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(57) Abstract: A wire comprising a wire core with a surface, the wire core having a coating layer superimposed on its surface, wherein the wire core itself consists of a material selected from the group consisting of pure copper, doped copper with a copper content of >99.8 wt.-% and copper alloys with a copper content of at least 98 wt.-%, wherein all amounts in wt.-% are based on the total weight of the core, and wherein the coating layer is a triple-layer comprised of a 1 to 100 nm thick inner layer of gold, a 25 to 300 nm thick intermediate layer of palladium and a 1 to 50 nm thick outer layer of gold.



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## Coated Wire

The invention relates to a coated wire comprising a copper or copper-based wire core and a coating layer superimposed on the surface of the core. The invention further relates to a process for manufacturing such coated wire.

5

The use of bonding wires in electronics and microelectronics applications is well-known state of the art. While bonding wires were made from gold in the beginning, nowadays less expensive materials are used such as copper, copper alloys, silver and silver alloys. Such wires may have a metal coating. For example, WO 2017/123153 A2  
10 discloses bonding wires having a wire core of a copper alloy the wire core having a double-layered coating of an inner palladium and an outer gold coating layer.

With respect to wire geometry, most common are bonding wires of circular cross-section and bonding ribbons which have a more or less rectangular cross-section. Both  
15 types of wire geometries have their advantages making them useful for specific applications.

In the course of wire bonding it is typical that a ball bond (1<sup>st</sup> bond) and a stitch bond (2<sup>nd</sup> bond, wedge bond) are formed. During bond forming a certain force (typically  
20 measured in grams) is applied, supported by application of ultrasonic energy (typically measured in mA). The mathematical product of the difference between the upper and the lower limits of the applied force and the difference between the upper and the lower limits of the applied ultrasonic energy in a wire bonding process defines the wire bonding process window:

25

*(Upper limit of applied force - Lower limit of applied force) · (Upper limit of applied ultrasonic energy - Lower limit of applied ultrasonic energy) = Wire bonding process window.*

30

The wire bonding process window defines the area of force/ultrasonic energy combinations which allow formation of a wire bond that meets specifications, i.e. which

passes the conventional tests like conventional pull tests, ball shear test and ball pull test to name only few.

The stitch bond process window area is the product of the difference between the upper and the lower limits of the force used in the stitch bonding and the difference between the upper and the lower limits of the applied ultrasonic energy, wherein the resulting bond has to meet certain pull test specifications, e.g. a pull force of 2 grams, no non-stick on lead, etc.

For industrial applications it is desirable to have a wide wire bonding process window (force in g versus ultrasonic energy in mA) for reasons of wire bonding process robustness. A wide wire bonding process window is desired for ball bonding as well as stitch bonding.

It is an object of the invention to provide a wire having a copper or copper-based wire core with some sort of palladium coating. The wire shall be suitable for use in wire bonding applications, the wire being improved in particular in FAB (free air ball) sphericity (formation of axi-symmetrical FAB) and palladium coverage of the FAB. The wire shall have a wide stitch bonding window.

The term "axi-symmetrical FAB" is used herein. It means a solidified spherical FAB which does not show any of the following defects:

- pointed tip (outflow of molten metal at the FAB tip),
- apple-bite tip (inflow of molten metal at the FAB tip),
- peach tip (two plateaus with distinct hemisphere at FAB tip),
- FAB tilted from wire axis with an angle of less than 5 °, preferably  $\leq 1^\circ$ .

The term "spherical FAB" is used herein. It shall not be understood absolute; rather, it shall be understood to include FAB of true spherical shape as well as FAB of essentially spherical shape, i.e. FAB exhibiting an aspect ratio (quotient of the longest and the shortest diagonal (or diameter) along the FAB radial axes) in the range of from 1:1 (true spherical) to 1.1:1 (essentially spherical).

The skilled person knows that good FAB sphericity is an important precondition for preventing the occurrence of an undesired OCB (off-center-ball) phenomenon during ball bonding.

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The term “palladium coverage” is used herein. It refers to the palladium coverage on the copper FAB from the neck of the wire to the FAB tip and it is expressed as percentage of surface covered. It can be determined by cross-sectioning the FAB, followed by EDX dot mapping (energy dispersive X-ray analysis dot mapping) of a unit attached to SEM  
10 (scanning electron microscopy), followed by calculating the % of Pd spread-over on the copper FAB using the circle method or the angle method by the software IMAGE analyzer (SmartSEM Version 5.0.5 & Stream Basic 1.7).

A contribution to the solution of the aforementioned object is provided by the subject-matter of the category-forming claims. The dependent sub-claims of the category-forming claims represent preferred embodiments of the invention, the subject-matter of  
15 which also makes a contribution to solving the objects mentioned above.

In a first aspect, the invention relates to a wire comprising a wire core (hereinafter also  
20 called “core” for short) with a surface, the wire core having a coating layer superimposed on its surface, wherein the wire core itself consists of a material selected from the group consisting of pure copper, doped copper with a copper content of >99.8 wt.-% (weight-%, % by weight) and copper alloys with a copper content of at least 98 wt.-%, wherein all amounts in wt.-% are based on the total weight of the core, and  
25 wherein the coating layer is a triple-layer comprised of a 1 to 100 nm thick inner layer of gold, a 25 to 300 nm thick intermediate layer of palladium and a 1 to 50 nm thick outer layer of gold.

The wire used in the process of the invention is a bonding wire for bonding in  
30 microelectronics. It is preferably a one-piece object. Numerous wire shapes are possible. Preferred shapes are – in cross-sectional view – round, ellipsoid and rectangular shapes. The term “wire” or “bonding wire” used herein comprises all shapes

of cross-sections and all usual wire diameters, though bonding wires with circular cross-section and thin diameters are preferred. The average cross-section is in the range of for example from 50 to 5024  $\mu\text{m}^2$  or preferably 110 to 2400  $\mu\text{m}^2$ ; accordingly in case of the preferred circular cross-sections, the average diameter is in the range of, for  
5 example, 8 to 80  $\mu\text{m}$  or preferably 12 to 55  $\mu\text{m}$ .

The average diameter or, simply stated, the diameter of a wire or wire core can be determined by the "sizing method". According to this method the physical weight of the wire for a defined length is determined. Based on this weight, the diameter of a wire or  
10 wire core is calculated using the density of the wire material. The diameter is calculated as arithmetic mean of five measurements on five cuts of a particular wire.

It is important that the wire comprises a wire core with a surface, the wire core having a triple-layered coating superimposed on its surface, wherein the wire core itself consists  
15 of a material selected from the group consisting of pure copper, doped copper with a copper content of >99.8 wt.-% and copper alloys with a copper content of at least 98 wt.-%, wherein all amounts in wt.-% are based on the total weight of the core, and wherein the triple-layered coating is comprised of a 1 to 100 nm thick inner layer of gold, a 25 to 300 nm thick intermediate layer of palladium and an 1 to 50 nm thick outer layer  
20 of gold. For brevity, this coated wire is also called "wire" herein for short.

The term "pure copper" is used herein. It shall mean copper having a purity in the range of from 99.95 to 100 wt.-%. It may comprise further components (components other than copper) in a total amount of up to 500 wt.-ppm (weight-ppm, ppm by weight).  
25

The term "doped copper" is used herein. It shall mean a copper type consisting of copper in an amount in the range of from >99.8 to 99.997 wt.-% and at least one doping element (dopant) in a total amount of up to <2000 wt.-ppm, for example, of from 30 to <2000 wt.-ppm. It may comprise further components (components other than copper and the at least one doping element) in a total amount of up to 500 wt.-ppm.  
30

The term “copper alloy” is used herein. It shall mean an alloy consisting of copper in an amount in the range of from 98 to 99.8 wt.-% and at least one alloying element in a total amount of from 0.2 to 2 wt.-%. It may comprise at least one doping element (other than the at least one alloying element) in a total amount of up to <2000 wt.-ppm, for example, of from 30 to <2000 wt.-ppm. It may comprise further components (components other than copper, the at least one alloying element and the at least one doping element) in a total amount of up to 500 wt.-ppm.

Examples of preferred alloying elements include palladium, gold, nickel, platinum and, in particular, silver.

Examples of preferred doping elements include nickel, platinum, palladium, gold, silver, aluminium, magnesium and, in particular, phosphorus.

As already mentioned, the core of the wire may comprise so-called further components in a total amount of up to 500 wt.-ppm. The further components, often also referred as “inevitable impurities”, are minor amounts of chemical elements and/or compounds which originate from impurities present in the raw materials used or from the wire manufacturing process. The low total amount of 0 to 500 wt.-ppm of the further components ensures a good reproducibility of the wire properties. Further components present in the core are usually not added separately. Each individual further component may be comprised in an amount of less than 30 wt.-ppm, preferably less than 15 wt.-ppm, based on the total weight of the wire core.

In line with the aforementioned, the wire core consists of pure copper, of doped copper, or of a copper alloy.

In a preferred embodiment, the wire core consists of a copper alloy. It is preferred that such copper alloy comprises  $\geq 0.2$  wt.-% or even  $\geq 0.5$  wt.-% of silver as an alloying element and most preferably it comprises also 40 to 85 wt.-ppm or even 70 to 85 wt.-ppm of phosphorus as dopant. In a most preferred embodiment, the wire core consists of a copper alloy, in particular of a copper alloy comprising  $\geq 0.2$  wt.-% or even  $\geq 0.5$  wt.-

% of silver as one single alloying element and most preferably also comprising 40 to 85 wt.-ppm or even 70 to 85 wt.-ppm of phosphorus as one single dopant; i.e. it is most preferred that the copper alloy consists of copper and  $\geq 0.2$  wt.-% or even  $\geq 0.5$  wt.-% of alloying silver and, in particular also of 40 to 85 wt.-ppm or even 70 to 85 wt.-ppm of phosphorus as dopant. In accordance with the disclosure above, the silver content of such copper alloy cannot exceed an upper limit of 2 wt.-% and the preferred upper limit is 1.5 wt.-% for the alloying silver. To summarize it in other words, the following embodiments are preferred and are listed in the order of preference and ascending numbering:

1. The copper alloy comprises  $\geq 0.2$  wt.-% of silver as alloying element.
2. The copper alloy comprises  $\geq 0.2$  wt.-% of silver as alloying element and 40 to 85 wt.-ppm of phosphorus as dopant.
3. The copper alloy consists of copper and  $\geq 0.2$  wt.-% of silver as alloying element.
4. The copper alloy consists of copper,  $\geq 0.2$  wt.-% of silver as alloying element and 40 to 85 wt.-ppm of phosphorus as dopant.

The skilled person will understand that the afore disclosed preferences regarding lower and upper wt.-% and wt.-ppm levels do apply for these four embodiments.

The core of the wire is a homogeneous region of bulk material. Since any bulk material always has a surface region which might exhibit different properties to some extent, the properties of the core of the wire are understood as properties of the homogeneous region of bulk material. The surface of the bulk material region can differ in terms of morphology, composition (e.g. sulfur, chlorine and/or oxygen content) and other features. The surface is an interface region between the wire core and the triple-layered coating superimposed on the wire core. Typically, the triple-layered coating is completely superimposed on the wire core's surface. In the region of the wire between its core and the triple-layered coating superimposed thereon a combination of materials of both, the core and the triple-layered coating, can be present.

The triple-layered coating superimposed on the surface of the wire is comprised of a 1 to 100 nm thick inner layer of gold, a 25 to 300 nm thick intermediate layer of palladium and a 1 to 50 nm thick outer layer of gold. Preferably, the triple-layered coating

superimposed on the surface of the wire is comprised of a 2 to 10 nm thick inner layer of gold, a 50 to 100 nm thick intermediate layer of palladium and a 2 to 10 nm thick outer layer of gold. In this context the term “thick” or “coating layer thickness” means the size of the coating layer in perpendicular direction to the longitudinal axis of the core.

5

The inner layer of gold may account for 0.04 to 4.2 wt.-% of the triple-coated wire. The intermediate layer of palladium may account for 0.5 to 7.6 wt.-% of the triple-coated wire. The outer layer of gold may account for 0.04 to 4.2 wt.-% of the triple-coated wire.

10 In case of a wire core diameter of, for example, 20  $\mu\text{m}$  the triple-layered coating may be comprised of a 1 to 20 nm thick inner layer of gold, a 25 to 120 nm thick intermediate layer of palladium and a 1 to 5 nm thick outer layer of gold. With increasing wire core diameter said coating layers' thickness ranges will typically also increase within the aforesaid ranges.

15

Concerning the composition of said triple-layered coating, the gold content of its inner and its outer layer is, for example, at least 50 wt.-%, preferably at least 95 wt.-%, based on the total weight of the respective gold coating layer. Particularly preferred, the inner and the outer coating layer consists of pure gold. Pure gold usually has less than 1 wt.-% of further components (components other than the gold), based on the total weight of the respective gold coating layer. The palladium content of the intermediate layer is, for example, at least 50 wt.-%, preferably at least 95 wt.-%, based on the total weight of the intermediate layer. Particularly preferred, the intermediate layer consists of pure palladium. Pure palladium usually has less than 1 wt.-% of further components (components other than palladium), based on the total weight of the intermediate layer.

20

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In another aspect, the invention relates also to a process for the manufacture of the triple-coated wire of the invention in any of its embodiments disclosed above. The process comprises at least the steps (1) to (5):

30

(1) providing a precursor item consisting of a material of the desired wire core composition, i.e. a wire core composition as desired and selected accordingly among the afore disclosed embodiments,

(2) elongating the precursor item to form an elongated precursor item, until an intermediate cross-section in the range of from 7850 to 49063  $\mu\text{m}^2$  or an intermediate diameter in the range of from 100 to 250  $\mu\text{m}$ , preferably 130 to 140  $\mu\text{m}$  is obtained, (3) depositing a triple-layered coating of an inner layer (base layer) of gold, an intermediate layer of palladium and an outer layer (top layer) of gold on the surface of the elongated precursor item obtained after completion of process step (2), (4) further elongating the triple-coated precursor item obtained after completion of process step (3) until a desired final cross-section or diameter is obtained, and (5) finally strand annealing the triple-coated precursor obtained after completion of process step (4) at an oven set temperature in the range of from 200 to 600 °C for an exposure time in the range of from 0.4 to 0.8 seconds to form the triple-coated wire.

The term “strand annealing” is used herein. It is a continuous process allowing for a fast production of a wire with high reproducibility. In the context of the invention, strand annealing means that the annealing is done dynamically while the coated precursor to be annealed is pulled or moved through a conventional annealing oven and spooled onto a reel after having left the annealing oven. Here, the annealing oven is typically in the form of a cylindrical tube of a given length. With its defined temperature profile at a given annealing speed which may be chosen in the range of, for example, from 10 to 60 meters/minute the annealing time/oven temperature parameters can be defined and set.

The term “oven set temperature” is used herein. It means the temperature fixed in the temperature controller of the annealing oven. The annealing oven may be a chamber furnace type oven (in case of batch annealing) or a tubular annealing oven (in case of strand annealing).

This disclosure distinguishes between precursor item, elongated precursor item, triple-coated precursor item, triple-coated precursor and triple-coated wire. The term “precursor item” is used for those wire pre-stages which have not reached the desired final cross-section or final diameter of the wire core, while the term “precursor” is used for a wire pre-stage at the desired final cross-section or the desired final diameter. After completion of process step (5), i.e. after the final strand annealing of the triple-coated

precursor at the desired final cross-section or the desired final diameter a triple-coated wire in the sense of the invention is obtained.

The precursor item as provided in process step (1) may consist of pure copper.

- 5 Typically, such precursor item is in the form of a rod having a diameter of, for example, 2 to 25 mm and a length of, for example, 2 to 100 m. Such copper rod can be made by continuous casting copper using an appropriate mold, followed by cooling and solidifying.
- 10 In the alternative, the precursor item as provided in process step (1) may consist of doped copper or of a copper alloy, as disclosed above for the wire core composition. Such precursor items can be obtained by alloying, doping or alloying and doping copper with the desired amount of the required components. The doped copper or copper alloy can be prepared by conventional processes known to the person skilled in the art of
- 15 metal alloys, for example, by melting together the components in the desired proportional ratio. In doing so, it is possible to make use of one or more conventional master alloys. The melting process can for example be performed making use of an induction furnace and it is expedient to work under vacuum or under an inert gas atmosphere. The melt so-produced can be cooled to form a homogeneous piece of
- 20 copper based precursor item. Typically, such precursor item is in the form of a rod having a diameter of, for example, 2 to 25 mm and a length of, for example, 2 to 100 m. Such rod can be made by continuous casting said doped copper or (doped) copper alloy melt using an appropriate mold, followed by cooling and solidifying.
- 25 In process step (2) the precursor item is elongated to form an elongated precursor item, until an intermediate cross-section in the range of from 7850 to 49000  $\mu\text{m}^2$  or an intermediate diameter in the range of from 100 to 250  $\mu\text{m}$ , preferably 130 to 140  $\mu\text{m}$  is obtained. Techniques to elongate a precursor item are known. Preferred techniques are rolling, swaging, die drawing or the like, of which die drawing is particularly preferred. In
- 30 the latter case the precursor item is drawn in several process steps until the desired intermediate cross-section or the desired intermediate diameter is reached. Such wire die drawing process is well known to the person skilled in the art. Conventional tungsten

carbide and diamond drawing dies may be employed and conventional drawing lubricants may be employed to support the drawing.

- 5 Step (2) may include one or more sub-steps of intermediate batch annealing of the elongated precursor item at an oven set temperature in the range of from 400 to 800 °C for an exposure time in the range of from 50 to 150 minutes. The intermediate batch annealing may be performed, for example, with a rod drawn to a diameter of about 2 mm and coiled on a drum.
- 10 The optional intermediate batch annealing of process step (2) may be performed under an inert or reducing atmosphere. Numerous types of inert atmospheres as well as reducing atmospheres are known in the art and are used for purging the annealing oven. Of the known inert atmospheres, nitrogen or argon is preferred. Of the known reducing atmospheres, hydrogen is preferred. Another preferred reducing atmosphere
- 15 is a mixture of hydrogen and nitrogen. Preferred mixtures of hydrogen and nitrogen are 90 to 98 vol.-% nitrogen and, accordingly, 2 to 10 vol.-% hydrogen, wherein the vol.-% total 100 vol.-%. Preferred mixtures of nitrogen/hydrogen are equal to 90/10, 93/7, 95/5 and 97/3 vol.-%/vol.-%, each based on the total volume of the mixture.
- 20 In process step (3) a triple-layered coating comprised of an inner layer (base layer) of gold, an intermediate layer of palladium and an outer layer (top layer) of gold is deposited on the surface of the elongated precursor item obtained after completion of process step (2) so as to superimpose the triple-layered coating over said surface.
- 25 The skilled person knows how to calculate the thickness of such triple-layered coating on an elongated precursor item to finally obtain the triple-layer coating in the layer thickness disclosed for the embodiments of the wire, i.e. after finally elongating the triple-layer coated precursor item. The skilled person knows numerous techniques for forming a triple-layered gold-palladium-gold coating according to the embodiments on a
- 30 copper or copper alloy surface. Preferred techniques are plating, such as electroplating and electroless plating, deposition of the material from the gas phase such as

sputtering, ion plating, vacuum evaporation and physical vapor deposition, and deposition of the material from the melt. Electroplating is the preferred technique.

In process step (4) the triple-layer coated precursor item obtained after completion of process step (3) is further elongated until the desired final cross-section or diameter of the wire is obtained. Techniques to elongate the triple-layer coated precursor item are the same elongation techniques like those mentioned above in the disclosure of process step (2).

In process step (5) the triple-layer coated precursor obtained after completion of process step (4) is finally strand annealed at an oven set temperature in the range of from 200 to 600 °C, preferably 200 to 400 °C for an exposure time in the range of from 0.4 to 0.8 seconds to form the triple-layer coated wire.

In a preferred embodiment, the finally strand annealed triple-layer coated precursor, i.e. the still hot triple-layer coated wire is quenched in water which, in an embodiment, may contain one or more additives, for example, 0.01 to 0.07 volume-% of additive(s). The quenching in water means immediately or rapidly, i.e. within 0.2 to 0.6 seconds, cooling the finally strand annealed triple-layer coated precursor from the temperature it experienced in process step (v) down to room temperature, for example by dipping or dripping.

After completion of process step (5) and the optional quenching the triple-layer coated wire is finished. In order to fully benefit from its properties, it is expedient to either use it immediately for wire bonding applications, i.e. without delay, for example, within no longer than 28 days after completion of process step (5), i.e. without delay, for example, within <1 to 5 hours after completion of process step (5) and then stored for further use as bonding wire. Storage in vacuum sealed condition should not exceed 12 months. After opening the vacuum seal the wire should be used for wire bonding within no longer than 28 days.

It is preferred that all process steps (1) to (5) as well as spooling and vacuum sealing are carried out under clean room conditions (US FED STD 209E cleanroom standards, 1k standard).

- 5 The following non-limiting examples illustrate the invention. These examples serve for exemplary elucidation of the invention and are not intended to limit the scope of the invention or the claims in any way.

### Examples

10

Preparation of free air ball (FAB):

- It was worked according to the procedures described in the KNS Process User Guide for FAB (Kulicke & Soffa Industries Inc, Fort Washington, PA, USA, 2002, 31 May 2009). FAB was prepared by performing conventional electric flame-off (EFO) firing by standard firing (single step, 17.8  $\mu\text{m}$  wire, EFO current of 50 mA, EFO time 200  $\mu\text{s}$ , under 95 vol.-% nitrogen/5 vol.-% hydrogen atmosphere).

### Test methods

- All tests and measurements were conducted at  $T = 20\text{ }^{\circ}\text{C}$  and a relative humidity  $\text{RH} = 50\text{ }\%$ .

#### A. FAB morphology

The formed FAB was examined by scanning electron microscope (SEM) with a magnification of 1000.

- 25 Evaluation:

++, very good (round ball)

+, good (round ball);

0, acceptable (not perfectly round, but no obvious plateau on the FAB surface);

-, peach ball

- 30 --, severe peach ball

The term "peach ball" used herein shall mean formation of two plateaus with distinct hemisphere at FAB tip.

### B. Bonded Ball Shape

The formed FAB descended to a Al-0.5wt.-%Cu bond pad from a predefined height (tip of 203.2  $\mu\text{m}$ ) and speed (contact velocity of 6.4  $\mu\text{m}/\text{sec}$ ). Upon touching the bond pad, a set of defined bonding parameters (bond force of 100 g, ultrasonic energy of 95 mA and bond time of 15 ms) took into effect to deform the FAB and formed the bonded ball.

After forming the ball, the capillary rose to a predefined height (kink height of 152.4  $\mu\text{m}$  and loop height of 254  $\mu\text{m}$ ) to form the loop. After forming the loop, the capillary descended to the lead to form the stitch. After forming the stitch, the capillary

the wire clamp closed to cut the wire to make the predefined tail length (tail length extension of 254  $\mu\text{m}$ ). For each sample five bonded wires were optically inspected using a microscope with a magnification of 1000.

Evaluation:

++, perfectly round;

+, round;

0, acceptable;

-, flowery.

### C. Off center ball (OCB)

The same method as described in Method B was applied, but instead of inspecting the roundness of the ball, the centricity of the ball was determined. For each sample 2000 bonded wires were optically inspected.

Evaluation:

++, perfect centered

+, centered;

0, acceptably off-centered;

-, off-centered;

--, very off-centered.

### D. Pd distribution on the FAB

The FAB was first potted using cold-mounting epoxy, cross-sectioned by standard metallographic techniques. A multi-prep semi-automatic polisher was used with low force and optimal speed to grind and polish the sample with minimum deformation strain

on the sample surface. Finally the polished sample was EDX dot mapped (energy dispersive X-ray analysis dot mapping) of a unit attached to SEM (scanning electron microscopy), followed by calculating the % of Pd spread-over on the copper FAB using the circle method or the angle method by the software IMAGE analyzer, (SmartSEM  
5 Version 5.0.5 & Stream Basic 1.7) with a magnification of about 1000. Method E is preferred than method D. For each sample five FABs were optically inspected.

Visual evaluation:

+++, Pd almost homogeneously covers the FAB shell with Pd coverage  $\geq 90$  % of FAB height;

10 ++, Pd very homogeneously covers the FAB shell with Pd coverage  $\geq 80$  % of FAB height;

+, Pd homogeneously covers the FAB shell with Pd coverage  $\geq 70$  % of FAB height;

0, Pd partially covers the FAB shell and diffuses partially into the ball with Pd coverage of FAB height between 50 and 70%;

15 -, major diffusion of Pd into the ball with formation of Cu-Pd alloy, with Pd coverage of FAB height  $\leq 50$ %;

-- major diffusion of Pd into the ball with formation of Cu-Pd alloy, with Pd coverage of FAB height  $\leq 30$ %.

20 Comparative wire sample 1:

A quantity of copper and phosphorus of at least 99.99 % purity ("4N") each was melted in a crucible in a vacuum oven at about 1200°C. Then a wire core precursor item in the form of a 8 mm rod was continuous cast from the melt. The rod was then drawn in several drawing steps to form a wire core precursor having a circular cross-section with  
25 a diameter of 200  $\mu\text{m}$ . The wire core precursor was electroplated with a double layer coating consisting of a 700 nm thick inner palladium layer and a 30 nm thick outer gold layer and thereafter further drawn to a final diameter of 17.8  $\mu\text{m}$  with a final palladium coating layer thickness of 75 nm and final gold coating layer thickness of 4 nm, followed by a final strand annealing at an oven set temperature of 530 °C for an exposure time of  
30 0.8 seconds, immediately followed by quenching the so-obtained coated wire in water containing 500 wt.-ppm of surfactant.

Inventive wire samples 1 to 8:

A quantity of copper, silver and phosphorus of at least 99.99 % purity ("4N") each were melted in a crucible in a vacuum oven at about 1200°C. Then a wire core precursor item in the form of 8 mm rods was continuous cast from the melt. The rods were then drawn  
5 in several drawing steps to form a wire core precursor having a circular cross-section with a diameter of 200 µm. The wire core precursor was electroplated with a triple layer coating consisting of a 30 nm thick inner gold layer, a 700 nm thick intermediate palladium layer and a 30 nm thick outer gold layer and thereafter further drawn to a final  
10 diameter of 17.8 µm with a final palladium coating layer thickness of 75 nm and final gold coating layer thicknesses of 4 nm, followed by a final strand annealing at an oven set temperature of 530 °C for an exposure time of 0.8 seconds, immediately followed by quenching the so-obtained coated wires in water containing 500 wt.-ppm of surfactant.

Table 1 shows the composition of the wire cores.

| Table 1 |                                                         |
|---------|---------------------------------------------------------|
| Sample: | Wire core composition:                                  |
| Ref1    | Cu doped with 75 wt.-ppm P                              |
| 1       | Cu doped with 75 wt.-ppm P                              |
| 2       | Cu alloyed with 0.1 wt.% Ag and doped with 75 wt.-ppm P |
| 3       | Cu alloyed with 0.2 wt.% Ag, not doped with P           |
| 4       | Cu alloyed with 0.2 wt.% Ag and doped with 40 wt.-ppm P |
| 5       | Cu alloyed with 0.2 wt.% Ag and doped with 75 wt.-ppm P |
| 6       | Cu alloyed with 0.3 wt.% Ag and doped with 75 wt.-ppm P |
| 7       | Cu alloyed with 0.4 wt.% Ag and doped with 75 wt.-ppm P |
| 8       | Cu alloyed with 0.5 wt.% Ag and doped with 75 wt.-ppm P |

Table 2 below shows certain test results.

| Table 2                    |        |    |    |    |    |    |    |    |     |
|----------------------------|--------|----|----|----|----|----|----|----|-----|
|                            | Sample |    |    |    |    |    |    |    |     |
|                            | Ref1   | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8   |
| FAB morphology             | ++     | ++ | ++ | +  | +  | ++ | ++ | ++ | ++  |
| Bonded ball shape          | ++     | ++ | ++ | +  | +  | ++ | ++ | ++ | ++  |
| OCB                        | ++     | ++ | ++ | +  | ++ | ++ | ++ | ++ | ++  |
| Pd distribution on the FAB | +      | +  | ++ | ++ | ++ | ++ | ++ | ++ | +++ |
| Stitch bond window (mA·g)  | ++     | ++ | ++ | ++ | ++ | ++ | ++ | ++ | ++  |

5 +GOOD, ++ VERY GOOD, +++ EXCELLENT

**CLAIMS**

1. A wire comprising a wire core with a surface, the wire core having a coating layer superimposed on its surface, wherein the wire core itself consists of a material selected from the group consisting of pure copper, doped copper with a copper content of >99.8 wt.-% and copper alloys with a copper content of at least 98 wt.-%, wherein all amounts in wt.-% are based on the total weight of the core, and wherein the coating layer is a triple-layer comprised of a 1 to 100 nm thick inner layer of gold, a 25 to 300 nm thick intermediate layer of palladium and a 1 to 50 nm thick outer layer of gold.
2. The wire of claim 1 having an average cross-section in the range of 50 to 5024  $\mu\text{m}^2$ .
3. The wire of claim 1 or 2 having a circular cross-section with an average diameter in the range of 8 to 80  $\mu\text{m}$ .
4. The wire of any one of claims 1 to 3, wherein the wire core consists of a copper alloy comprising  $\geq 0.2$  wt.-% of silver as alloying element.
5. The wire of any one of claims 1 to 3, wherein the wire core consists of a copper alloy comprising  $\geq 0.2$  wt.-% of silver as alloying element and 40 to 85 wt.-ppm of phosphorus as dopant.
6. The wire of any one of claims 1 to 3, wherein the wire core consists of a copper alloy consisting of copper and  $\geq 0.2$  wt.-% of silver as alloying element.
7. The wire of any one of claims 1 to 3, wherein the wire core consists of a copper alloy consisting of copper,  $\geq 0.2$  wt.-% of silver as alloying element and 40 to 85 wt.-ppm of phosphorus as dopant.
8. The wire of any one of the preceding claims, wherein the triple-layered coating superimposed on the surface of the wire is comprised of a 2 to 10 nm thick inner layer

of gold, a 50 to 100 nm thick intermediate layer of palladium and a 2 to 10 nm thick outer layer of gold.

9. A process for the manufacture of the triple-coated wire of any one of the preceding claims, wherein the process comprises at least the steps (1) to (5):

(1) providing a precursor item consisting of a material of the desired wire core composition,

(2) elongating the precursor item to form an elongated precursor item, until an intermediate cross-section in the range of from 7850 to 49063  $\mu\text{m}^2$  or an intermediate diameter in the range of from 100 to 250  $\mu\text{m}$  is obtained,

(3) depositing a triple-layered coating of an inner layer of gold, an intermediate layer of palladium and an outer layer of gold on the surface of the elongated precursor item obtained after completion of process step (2),

(4) further elongating the triple-coated precursor item obtained after completion of process step (3) until a desired final cross-section or diameter is obtained, and

(5) finally strand annealing the triple-coated precursor obtained after completion of process step (4) at an oven set temperature in the range of from 200 to 600 °C for an exposure time in the range of from 0.4 to 0.8 seconds to form the triple-coated wire, wherein step (2) may include one or more sub-steps of intermediate batch annealing of the elongated precursor item at an oven set temperature in the range of from 400 to 800 °C for an exposure time in the range of from 50 to 150 minutes.

10. The process of claim 9, wherein the final strand annealing is performed at an oven set temperature in the range of from 200 to 400 °C.

# INTERNATIONAL SEARCH REPORT

International application No.

**PCT/SG2018/050572**

## A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B23K; C22C 9/00; C22F1/00; C23C 28/00; C25D; H01L

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)

FAMPAT, COMPENDEX, INSPEC, ACS, IEEE: Wire, triple-layer coating, copper, gold, palladium, 线, 涂层, 金, 钯, 铜, and related terms.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                         | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | WO 2017/123153 A2 (HERAEUS MATERIALS SINGAPORE PTE LTD) 20 July 2017<br>Examples 1, 2; Tables 1, 2                                         | 1-10                  |
| X         | CN 106486455 A (PREC PACKAGING MAT CORP) 8 March 2017<br>Paragraphs [0040], [0079]-[0083] of the machine translation                       | 9, 10                 |
| A         | CN 105762129 A (SHANDONG KEDADINGXIN ELECTRONIC TECH CO LTD) 13 July 2016<br>Paragraphs [0009]-[0012]; Figure 1 of the machine translation |                       |
| A         | WO 2016/093769 A1 (HERAEUS MATERIALS SINGAPORE PTE LTD) 16 June 2016<br>Example 1                                                          |                       |

☐ 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

10/12/2018 (day/month/year)

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International application No.

**PCT/SG2018/050572**

## Supplemental Box (Classification of Subject Matter)

Int. Cl.

**C23C 28/02 (2006.01)**

**C25D 5/10 (2006.01)**

B23K 35/30 (2006.01)

B23K 35/40 (2006.01)

C22C 9/00 (2006.01)

C25D 7/06 (2006.01)

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/SG2018/050572**

*Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.*

| <b>Patent document<br/>cited in search report</b> | <b>Publication date</b> | <b>Patent family<br/>member(s)</b>                                        | <b>Publication date</b>                              |
|---------------------------------------------------|-------------------------|---------------------------------------------------------------------------|------------------------------------------------------|
| WO 2017/123153 A2                                 | 20/07/2017              | TW 201736606 A<br>KR 20180101468 A<br>SG 10201600329S A<br>CN 108474058 A | 16/10/2017<br>12/09/2018<br>30/08/2017<br>31/08/2018 |
| CN 106486455 A                                    | 08/03/2017              | TW 201710565 A                                                            | 16/03/2017                                           |
| CN 105762129 A                                    | 13/07/2016              | NONE                                                                      |                                                      |
| WO 2016/093769 A1                                 | 16/06/2016              | SG 10201408302Q A<br>TW 201633481 A                                       | 28/07/2016<br>16/09/2016                             |