i

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, H01B1/00, H01B1/22

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	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

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.
Y	JP 10-021744 A (MITSUBOSHI BELTING LTD.) 23 January 1998, claims, paragraph [0012] (Family: none)	1-7
Y	JP 2011-094236 A (DOWA HOLDINGS CO., LTD.) 12 May 2011, claims, paragraph [0015] (Family: none)	1-7

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
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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 20.05.2019	Date of mailing of the international search report 28.05.2019
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2017074598 A **[0004]**
- JP 2014167145 A **[0004]**