Silver paste

The invention relates to a silver paste, which has a high suitability as interconnection material in electronics applications, where electronic components (electronic parts) have to be interconnected to each other.

Examples of electronic components in the sense of the present disclosure include diodes, LEDs (light-emitting diodes), semiconductor dies (semiconductor chips), IGBTs (insulated-gate bipolar transistors, bipolar transistors with an insulated gate electrode), MOSFETs (metal-oxide-semiconductor field-effect transistors), ICs (integrated circuits), sensors, heat dissipators which may also be called “heat spreaders” (e.g. heat sinks; metal lids, in particular metal lids such as those employable for interconnecting to a semiconductor generating heat when in operation; graphene films, in particular graphene films such as those employable for interconnecting to a semiconductor generating heat when in operation; metal lids interconnected to a heat sink; graphene films interconnected to a heat sink; metal lids interconnected to a semiconductor; graphene films interconnected to a semiconductor), resistors, capacitors, coils, connecting elements (e.g. clips), base plates, antennas, and the like. Further examples of electronic components include substrates such as lead frames, PCBs (printed circuit boards), flexible electronics, ceramic substrates, metal-ceramic substrates, such as DCB substrates (direct copper-bonded substrates), IMS (insulated metal substrates), glass substrates and the like. The electronic components have contact surfaces via which they can be interconnected (bonded) to each other, typically as a sandwich assembly with an interconnection material in between. Examples of interconnection materials include solder materials, sinter materials and electrically conductive adhesives. Said contact surfaces are often metallic contact surfaces, wherein the electronic components may consist of metal or may at least have a metallic contact surface. However, in some cases the contact surfaces may be non-metallic.

Electrically conductive silver adhesives are known as interconnection materials that can be used in electronics applications. WO 2016/018191 A1 discloses such an electrically conductive composition especially for use as a hardenable electrically conductive adhesive. The electrically conductive composition comprises metal containing particles, at least one epoxy resin, at least one hardener for the at least one epoxy resin, and at least one lactone. However, there is room for improvement, in particular with regard to the thermal conductivity of such adhesives in the cured (hardened) state.

The terms “curing, cured, curable, etc.” used in this disclosure are synonymous with “hardening, hardened, hardenable, etc.” also used in this disclosure.

The invention relates to a silver paste which can be used as an interconnection material in electronics applications and which in the hardened state is distinguished by an outstanding thermal conductivity in the range of, for example, 30 to 100 $Wm^{-1}K^{-1}$; hence, it is especially useful in electronics applications where heat dissipation is required or, more precisely, where heat is generated within an active electronic component during operation (e.g. a semiconductor die in operation) and needs to be effectively dissipated from it, e.g. making use of a heat dissipator interconnected to it. In other words, apart from its mechanical interconnection capability and its electrical conductivity, the hardened silver paste can function as a highly effective thermal interface material (TIM) between an electronic heat source like a semiconductor die in operation and a heat dissipator. The thermal conductivity can be determined by a method as defined in industry standard ASTM D5470.

The silver paste of the invention consists of
(i) 5 to 15 wt% (weight percent, % by weight), preferably 5 to 13 wt% of at least one organic solvent,
(ii) 75 to 90 wt%, preferably 80 to 90 wt% of silver particles,
(iii) 5 to 10 wt% of a curable epoxy resin / hardener system, and
(iv) 0 to 2 wt% of at least one constituent other than constituents (i) to (iii),
wherein the curable epoxy resin / hardener system (iii) consists of no or at least one non-elastomer-modified epoxy resin (iiia), at least one elastomer-modified epoxy resin (iiib), and at least one hardener (iiic),
wherein the weight ratio of epoxy resins (iiia) and (iiib) is ≤1.0, preferably ≤0.7, and wherein the at least one hardener (iiic) is selected from the group consisting of amine hardeners (iiic1) or from the group consisting of anhydride hardeners (iiic2).

Accordingly, depending on the presence or absence of constituents (iiia) and/or (iv), the silver paste of the invention may consist of constituents (i) plus (ii) plus (iiib) plus (iiic1) or of constituents (i) plus (ii) plus (iiib) plus (iiic2) or of constituents (i) plus (ii) plus (iiia) plus (iiib) plus (iiic1) or of constituents (i) plus (ii) plus (iiia) plus (iiib) plus (iiic2) or of constituents (i) plus (ii) plus (iiib) plus (iiic1) plus (iv) or of constituents (i) plus (ii) plus (iiib) plus (iiic2) plus (iv) or of constituents (i) plus (ii) plus (iiia) plus (iiib) plus (iiic1) plus (iv) or of constituents (i) plus (ii) plus

(iiia) plus (iiib) plus (iiic2) plus (iv), and in each of these eight alternatives the sum of the weight percentages of the respective constituents is 100 weight percent.

In a preferred embodiment, the silver paste of the invention consists of
(i) 5 to 13 wt% of at least one organic solvent,
(ii) 80 to 90 wt% of silver particles,
(iii) 5 to 10 wt% of a curable epoxy resin / hardener system, and
(iv) 0 to 2 wt% of at least one constituent other than constituents (i) to (iii),
wherein the curable epoxy resin / hardener system (iii) consists of no or at least one non-elastomer-modified epoxy resin (iiia), at least one elastomer-modified epoxy resin (iiib), and at least one hardener (iiic),
wherein the weight ratio of epoxy resins (iiia) and (iiib) is ≤1.0, preferably ≤0.7, and wherein the at least one hardener (iiic) is selected from the group consisting of amine hardeners (iiic1) or from the group consisting of anhydride hardeners (iiic2).

As has been indicated already above, after application and curing, a layer obtained from the silver paste of the invention located between electronic components is characterized not only by the formation of a firm mechanical interconnection of the electronic components, but also by good electrical conductivity and in particular by excellent thermal conductivity in the range of, for example, 30 to 100 to $Wm^{-1}K^{-1}$. A best possible thermal conductivity is a very desirable property in the field of electronics, when it comes to dissipating heat from active electronic components during their operation.

As constituent (i) the silver paste of the invention comprises 5 to 15 wt%, preferably 5 to 13 wt% of at least one organic solvent, i.e. one organic solvent or a mixture of at least two organic solvents. Examples of the at least one organic solvent include alcohols, e.g. terpineols, tridecanols; glycol ethers, e.g. tripropylene glycol monomethyl ether, dipropylene glycol monobutyl ether, diethylene glycol monohexyl ether, butyl polyglycol; esters, e.g. dipropylene glycol methylether acetate, diethyl adipate, dibasic esters; aromatic hydrocarbons, e.g. toluene, xylene, ethylbenzene.

As constituent (ii) the silver paste of the invention comprises 75 to 90 wt%, preferably 80 to 90 wt% of silver particles.

The term "silver particles" used herein refers to particles of pure silver (silver with a purity of at least 99.90 wt%, preferably at least 99.95 wt%) or of a silver alloy having a silver content in the range of >90 wt%. Examples of alloying elements include gold, copper, platinum, palladium, rhodium, zinc and tin.

The shape of the silver particles may vary, i.e. the silver particles can be acicular particles (needles), granules, flakes (platelets) and/or particles having an ideal spherical shape (spheres), a substantially spherical shape, an elliptical shape, or an ovoid shape. The mean particle size of the silver particles can be in the range of, for example, 0.1 to 20 µm, preferably 0.2 to 10 µm, more preferred 0.2 to 8 µm.

The term "mean particle size" ("average particle size") used herein means the volume-average primary particle diameter (d50) that can be determined by laser diffraction. The Equivalent Circular Area Diameter (ECAD) can be conveniently used as a measure of particle diameter (see RENLIANG XU ET AL: "Comparison of sizing small particles using different technologies", POWDER TECHNOLOGY, ELSEVIER, BASEL (CH), Vol. 132, No. 2-3, June 24, 2003 (2003-06-24), pages 145-153). Laser diffraction measurements can be made using the wet determination method with an appropriate particle sizer, such as a Mastersizer 3000 or a Mastersizer 2000 from Malvern Instruments. In the wet determination method, particulate sample can be ultrasonically dispersed in ethanol as part of sample preparation.

Silver particles in flake form are preferred as constituent (ii). Silver flakes are flat silver particles exhibiting an aspect ratio of >5 : 1 or >10 : 1, even up to several hundreds : 1 as opposed to silver granules (aspect ratio typically between 1 : 1 and 5 : 1) or silver spheres (aspect ratio of 1:1).

The term "aspect ratio" as used herein refers to the shape of the silver particles (ii) and means the quotient of the largest and smallest linear dimensions of a silver particle. It can be determined by scanning electron microscopy and evaluation of the electron microscopic images by measuring the dimensions of a statistically reasonable number of, for example, 20 to 100 individual silver particles.

The silver particles or the silver flakes in particular can have a surface coating, for example, a coating of one or more fatty acids and/or one or more fatty acid derivatives. Said weight proportion of 75 to 90 wt%, preferably 80 to 90 wt% then includes the weight of the coating on

the silver particles or the silver flakes. Examples of fatty acid derivatives include fatty acid esters, fatty acid salts, fatty alcohols and fatty amines. Examples of said fatty acids include caprylic acid (octanoic acid), capric acid (decanoic acid), lauric acid (dodecanoic acid), myristic acid (tetradecanoic acid), palmitic acid (hexadecanoic acid), margaric acid (heptadecanoic acid), stearic acid (octadecanoic acid), arachinic acid (eicosanoic acid/icosanoic acid), behenic acid (docosanoic acid), and lignoceric acid (tetracosanoic acid).

Silver particles or silver flakes of type (ii) are commercially available, for example Silflake® 40-592, Silflake® 40-384 or Silflake® 40-394 from Technic, AA-192N from Metalor or FA-S-14, FA-D-3, FA-D-1 and FA-D-2 from Dowa Electronics Materials, to name only a few examples.

Non-flaky silver particles (silver particles other than silver flakes) are commercially available. Examples include 18060-NM2 from Ames Goldsmith and products AG 2.5-8F, AG 2.5-11F, Ag 3-11F, AG 4-1F, AG 4-8F, AG 4-11F from Dowa Electronics Materials and products K-79124P and K-79121P from Metalor.

As constituent (iii) the silver paste of the invention comprises 5 to 10 wt% of a curable epoxy resin / hardener system,
wherein the curable epoxy resin / hardener system (iii) consists of no or at least one non-elastomer-modified epoxy resin (iiia), at least one elastomer-modified epoxy resin (iiib), and at least one hardener (iiic),
wherein the weight ratio of epoxy resins (iiia) and (iiib) is ≤1.0, preferably ≤0.7, and wherein the at least one hardener (iiic) is selected from the group consisting of amine hardeners (iiic1) or from the group consisting of anhydride hardeners (iiic2).

It is essential, that the quotient of the weight of the at least one non-elastomer-modified epoxy resin (iiia) divided by the weight of the at least one elastomer-modified epoxy resin (iiib) is ≤1.0, i.e. it is even possible that said quotient equals 0 and that the curable epoxy resin / hardener system comprises even no non-elastomer-modified epoxy resin of type (iiia). It is preferred that the quotient is ≤0.7.

The curable epoxy resin / hardener system (iii) comprises those constituents of the silver paste of the invention which, after application and curing thereof, form a covalently crosslinked polymer matrix or polymer network, i.e. the cured epoxy resin / hardener system (iii').

This disclosure distinguishes between non-elastomer-modified epoxy resins of type (iiia) and elastomer-modified epoxy resins of type (iiib). Non-elastomer-modified epoxy resins of type (iiia) have epoxy end-groups, e.g. glycidyl end-groups. They do not comprise an elastomer-modification, i.e. they do not include a linear chainlike structure. In other words, non-elastomer-modified epoxy resins of type (iiia) do not include linear chainlike molecules with epoxy end-groups, e.g. glycidyl end-groups. Examples of linear chainlike structures include diene elastomer type structures like polyisoprene, polybutadiene, and polychloroprene; and non-diene elastomer type structures like butyl rubber (polyisobutylene), polysiloxanes (silicone rubber), polyurethane (polyurethane rubber), and fluoro-elastomers.

Examples of the at least one non-elastomer-modified epoxy resin (iiia) include bisphenol A epoxy resins and/or bisphenol F epoxy resins, novolac epoxy resins, and cycloaliphatic epoxy resins.

The at least one non-elastomer-modified epoxy resin (iiia) can have an epoxy equivalent weight in the range of, for example, 100 to 400 grams per equivalent.

Examples of bisphenol A epoxy resins include Araldite® GY 279 as well as Quatrex® 1010 commercially available from Huntsman or D.E.R.™ 331 as well as D.E.R.™ 732 commercially available from Dow Chemical, EPON™ 828 from Hexion and D.E.R.™ 383 from Olin.

Examples of bisphenol A/F epoxy resins include Araldite® GY 891, Araldite® PY 302-2 and Araldite® PY 3483 commercially available from Huntsman.

Examples of bisphenol F epoxy resins include Araldite® GY 281 commercially available from Huntsman and D.E.R.™ 354 commercially available from Olin.

An example of a novolac epoxy resin is D.E.N™ 431 commercially available from Olin.

Examples of cycloaliphatic epoxy resins include JER YX8000 commercially available from Mitsubishi Chemical and EPONEX™ Resin 1510 commercially available from Momentive Specialty Chemicals.

Elastomer-modified epoxy resins of type (iiib) have epoxy end-groups, e.g. glycidyl end-groups. They do comprise an elastomer-modification, i.e. they do include a linear chainlike structure. In

other words, elastomer-modified epoxy resins of type (iiib) do include linear chainlike molecules with epoxy end-groups, e.g. glycidyl end-groups. Examples of linear chainlike structures include diene elastomer type structures like polyisoprene, polybutadiene, and polychloroprene; and non-diene elastomer type structures like butyl rubber (polyisobutylene), polysiloxanes (silicone rubber), polyurethane (polyurethane rubber), and fluoro-elastomers.

The at least one elastomer-modified epoxy resin (iiib) can have an epoxy equivalent weight in the range of, for example, 200 to 1000 grams per equivalent.

Elastomer-modified epoxy resins of type (iiib) are commercially available. Examples include ED-502 and ED-506 commercially available from ADEKA, jER™ YX7105 and jER™ YX7110 from Mitsubishi Chemical, and X-22-163, X-22-163A, X-22-163B and KF-105 from Shin-Etsu Chemical.

The curable epoxy resin / hardener system comprises at least one hardener (iiic). The at least one hardener (iiic) is selected from the group consisting of amine hardeners (iiic1) or from the group consisting of anhydride hardeners (iiic2). Amine hardeners (iiic1) are preferred.

Examples of amine hardeners (iiic1) include monoamine hardeners having one primary amino group per molecule and polyamine hardeners with primary and/or secondary amino groups. Typical examples include diamines, triamines, and other polyamines with at least two amino groups in the molecule, where the amino groups are selected from primary and secondary amino groups. Secondary amino groups may be present as lateral or terminal functional groups or as a member of a heterocyclic ring. Examples of polyamine hardeners include dicyandiamide, diethylenetriamine, ethylenediamine, m-phenylenediamine, triethylenetetramine, aminoethylpiperazine, Jeffamine® D230 from Huntsman, and heterocyclic polyamine hardeners such as pyrazine and imidazole derivatives. Further examples include Curezol® 2MZ-H, 2MZ-CN, 2PZ, C17Z, 2E4MZ, 2E4MZ-CN or 2MA-OK from Shikoku Chemical.

Examples of anhydride hardeners (iiic2) include anhydrides of polycarboxylic acids such as, for example, methyltetrahydrophthalic acid or methylhexahydrophthalic acid.

It is expedient that the cured epoxy resin / hardener system (iii') (i.e. the curable epoxy resin / hardener system (iii) after having been cured) exhibits some desired elasticity. With regard to such elasticity of the cured epoxy resin / hardener system (iii') it is expedient, to combine the

constituents (iiia), (iiib) and (iiic) or (iiib) and (iiic) such, that the curable epoxy resin / hardener system (iii) as such after a heat treatment of 2 hours at 80°C followed by 2 hours at 200°C exhibits a glass transition temperature T_g in the range of -50 to +35°C, preferably of -50 to +10°C, measured by DSC (differential scanning calorimetry) in the temperature range of -80°C to +200°C with a heating rate of 10 K/min. In other words, in an advantageous embodiment, the silver paste of the invention comprises a curable epoxy resin / hardener system (iii) which as such after a heat treatment of 2 hours at 80°C followed by 2 hours at 200°C exhibits a glass transition temperature T_g in the range of -50 to +35°C, preferably of -50 to +10°C, measured by DSC in the temperature range of -80°C to +200°C with a heating rate of 10 K/min. The person skilled in the art is provided here with a selection rule enabling him to take a very targeted approach when composing a suitably composed epoxy resin / hardener system (iii) from the constituents (iiia) if any, (iiib) and (iiic2) or preferably from the constituents (iiia) if any, (iiib) and (iiic1) without an unreasonable effort or number of tests. To this end, the skilled person may or will typically perform a simple DOE (design of experiments) always maintaining a weight ratio of epoxy resins (iiia) and (iiib) of ≤1.0, preferably ≤0.7, and working with said heat treatment regime of 2 hours at 80°C followed by 2 hours at 200°C. The only variables in said DOE are (1) the selection of an epoxy resin (iiia) if any, (2) the selection of an epoxy resin (iiib) and (3) the selection of a hardener (iiic) and the proportion between those constituents.

As constituent (iv) the silver paste of the invention comprises 0 to 2 wt% of at least one constituent other than constituents (i) to (iii), i.e. it is possible that the silver paste of the invention comprises even no constituent of type (iv). Examples of such constituents of type (iv) include catalysts, reactive diluents (lactones, monoepoxides), rheological modifiers, and surface-active agents.

It is preferred that the silver paste of the invention does not comprise glass frit. It is also preferred that the silver paste of the invention does not comprise any silver precursor (thermally decomposable silver compound), e.g. no silver compound such as for example silver carbonate, silver lactate, silver formate, silver citrate or silver oxide.

Preferably, the viscosity of the silver paste of the invention is in the range of 15 to 60 mPa·s. The viscosity can be determined with a plate-plate rheometer with a plate diameter of 50 mm and a measuring gap of 400 µm (for example the plate-plate rheometer Physica MCR 150 from Anton-Paar) at 25°C and at a shear rate of 10 s^{-1}.

The silver paste of the invention may be prepared by mixing the constituents of type (i) to (iii) or, in case constituent (iv) is present (i.e. constituent (iv) totalling >0 to 2 wt% of the silver paste of the invention), it may be prepared by mixing the constituents of type (i) to (iv). Mixing equipment that can be used here includes stirrers and three-roller mills. The so prepared silver paste of the invention has a shelf life when stored at -20°C in the range of, for example, 1 to 12 months.

The silver paste of the invention can advantageously be used as an interconnection material in electronics applications. In particular, it can be used in such electronics and microelectronics applications in which electronic components or, more precisely, contact surfaces of electronic components need to be firmly mechanically interconnected to each other with the hardened interconnection material in between, in particular with the hardened interconnection material in between forming a highly efficient thermal path between said electronic components. To prevent misunderstandings, “hardened interconnection material in between” relates to a sandwich assembly of two electronic components with a hardened interconnection material in between thus forming a mechanical and thermally highly conductive interconnection (“TIM layer”) between said electronic components. For said purpose of serving as interconnection material in electronics applications, the silver paste of the invention can be applied between the contact surfaces of electronic components to be bonded to each other. The so prepared sandwich assembly can be heat treated so as to harden the silver paste between the electronic components. Examples of such electronic components include the aforementioned substrates and electronic components.

Examples of sandwich assemblies comprising an electronic component functioning as a heat source and a heat dissipator as a further electronic component with the cured silver paste of the invention as TIM in between include those listed in the following table:

Type of sandwich assembly		
Heat source:	**TIM layer**	**Heat dissipator:**
Semiconductor die*	Layer of cured silver paste of the invention	Metal lid** functioning as a heat dissipator or interconnected to a heat sink
Semiconductor die*	Layer of cured silver paste of the invention	Graphene film functioning as a heat dissipator or interconnected to a heat sink
Semiconductor die*	Layer of cured silver paste of the invention	Air- or water-cooled heat sink
Metal lid** interconnected to	Layer of cured silver paste	Air- or water-cooled heat

a semiconductor die* (in operation)	of the invention	sink
Graphene film interconnected to a semiconductor die* (in operation)	Layer of cured silver paste of the invention	Air- or water-cooled heat sink

* e.g. silicon die (in operation)

** e.g. a lid of copper, aluminum or nickel-coated copper

As has already been indicated, the invention relates also to a process for the manufacture of a sandwich assembly comprising or consisting of a first electronic component firmly mechanically interconnected to a second electronic component via a layer of the hardened silver paste of the invention. The manufacturing process comprises the subsequent steps:

(a) applying a layer of the silver paste of the invention to a contact surface of a first electronic component,

(b) optionally, drying the so-applied wet layer of the silver paste,

(c) placing a second electronic component with its contact surface onto the wet or dried layer of the silver paste so as to obtain a sandwich assembly comprising or consisting of the first electronic component and the second electronic component with the wet or dried layer of the silver paste in between, and

(d) drying and hardening the wet layer of the silver paste or hardening the dried layer of the silver paste by heat treating the sandwich assembly so as to obtain a sandwich assembly comprising or consisting of the first electronic component and the second electronic component with a layer of the hardened silver paste in between.

This disclosure distinguishes between dried silver paste and hardened silver paste. To prevent misunderstandings, dried silver paste is not or at best partly hardened and it shall not be confused with hardened silver paste.

The application of the silver paste of the invention according to step (a) can be carried out, for example, by printing, e.g. screen printing or stencil printing, or dispensing. The typical wet thickness of the so-applied silver paste of the invention is in the range of, for example, 40 to 260 µm.

After application, an optional drying step (b) is performed to remove any volatile compounds, such as in particular organic solvent (i). The drying parameters are, for example, 5 to 30 minutes at an object temperature of, for example, 50 to 80°C. Most preferred drying parameters

are 15 minutes at an object temperature of 50°C.The typical dry thickness of the silver paste of the invention is in the range of, for example, 34 to 220 µm.

After step (a) or after the optional drying step (b) step (c) is performed. In step (c) a second electronic component is placed with its contact surface onto the wet or dried layer of the silver paste so as to obtain a sandwich assembly comprising or consisting of the first electronic component and the second electronic component with the wet or dried layer of the silver paste in between.

In subsequent step (d) the wet layer of the silver paste is dried and cured or the already dried layer of the silver paste is only cured. The drying and curing or the curing without drying is performed via a heat treatment and without application of pressure. To this end, heat is applied to the sandwich assembly obtained in step (c) so as to reach a desired object temperature. The drying parameters are, for example, 1 to 3 hours at an object temperature of, for example, 50 to 150°C. Most preferred drying parameters are 2 hours at an object temperature of 80°C. The hardening parameters are, for example, 1 to 5 hours, preferably 1 to 3 hours at an object temperature of, for example, 150 to 250°C, preferably 180 to 220°C. Most preferred hardening parameters are 2 hours at an object temperature of 200°C. After conclusion of step (d) the typical final thickness of the hardened silver paste of the invention is in the range of, for example, 30 to 200 µm. In the course of thermally curing the dried silver paste of the invention two curing mechanisms take place: (1) curing of the curable epoxy resin / hardener system (iii) to form a covalently crosslinked polymer matrix or polymer network and (2) pressure-less sintering of the silver particles (ii). As a result, a hybrid material of sintered silver particles embedded in a cross-linked polymer network (i.e. the cured epoxy resin / hardener system (iii')) is formed. The hybrid material forms a firm mechanical interconnection and provides a remarkably efficient thermal path between the interconnected electronic components. Insofar the skilled person will understand the silver paste of the invention as a hybrid silver paste. The hybrid material is void-free or it exhibits only a small content of voids, for example, a volume share in the range of, for example, no more than 5 % volume of voids within the total volume of the hybrid material layer. The volume share of voids can be determined by X-ray (e.g. making use of a Nordson X-ray machine).

The hybrid material is flexible which allows for the reduction of CTE (coefficient of thermal expansion) mismatch between two electronic components of a sandwich assembly as has been described above. Said flexibility of the hybrid material goes along essentially with said desired

elasticity of its cured epoxy resin / hardener system (iii'); i.e. it is expedient when the silver paste of the invention after a heat treatment of 2 hours at 80°C followed by 2 hours at 200°C exhibits a glass transition temperature T_g in the range of -55 to +30°C, preferably of -55 to +5°C, measured by DSC in the temperature range of -80°C to +200°C with a heating rate of 10 K/min. To this end, it is expedient to select a curable epoxy resin / hardener system of type (iii) which after a heat treatment of 2 hours at 80°C followed by 2 hours at 200°C exhibits a glass transition temperature T_g in the range of -50 to +35°C, preferably of -50 to +10°C, measured by DSC in the temperature range of -80°C to +200°C with a heating rate of 10 K/min, and to combine the so selected curable epoxy resin / hardener system of type (iii) with silver particles of type (ii) accordingly.

The following combinations of types of a first electronic component with a second electronic component represent preferred combinations within the process for the manufacture of a sandwich assembly according to the invention:

- The first electronic component is a semiconductor die (in operation) and the second electronic component is a metal lid or a graphene film,
- The first electronic component is a semiconductor die (in operation) and the second electronic component is a metal lid interconnected to a heat sink or a graphene film interconnected to a heat sink,
- The first electronic component is a metal lid or a graphene film and the second electronic component is a heat sink,
- The first electronic component is a metal lid interconnected to a semiconductor die (in operation) or a graphene film interconnected to a semiconductor die (in operation) and the second electronic component is a heat sink,
- The second electronic component is a semiconductor die (in operation) and the first electronic component is a metal lid or a graphene film,
- The second electronic component is a semiconductor die (in operation) and the first electronic component is a metal lid interconnected to a heat sink or a graphene film interconnected to a heat sink,
- The second electronic component is a metal lid or a graphene film and the first electronic component is a heat sink,
- The second electronic component is a metal lid interconnected to a semiconductor die (in operation) or a graphene film interconnected to a semiconductor die (in operation) and the first electronic component is a heat sink.

Examples 1 to 4

Silver pastes were prepared by homogenously mixing the ingredients making use of a stirrer followed by using a three-roller mill. The so-prepared silver pastes were stored at -20°C and they exhibited a shelf-life of at least 2 months. The thermal conductivity, the electrical resistivity and the glass transition temperature T_g of each of the dried and cured silver pastes as well as the T_g of each of the silver pastes' underlying dried and cured epoxy resin / hardener system was measured. Drying and curing conditions were in each case: 2 hours at 80°C, followed by 2 hours at 200°C.

The thermal conductivity was measured via a lateral thermal material analyzer (LaTIMA®) system by Nanotest. The measurement principle of LaTIMA® is based on the TIMA® methodology defined in industry standard ASTM D5470. Three different spots of each sample are measured, and an average data is obtained for each of the samples.

The electrical resistivity was measured in Ωm according to the four point probe measurement (F.M.Smits, "Measurement of Sheet Resistivities with the Four-Point Probe", published in THE BELL SYSTEM TECHNICAL JOURNAL, MAY 1958, pages 711 -718, or the web-site: "http://en.wikipedia.org/wiki/Sheet_resistance").

DSC measurements were carried out in a temperature range of -80°C to +200°C with a heating rate of 10 K/min.

The results of said measurements can be found in Table 1.

Example 1 (according to the invention): A silver paste was prepared by mixing 7 pbw (parts by weight) of terpineol, 5 pbw of elastomer-modified epoxy resin ED-506 from ADEKA, 2 pbw of non-elastomer-modified epoxy resin EPON™ 828 from Hexion, 1 pbw of m-phenylenediamine and 85 pbw of silver flakes (FA-D-1, d50 = 4.2µm, Dowa Electronics Materials).

Example 2 (according to the invention): A silver paste was prepared by mixing 5.9 pbw of terpineol, 4 pbw of elastomer-modified epoxy resin X-22-163 from Shin-Etsu, 1 pbw of non-elastomer-modified epoxy resin D.E.R.™ 383 from Olin, and 84.5 pbw of silver flakes (FA-D-3, d50 = 5.6µm, Dowa Electronics Materials), 4.3 pbw of methyltetrahydrophthalic anhydride hardener and 0.3 pbw of 2-ethyl-4-methylimidazole catalyst.

Example 3 (according to the invention): A silver paste was prepared by mixing 7 pbw of terpineol, 3.5 pbw of elastomer-modified epoxy resin ED-506 from ADEKA, 3.5 pbw of non-elastomer-modified epoxy resin EPON™ 828 from Hexion, 1 pbw of m-phenylenediamine and 85 pbw of silver flakes (FA-D-1).

Comparative Example 4: A silver paste was prepared by mixing 5.9 pbw of terpineol, 5.0 pbw of non-elastomer-modified epoxy resin D.E.R.™ 383 from Olin, and 84.5 pbw of silver flakes (FA-D-3), 4.3 pbw of methyltetrahydrophthalic anhydride hardener and 0.3 pbw of 2-ethyl-4-methylimidazole catalyst.

Table 1

Example	Electrical resistivity (Ωm)	Thermal conductivity ($Wm^{-1}K^{-1}$)	T_g of cured epoxy resin / hardener system (°C)	T_g of hybrid material (cured silver paste) (°C)
1	0.7×10^{-7}	80	-17	-20
2	2.2×10^{-7}	50	-20	-25
3	1.1×10^{-7}	70	27	24
4	2.1×10^{-7}	52	80	74

Application of the silver pastes in a flip-chip package:

Each of the silver pastes 1 to 3 was dispensed on a nickel plate and a silicon chip (20 mm x 20 mm, 750 µm thickness) was placed on the center of the dispensed silver paste and pressed down until the silver paste had spread and covered the entire area underneath the silicon chip. The amount of dispensed silver paste was adjusted to achieve a wet layer thickness of 110 µm. The so obtained sandwich assembly was then heat treated to dry and harden the silver paste. To this end, the sandwich assembly was heated to 80°C and maintained at an object temperature of 80°C for 2 hours to remove the organic solvents and other volatiles in a first step. In a second step, the temperature was ramped up to an object temperature of 200°C and further maintained for 2 hours. A dry layer thickness of the dried and hardened silver paste of 85 µm was achieved in the resulting sandwich assembly consisting of the nickel plate firmly interconnected to the silicon chip.

Claims

1. A silver paste consisting of

(i) 5 to 15 wt% of at least one organic solvent,

(ii) 75 to 90 wt% of silver particles,

(iii) 5 to 10 wt% of a curable epoxy resin / hardener system, and

(iv) 0 to 2 wt% of at least one constituent other than constituents (i) to (iii),

wherein the curable epoxy resin / hardener system (iii) consists of no or at least one non-elastomer-modified epoxy resin (iiia), at least one elastomer-modified epoxy resin (iiib), and at least one hardener (iiic),

wherein the weight ratio of epoxy resins (iiia) and (iiib) is ≤1.0, and wherein the at least one hardener (iiic) is selected from the group consisting of amine hardeners (iiic1) or from the group consisting of anhydride hardeners (iiic2).

2. The silver paste of claim 1, wherein the proportion of the at least one organic solvent (i) is in the range of 5 to 13 wt% and the proportion of the silver particles (ii) is in the range of 80 to 90 wt%.

3. The silver paste of claim 1 or 2, wherein the silver particles (ii) are particles of pure silver or of a silver alloy having a silver content in the range of >90 wt%.

4. The silver paste of any one of the preceding claims, wherein the silver particles (ii) comprise acicular particles, granules, flakes, particles having an ideal spherical shape, particles having a substantially spherical shape, particles having an elliptical shape and/or particles having an ovoid shape.

5. The silver paste of any one of the preceding claims, wherein the silver particles (ii) have a mean particle size in the range of 0.1 to 20 µm.

6. The silver paste of any one of the preceding claims, wherein the at least one non-elastomer-modified epoxy resin (iiia) has an epoxy equivalent weight in the range of 100 to 400 grams per equivalent.

7. The silver paste of any one of the preceding claims, wherein the at least one elastomer-modified epoxy resin (iiib) has an epoxy equivalent weight in the range of 200 to 1000 grams per equivalent.

8. The silver paste of any one of the preceding claims, wherein the at least one hardener (iiic) is selected from the group consisting of amine hardeners (iiic1) or from the group consisting of anhydride hardeners (iiic2).

9. The silver paste of any one of the preceding claims, wherein the curable epoxy resin / hardener system (iii) as such after a heat treatment of 2 hours at 80°C followed by 2 hours at 200°C exhibits a glass transition temperature T_g in the range of -50 to +35°C measured by DSC in the temperature range of -80°C to +200°C with a heating rate of 10 K/min.

10. The silver paste of any one of the preceding claims - after a heat treatment of 2 hours at 80°C followed by 2 hours at 200°C - exhibiting a glass transition temperature T_g in the range of -55 to +30°C measured by DSC in the temperature range of -80°C to +200°C with a heating rate of 10 K/min.

11. A process for the manufacture of a sandwich assembly comprising or consisting of a first electronic component firmly mechanically interconnected to a second electronic component via a layer of the hardened silver paste of any one of the preceding claims, the manufacturing process comprising the subsequent steps:
(a) applying a layer of the silver paste of the invention to a contact surface of a first electronic component,
(b) optionally, drying the so-applied wet layer of the silver paste,
(c) placing a second electronic component with its contact surface onto the wet or dried layer of the silver paste so as to obtain a sandwich assembly comprising or consisting of the first electronic component and the second electronic component with the wet or dried layer of the silver paste in between, and
(d) drying and hardening the wet layer of the silver paste or hardening the dried layer of the silver paste by heat treating the sandwich assembly so as to obtain a sandwich assembly comprising or consisting of the first electronic component and the second electronic component with a layer of the hardened silver paste in between.

12. The process of claim 11, wherein the electronic components are selected from the group consisting of diodes, LEDs, semiconductor dies, IGBTs, MOSFETs, ICs, sensors, heat dissipators, resistors, capacitors, coils, connecting elements, base plates, antennas, lead frames, PCBs, flexible electronics, ceramic substrates, metal-ceramic substrates, DCB substrates, IMS and glass substrates.

13. The process of claim 11,
wherein the first electronic component is a semiconductor die (in operation) and the second electronic component is a metal lid or a graphene film
or
wherein the first electronic component is a semiconductor die (in operation) and the second electronic component is a metal lid interconnected to a heat sink or a graphene film interconnected to a heat sink
or
wherein the first electronic component is a metal lid or a graphene film and the second electronic component is a heat sink
or
wherein the first electronic component is a metal lid interconnected to a semiconductor die (in operation) or a graphene film interconnected to a semiconductor die (in operation) and the second electronic component is a heat sink
or
wherein the second electronic component is a semiconductor die (in operation) and the first electronic component is a metal lid or a graphene film
or
wherein the second electronic component is a semiconductor die (in operation) and the first electronic component is a metal lid interconnected to a heat sink or a graphene film interconnected to a heat sink
or
wherein the second electronic component is a metal lid or a graphene film and the first electronic component is a heat sink
or
wherein the second electronic component is a metal lid interconnected to a semiconductor die (in operation) or a graphene film interconnected to a semiconductor die (in operation) and the first electronic component is a heat sink.

14. The process of claim 13, wherein the heat sink is selected from the group consisting of air-cooled heat sinks and water-cooled heat sinks.

15. The process of any one of claims 11 to 14, wherein the silver paste is applied by printing or dispensing.