



(51) International Patent Classification:
C09J 9/00 (2006.01)

(21) International Application Number:
PCT/CN2015/088444

(22) International Filing Date:
28 August 2015 (28.08.2015)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except SC): **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 974 Centre Rd., Wilmington, Delaware, 19805 (US).

(72) Inventors; and

(71) Applicants (for SC only): **MU, Minfang** [CN/CN]; 558 Jinping Road, No. 130, Minhang District, Shanghai, 200240 (CN). **FENG, Dan** [CN/CN]; 102, Bidg. 6, Lane 180, Liangxiu Road, Pudong New District, Shanghai 201203 (CN). **RODRIGUEZ-PARADA, Jose M** [US/US]; 160 Ramunno Circle, Hockessin, Delaware 19707 (US).

(74) Agent: **NTD PATENT & TRADEMARK AGENCY LIMITED**; 10th Floor, Block A, Investment Plaza, 27 Jinrongdajie, Xicheng District, Beijing 100033 (CN).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: COATED COPPER PARTICLES AND USE THEREOF

(57) Abstract: Coated copper particles formed of copper cores that are surface coated with a coating composition comprising one or more conductive oxides. Electrically conductive adhesives (ECA) comprising: (a) organic binder, (b) surface coated copper particles, and optional (c) solvent.



WO 2017/035709 A1

TITLE**COATED COPPER PARTICLES AND USE THEREOF****FIELD OF THE INVENTION**

5 The invention relates to coated copper particles and electrically conductive adhesives comprising the same.

BACKGROUND OF THE INVENTION

10 Electrically conductive materials are used for a variety of purposes in the fabrication and assembly of electronic devices, integrated circuits, semiconductor devices, passive components, solar cells, and/or light emitting diodes.

 In general, electrically conductive adhesives (ECAs) provide a mechanical bond between two surfaces and conduct electricity. Typically, ECA formulations are made of organic binder resins filled with electrically conductive metal fillers.

15 The binder resins generally provide a mechanical bond between two substrates, while the electrically conductive fillers generally provide the desired electrical interconnection.

 Typical electrically conductive adhesives require high loadings of electrically conductive fillers which are normally made from expensive conductive
20 metals, such as silver. Silver-coated metal fillers, e.g. silver-coated copper fillers also have been developed and used in the art. However, the electrical conductivity of adhesive formulations, comprising silver-coated fillers is often significantly reduced compared with formulations based on filler materials made of silver.

25 Hence, there is still a need to develop new conductive fillers for electrically conductive adhesives to reduce the use of expensive conductive metals, such as silver, and to provide good electrical conductivity.

BRIEF SUMMARY OF THE INVENTION

30 Provided herein are coated copper particles comprised of copper cores that are surface coated with about 0.15-4.5 parts by weight of a coating

composition, relative to 100 parts by weight of the copper particles, wherein the coating composition comprising at least one conductive oxide.

In one embodiment of the coated copper particles, the copper cores have a particle size distribution D50 ranging from about 0.08-50 μm . Or, the copper
5 cores have a particle size distribution D50 ranging from about 0.5-35 μm . Or, the copper cores have a particle size distribution D50 ranging from about 0.5-20 μm .

In one embodiment of the coated copper particles, the conductive oxide is selected from the group consisting of metal oxides, doped metal oxides, and combinations of two or more thereof.

10 In a further embodiment of the coated copper particles, the conductive oxide is selected from the group consisting of selected from the group consisting of antimony doped tin oxide (ATO), indium tin oxide (ITO), gallium doped zinc oxide (GZO), aluminum doped zinc oxide (AZO), fluorine doped tin oxide (FTO), and combinations of two or more thereof.

15 In a further embodiment of the coated copper particles, the copper cores that are surface coated with about 0.15-3 parts by weight of a coating composition, relative to 100 parts by weight of the copper particles.

Further provided herein is an electrically conductive adhesive comprising (a) organic binder, (b) the coated copper particles described above, and optional
20 (c) solvent.

In one embodiment of the electrically conductive adhesive, the weight ratio of the coated copper particles to the organic binder is in the range of about 95:5–70:30. Or, the weight ratio of the coated copper particles to the organic binder is in the range of about 95:5 – 75:25. Or, the weight ratio of the coated copper
25 particles to the organic binder is in the range of about 95:5 – 82:18.

In a further embodiment of the electrically conductive adhesive, the organic binder comprises an organic material selected from the group consisting of thermoset resins, thermoplastic resins, elastomers, and combinations of two or more thereof.

30 In a yet further embodiment of the electrically conductive adhesive, the organic binder further comprises at least one cross-linking agent.

In a yet further embodiment of the electrically conductive adhesive, the optional solvent is included at a balance amount.

Yet further provided herein is a bonded assembly comprising two substrates aligned in a spaced apart relationship, each of which having an inwardly facing surface and an outwardly facing surface, wherein, the inwardly facing surfaces of each of the two substrates are bonded by an electrically conductive bond, and wherein, the electrically conductive bond is formed by curing the electrically conductive adhesive described above.

Yet further provided herein is an article comprising the bonded assembly described above.

In one embodiment, the article is selected from the group consisting of electronic devices, integrated circuits, semiconductor devices, solar cells, and light emitting diodes.

Yet further provided herein is a method for forming a bonded assembly, which comprises: a) providing two substrates aligned in a spaced apart relationship, each of which having an inwardly facing surface and an outwardly facing surface; b) placing the electrically conductive adhesive described above between the inwardly facing surfaces of each of the two substrates; and c) curing the electrically conductive adhesive to form an electrically conductive bond between the two substrates.

DETAILED DESCRIPTION OF THE INVENTION

Disclosed herein are coated copper particles formed of copper cores that are surface coated with a coating composition comprising one or more conductive oxides. Further disclosed herein are electrically conductive adhesives (ECA) comprising: (a) organic binder, (b) surface coated copper particles, and optional (c) solvent.

Coated Copper Particles

The copper cores can be pure copper, or a copper alloy with nickel, silver, aluminum, zinc, tin, silicon, iron, manganese, germanium, boron, or mixture

thereof. Among them, copper alloys with zinc, tin, aluminum, silicon, or mixtures thereof are preferred. In those embodiments, wherein the copper core is in the form of a copper alloy, the copper alloy need to contain at least about 70 wt% copper in one embodiment, at least about 75 wt% copper in another embodiment, or at least about 80 wt% copper in yet another embodiment.

A skilled person would recognize that the choice of raw materials could unintentionally include impurities that may be incorporated into the copper core during processing. For example, the impurities may be present in the range of hundreds to thousands of parts per million. Impurities commonly occurring in industrial metals used herein are known to one of ordinary skill.

The copper cores used herein may be of any shape. For example, it can be spherical, flaky, or irregular in shape.

In one embodiment, the copper cores used herein are spherically shaped, or have an isometric shape, i.e. a shape, in which, generally speaking, the extension (particle size) is approximately the same in any direction. In particular, for a particle to be isometric, the ratio of the maximum and minimum length of chords intersecting the geometric center of the convex hull of the particle should not exceed the ratio of the least isometric regular polyhedron, i.e. the tetrahedron. Particle shapes are often times defined by aspect ratios, which is expressed by particle major diameter/particle thickness. In accordance with the present disclosure, such spherically shaped copper cores may have an aspect ratio ranging from about 1-3, or from about 1-2.

In a further embodiment, the copper cores used herein are flaky shaped. The flaky copper cores used herein may have an aspect ratio ranging from about 5-1000, or about 5-600, or about 5-200.

In addition, the copper cores used herein may have a particle size distribution (PSD) D50 from about 0.08-50 μm , or about 0.5-35 μm , or about 0.5-20 μm . Particle size distribution D50 is also known as the median diameter or the medium value of the particle size distribution, it is the value of the particle diameter at 50% in the cumulative distribution. For example, if D50=5.4 μm , then 50 volume% of the particles in the sample have an averaged diameter larger

than 5.4 μm , and 50 volume% of the particles have an averaged diameter smaller than 5.4 μm . Particle size distribution D50 of a group of particles can be determined using light scattering methods following, for example, ASTM B822-10.

The conductive oxides used herein may be metal oxides or doped metal oxides. By "doped metal oxides", it is meant that one element within the base metal oxides is partially replaced by a different element (also called doping agent or dopant). And the doping level is the amount of the dopant expressed as atom percentage, based on the total amount of the one element in the base metal oxide. In other words, in doped metal oxide " $\text{M}_x\text{O}_y : z \text{ at\% D}$ ", $z \text{ at\%}$ of element M or element O in the base metal oxide M_xO_y is replaced by D. For example, in SnO_2 : 10 at% Sb, 10 at% of Sn in base oxide SnO_2 was replaced by Sb, while in SnO_2 : 2 at% F, 2 at% of O in base oxide SnO_2 was replaced by F

In one embodiment, the conductive oxides used herein are doped metal oxides. For example, the metal oxides may be selected from tin oxide (SnO_2), zinc oxide (ZnO), indium oxide (In_2O_3), cadmium oxide (CdO), nickel oxide (NiO), chromium oxide (Cr_2O_3), molybdenum oxide (MoO_3), etc., while the doping agents may be selected from antimony, indium, gallium, fluorine, aluminum, lithium, iron, phosphorous, arsenic, boron, silicon, germanium, titanium, yttrium, zirconium, hafnium, scandium, etc. And, the doping level may be up to about 20 at%, or about 0.1-15 at%. Exemplary doped oxides useful herein may include, without limitation, antimony doped tin oxide (SnO_2 :Sb, or ATO), indium tin oxide (In_2O_3 :Sn, or ITO), gallium doped zinc oxide (ZnO :Ga, or GZO), aluminum doped zinc oxide (ZnO :Al, or AZO), fluorine doped tin oxide (SnO_2 :F, or FTO), and combinations of two or more thereof.

In accordance with the present disclosure, the copper cores may be surface coated with about 0.15-4.5 parts by weight or about 0.15-3 parts by weight of the coating composition, relative to 100 parts by weight of the spherical copper core. And the coating composition is attached to and covers at least about 50%, or at least about 60%, or at least about 80% of the surface area of the spherical copper cores. Also, the thickness of the coating composition over

the spherical copper cores may range from about 1-400 nm, or about 1-200 nm, or about 1-100 nm.

Further, in addition to the one or more conductive oxides, the coating composition may further contain other suitable materials, such as, metals, conductive or semi-conductive inorganic compounds (e. g. nitrides, carbides, sulfides, phosphides, germanides, selenides, etc.), conductive polymers (e.g. poly(p-phenylene vinylene) (PPV), poly(3,4-ethylenedioxythiophene) (PEDOT), etc.), non-metallic elementals (e.g. carbon, boron, phosphorus, sulfur, germanium, silicon, selenium, etc.).

The coated copper particles may be manufactured by any suitable process, for example, wet coating, dry coating, melt coating, encapsulation, vapor processing, plasma processing, or a combination of two or more of these techniques. The coating equipment includes fluidized-bed coater, spouted bed coater, wurster, rotating drum, pan and disc coater, fluidized bed reactor with chemical vapor deposition, and plasma enhanced chemical vapor deposition.

Worth mentioning is that prior to the coating process, it is preferred that the surface of the spherical copper cores are cleaned to remove surface oxides. Such cleaning process may include, without limitation, thermal annealing, chemical reaction, mechanical polishing, etc.

Organic Binders

In forming the ECA disclosed herein, the coated copper particles are dispersed in the matrix formed by organic binder. The organic binder may be any organic material or organic material composition with rheological properties that could provide stable dispersion of the coated particles, appropriate viscosity and thixotropy for applying the conductive adhesive to a substrate, appropriate wettability on the substrate, good adhesion to the substrate, and appropriate curing profile to meet proper processing conditions.

Suitable organic materials may be small molecules, oligomers, or polymers. For example, thermoset resins (e.g. epoxy, phenolic resin, polyimide, cyanate ester, silicone resin, maleimide, saturated polyester, etc.), thermoplastic

resins (e.g. acrylic, polyurethane, unsaturated polyester, etc.), or elastomers (e.g. fluoroelastomer, silicone rubber, natural rubber, butyl rubber, polyisobutylene rubber, etc.), or mixtures thereof, may be used herein.

The organic binders also may contain crosslinking agents. Suitable crosslinking agents may include, without limitation, phenol, amines, anhydrides, modified amines, polyfunctional aziridines, silicone epoxides, peroxides, aliphatic azo compound, ammonium carbonate, organosilane, etc.

The organic binders may further contain thickeners, stabilizers, surfactants, de-gas agents, and/or other common additives.

Solvent

In some embodiments, solvents also may be included in the ECA for improved filler dispersion and/or processability. Suitable solvents may include, without limitation, alcohol (e.g., ethanol), ketone (e.g., methyl isobutyl ketone, methyl ethyl ketone, diisobutyl ketone, or acetone), ether, esters, organic acids, amines, alkanes, benzenes, aldehydes, amides, and mixtures thereof. It is within any skilled person's ability to choose suitable solvents or solvent mixtures for the different binder systems.

Electrically Conductive Adhesives (ECA)

The ECA disclosed herein comprise (a) organic binder, (b) the surface coated copper particles (as described above), and optional (c) solvent.

In forming the ECA, the weight ratio of the surface coated copper particles to the organic binder may be in the range of about 95:5 – 70:30 in one embodiment, or about 95:5 – 75:25 in another embodiment, or about 95:5 – 82:18 in yet another embodiment.

In accordance with the present disclosure, the optional solvent may be included in a balance amount.

Further, the ECA disclosed herein may further comprise other suitable additives, such as, metal powders, conductive carbons (e.g. carbon black, graphene, carbon nanotubes, etc.), conductive polymers (e.g. poly(p-phenylene

vinylene) (PPV), poly(3,4-ethylenedioxythiophene) (PEDOT), etc.), conductive or semi-conductive inorganic compound powders (e. g. nitrides, carbides, sulfides, phosphides, germanides, selenides, etc.), non-metallic elements (e.g. boron, phosphorus, sulfur, germanium, silicon, selenium, etc.), coupling agents (e.g. silane), and insulating polymeric or inorganic powders.

The ECA may be prepared by any suitable process. For example, the ECA may be prepared by simply mixing and dispersing the surface coated copper particles in the organic binder or the organic binder with solvent.

10 Electrically Conductive Bonds and Articles comprising the Same

The ECA disclosed herein, when cured, can form electrically conductive bonds between two substrates. Such electrically conductive bonds provide electrically conductive connections between the two substrates.

The ECA disclosed herein can be cured by any suitable curing process, such as, thermal curing or radiation curing. For example, thermal curing may be conducted using infrared, laser, microwave, hot shoe, hot gas, flame, oven, induction, ultrasonic, resistance heating, thermal additive based heating, autoclave, vacuum laminator, etc., while radiation curing may be conducted using high energy electromagnetic radiation (e.g., gamma ray, X-ray, ultraviolet, accelerated electron beams, etc.). For example, the ECA disclosed herein may be cured in about 0.1 sec to 180 min at a temperature of about 20-250°C in one embodiment, or about 20-220°C in another embodiment, or about 20-200°C in yet another embodiment.

As demonstrated by the examples below, electrically conductive bonds formed by the ECA incorporating copper particles that are surface coated with conductive oxides exhibit very much increased conductivity, when compared to the electrically conductive bonds formed by ECA incorporating copper particles that are surface coated with silver, at comparable total loadings of the electrically conductive powders.

Thus, also disclosed herein are bonded assemblies comprising two substrates aligned in a spaced apart relationship, each of which having an

inwardly facing surface and an outwardly facing surface, wherein between the inwardly facing surfaces of each of the two substrates an electrically conductive bond is formed by the ECA disclosed herein.

Further disclosed herein are articles comprising such bonded assemblies, which include, without limitation, electronic devices, integrated circuits, semiconductor devices, solar cells, and light emitting diodes. The articles also may be other devices employing the ECA disclosed herein, which may be used in a wide variety of applications, including energy production, personal computers, control systems, telephone networks, automotive electronics, displays, semiconductor packages, passive devices, and handheld devices.

EXAMPLES

Electrically Conductive Particles:

- Cu(S)/Ag: spherical copper cores (D50=3.1-3.6 μm ; aspect ratio=1.05) that were surface coated with various loadings of silver. The particles were manufactured by Ningbo Guangbo New Nanomaterials Stock Co., Ltd. (China) using electroless plating process.
- Cu(S)/ATO: spherical copper cores (D50=5.4 μm ; aspect ratio=1.12) that were surface coated with various loadings of antimony doped tin oxide (ATO, SnO_2 : 10 at% Sb) nanoparticles (D50=20-40 nm) by dry coating process in a chamber protected by inert gas (with rotor speed of 5500 rpm and duration of 3 minutes). The spherical copper core particles were purchased from Mitsui Mining & Smelting Co., Ltd. (Japan), while the ATO nanoparticles were purchased from Hangzhou Wanjiang New Material Co., Ltd. (China).
- Cu(F)/ATO: flaky copper cores (D50=3.5 μm ; aspect ratio=10.45) that were surface coated with various loadings of ATO nanoparticles by dry coating process in a chamber protected by inert gas (with rotor speed of 5500 rpm and duration of 3 minutes). The flaky copper core particles were purchased from Mitsui Mining & Smelting Co., Ltd. (Japan).

- Cu(S)/ITO: spherical copper cores (D50=5.4 μm ; aspect ratio=1.12) that were surface coated with various loadings of indium doped tin oxide (ITO, In_2O_3 : 9 at% Sn) nanoparticles (D50=20-40 nm) by dry coating process in a chamber protected by inert gas (with rotor speed of 5500 rpm and duration of 3 minutes). The ITO nanoparticles were purchased from Hangzhou Wanjing New Material Co., Ltd. (China).
- Cu(S)/GZO: spherical copper cores (D50=5.4 μm ; aspect ratio=1.12) that were surface coated with various loadings of gallium doped zinc oxide (GZO, ZnO: 2.6 at% Ga) nanoparticles (D50=20-40 nm) by dry coating process in a chamber protected by inert gas (with rotor speed of 5500 rpm and duration of 3 minutes). The GZO nanoparticles were purchased from Forsman Scientific (Beijing) Co., Ltd.. (China).

Electrically Conductive Adhesives (ECA):

Various ECAs were prepared as follows: (i) compounding 80 g of Viton® GF 200S resin (a fluoroelastomer obtained from E.I. du Pont de Nemours and Company (U.S.A.) (hereafter "DuPont")), 20 g of Vamac® resin (an ethylene/methyl acrylate copolymer having a Mooney viscosity (ML1+4, 100°C) of 22, which was obtained from DuPont), 2 g of 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1.5 g of TAIC (triallyl isocyanurate, obtained from DuPont under the trade name Diak™ 7), 0.1 g of butylated hydroxytoluene, 0.1 g of 4,4'-Bis(α , α -dimethylbenzyl) diphenylamine (obtained from Chemtura Corp. (U.S.A.) under the trade name Naugard™ 445), 2 g of MgO in a two roll mill at room temperature for 20 minutes and dissolving 2 g of the above as-made mixture in 3 g of MIBK (methyl isobutyl ketone obtained from Sinopharm Chemical Reagent Co., Ltd. (China)) to form a solution; (ii) adding various amounts of the surface coated copper particles into the solution obtained from step (i); (iii) mixing the mixture by a mixer (manufactured by Thinky USA Inc. (U.S.A.) with the model name ARE-310) at 2000 rpm for 1 min; (iv) repeating the mixing step 2 more times to obtain the electrically conductive adhesive (ECA).

Measurement of Resistivity:

To determine the resistivity of the ECA as prepared above, the ECA was blade-cast on an insulating glass slide (25.4 x 76.2 x 1.2 mm) to form a 50-80 μm thick ECA bar (4 mm wide and 40 mm long); dried at 70°C for 1 min and 100°C
 5 for 5-10 min; and cured in vacuum laminator at about 145-165°C for about 30-60 min.

The sheet resistance of the cured ECA bar was measured by a four-probe method using a sheet resistivity meter (manufactured by Napson Corp. (Japan) with the model name QT-70/5601Y) and the thickness of the cured ECA bar was
 10 measured using a Veeco Surface Profiler (manufactured by Veeco Instruments Inc. with the model name Dektak XT). The resistivity of the cured ECA bar was calculated by the equation below and tabulated in Table 1:

$$\begin{aligned} \rho \text{ (Resistivity)} &= \text{sheet resistance} \times \text{thickness} \times \text{geometry correction} \\ &= \text{sheet resistance} \times \text{thickness} \times 3.2248/4.5324 \end{aligned}$$

15

As demonstrated herein, electrically conductive bonds formed by the ECA incorporating copper particles that are surface coated with conductive oxides (E1-E9) exhibit very increased conductivity, when compared to the electrically
 20 conductive bonds formed by ECA incorporating copper particles that are surface coated with silver (CE1), at comparable total loadings of the electrically conductive powders. It also demonstrated that the coating of the conductive oxides over the copper cores also affect the conductivity of the electrically conductivity bonds formed therefrom. That is the coating level needs to be
 25 maintained above 0.1 parts by weight and below 5 parts by weight, relative to 100 parts by weight of the copper cores.

Table 1

Samples	Coated Cu Particles (¹ coating ratio)	Weight Ratio of Coated Cu Particles:Binder	² Resistivity (ohm-cm)
CE1	Cu(S)/Ag (1.4 phr)	80:20	Over limit
CE2	Cu(S)/ATO (0.1 phr)	85:15	Over limit

E1	Cu(S)/ATO (0.2 phr)	85:15	6.86E-02
E2	Cu(S)/ATO (0.8 phr)	85:15	1.28E-02
E3	Cu(F)/ATO (0.8 phr)	85:15	4.07E-02
E4	Cu(S)/ATO (1.4 phr)	85:15	6.22E-02
E5	Cu(S)/ATO (2.5 phr)	85:15	9.39E-02
CE3	Cu(S)/ATO (5 phr)	85:15	Over limit
E6	Cu(S)/ATO (0.8 phr)	80:20	8.24E-01
E7	⁵ Cu(S)/ATO (1.4 phr)	80:20	1.03E+00
E8	Cu(S)/GZO (0.8 phr)	85:15	5.89E-02
E9	Cu(S)/ITO (0.8 phr)	85:15	1.32E-02

- ¹Coating Ratio was recorded using phr (per hundred rubber) value, or parts by weight of the coating material, relative to 100 parts by weight of the particle core;
- ²Resistivity was recorded as over limit when the resistivity was 1.0E+06 ohm or higher at 80-100 μ m thickness;
- 5 • ³The rotor speed was set at 7000 rpm when the coated particles were prepared.

WHAT IS CLAIMED IS:

1. Coated copper particles comprised of copper cores that are surface coated with about 0.15-4.5 parts by weight of a coating composition, relative to 100 parts by weight of the copper cores, and wherein, the coating composition comprises at least one conductive oxide.
2. The coated copper particles of Claim 1, wherein, the copper cores have a particle size distribution D50 ranging from about 0.08-50 μm .
3. The coated copper particles of Claim 2, wherein, the copper cores have a particle size distribution D50 ranging from about 0.5-35 μm .
4. The coated copper particles of Claim 3, wherein, the copper cores have a particle size distribution D50 ranging from about 0.5-20 μm .
5. The coated copper particles of Claim 1, wherein, the at least one conductive oxide is selected from the group consisting of metal oxides, doped metal oxides, and combinations of two or more thereof.
6. The coated copper particles of Claim 5, wherein, the at least one conductive oxide is selected from the group consisting of selected from the group consisting of antimony doped tin oxide (ATO), indium tin oxide (ITO), gallium doped zinc oxide (GZO), aluminum doped zinc oxide (AZO), fluorine doped tin oxide (FTO), and combinations of two or more thereof.
7. The coated copper particles of Claim 1, wherein, the copper cores are surface coated with about 0.15-3 parts by weight of the coating composition, relative to 100 parts by weight of the copper cores.

8. An electrically conductive adhesive comprising (a) organic binder, (b) the coated copper particles recited in any one of Claims 1-7, and optional (c) solvent.
- 5 9. The electrically conductive adhesive of Claim 8, wherein, the weight ratio of the coated copper particles to the organic binder is in the range of about 95:5– 70:30.
- 10 10. The electrically conductive adhesive of Claim 9, wherein, the weight ratio of the coated copper particles to the organic binder is in the range of about 95:5 – 75:25.
- 15 11. The electrically conductive adhesive of Claim 10, wherein, the weight ratio of the coated copper particles to the organic binder is in the range of about 95:5 – 82:18.
- 20 12. The electrically conductive adhesive of Claim 8, wherein, the organic binder comprises an organic material selected from the group consisting of thermoset resins, thermoplastic resins, elastomers, and combinations of two or more thereof.
- 25 13. The electrically conductive adhesive of Claim 12, wherein, the organic binder further comprises at least one cross-linking agent.
- 30 14. The electrically conductive adhesive of Claim 8, wherein the optional solvent is included at a balance amount.
15. A bonded assembly comprising two substrates aligned in a spaced apart relationship, each of which having an inwardly facing surface and an outwardly facing surface, wherein, the inwardly facing surfaces of each of the two substrates is bonded by an electrically conductive bond, and

wherein, the electrically conductive bond is formed by curing the electrically conductive adhesive recited in any one of Claim 8-14.

16. An article comprising the bonded assembly of Claim 15.

5

17. The article of Claim 16, which is selected from the group consisting of electronic devices, integrated circuits, semiconductor devices, solar cells, and light emitting diodes.

10

18. A method for forming a bonded assembly comprising:

a) providing two substrates aligned in a spaced apart relationship, each of which having an inwardly facing surface and an outwardly facing surface;

15

b) placing the electrically conductive adhesive recited in any one of Claims 8-14 between the inwardly facing surfaces of each of the two substrates; and

c) curing the electrically conductive adhesive to form electrically conductive bond between the two substrates.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2015/088444

A. CLASSIFICATION OF SUBJECT MATTER

C09J 9/00(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)

C09J 9/-

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

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

EPODOC;WPI;CNPAT;CNKI;CA:E.I.DO PONT,MU Minfang,FENG Dan,RODRIGUEZ-PARADA Jose M,copper particle, conductive oxide,doped metal oxide,organic binder,conductive adhesive,electronic device,integrated circuit,semiconductor device,solar cell, light emitting diode

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2014/140430 A2 (INKRON LTD. ET AL) 18 September 2014 (2014-09-18) Page 21 paragraph 6, Page 22 paragraph 1, claims 3、 5、 6、 13	1-14
Y	WO 2014/140430 A2 (INKRON LTD. ET AL) 18 September 2014 (2014-09-18) Page 21 paragraph 6, Page 22 paragraph 1, claims 3、 5、 6、 13	15-18
Y	US 2013/0224474 A1 (HENKEL AG & CO. KGAA) 29 August 2013 (2013-08-29) Page 7 paragraphs [0105]、 [0108]	15-18
A	CN 102723121 A (ETERNAL CHEM CO., LTD.) 10 October 2012 (2012-10-10) Page 2 paragraph [0007]	1-18



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

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“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

16 May 2016

Date of mailing of the international search report

26 May 2016

Name and mailing address of the ISA/CN

STATE INTELLECTUAL PROPERTY OFFICE OF THE
P.R.CHINA
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088, China

Authorized officer

KONG, Deming

Facsimile No. (86-10)62019451

Telephone No. (86-10)61648524

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2015/088444

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)	
WO	2014/140430	A2	18 September 2014	EP	2971231	A2	20 January 2016
				US	2014264191	A1	18 September 2014
				FI	20135253	A	16 September 2014
				WO	2014140430	A3	30 April 2015
US	2013/0224474	A1	29 August 2013	WO	2012107556	A2	16 August 2012
				CN	103347974	A	09 October 2013
				EP	2673330	B1	19 November 2014
				JP	2014510803	A	01 May 2014
				WO	2012107556	A3	11 October 2012
				KR	20140048843	A	24 April 2014
				EP	2487215	B1	24 July 2013
				EP	2673330	A2	18 December 2013
				EP	2487215	A1	15 August 2012
				TW	201233764	A	16 August 2012
CN	102723121	A	10 October 2012	CN	102723121	B	18 March 2015
				TW	201319213	A	16 May 2013
				TW	I432551	B	01 April 2014