

COATED COPPER (Cu) WIRE FOR BONDING APPLICATIONS

The present invention relates to a wire which has an average diameter in the range of from 8 to 80 μm , wherein the wire comprises at least a core with a surface, a first coating layer with a layer surface and a further coating layer, wherein A) the core comprises copper and elemental phosphorus; B) the first coating layer is composed of at least one element selected from the group comprising of palladium, platinum and silver, wherein the first coating layer is superimposed over the surface of the core; C) the further coating layer is superimposed over the layer surface of the first coating layer of core; wherein the further coating layer is composed of at least one element selected from silver and gold and wherein the composition of the further coating layer is different from the composition of the first coating layer; characterized in that at least one, two, three or all of the following conditions are met: A1) the ratio of the average grain size of the crystal grains in the core, measured in longitudinal direction, and the diameter of the wire is in the range of from 0.14 – 0.28 ($\mu\text{m}/\mu\text{m}$), and the relative standard deviation of the average grain size is less than 0.9; or A2) the degree of recrystallization of the crystal grains in the core, measured in longitudinal direction, is in the range of from 50 to 95 %; or A3) the fraction of twin boundaries, measured in longitudinal direction, is in the range of from 2 to 25 %; or A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each % with respect to the total number of crystals with orientation parallel to the drawing direction of the wire. The present invention further relates to a method for manufacturing a wire as aforementioned and to an electric device comprising the wire of the invention.

Bonding wires are used in the manufacture of semiconductor devices for electrically interconnecting an integrated circuit and a printed circuit board during semiconductor device fabrication. Further, bonding wires are used in power electronic applications to electrically connect transistors, diodes and the like with pads or pins of the housing. While bonding wires were made from gold in the beginning, nowadays less expensive materials are used such as copper. While copper wire provides very good electrical and thermal conductivity, ball-bonding as well as wedge-bonding of copper wire has its challenges. Moreover, copper wires are susceptible to oxidation.

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 types of wire geometries have their advantages making them useful for specific applications. Thus, both types of geometry have their share in the market. For example, bonding ribbons have a larger contact area for a given cross-sectional area. However, bending of the ribbons is limited and orientation of the ribbon must be observed when bonding in order to arrive at acceptable electrical contact between the ribbon and the element to which it is bonded. Turning to bonding wires, these are more flexible to bending. However, bonding involves either welding and/or larger deformation of the wire in the bonding process, which can cause harm or even destroy the bonding pad and underlying electric structures of the element, which is bonded thereto.

Some recent developments were directed to bonding wires having a copper core and a protective coating layer. As core material, copper is chosen because of high electric conductivity. With regard to the coating layer, palladium is a possible choice. These coated bonding wires combine the advantages of the copper wire with less sensitivity to oxidation.

Nevertheless, there is an ongoing need for further improving bonding wire technology with regard to the bonding wire itself and the bonding processes.

Accordingly, it is an object of the invention to provide improved bonding wires.

Another object of the invention is to provide a bonding wire which has good processing properties and which has no specific needs when interconnecting.

Another object of the invention is to provide a bonding wire which has excellent electrical and thermal conductivity.

Another object of the invention is to provide a bonding wire which exhibits an improved reliability.

Another object of the invention is to provide a bonding wire which exhibits excellent bondability.

Another object of the invention is to provide a bonding wire which shows an improved bondability with respect to a stitch bonding.

5 Another object of the invention is to provide a bonding wire which shows an improved bondability with respect to a second bonding which is a stitch bonding, whilst the bonding performance for a first bonding which was a ball bonding is at least sufficient.

Another object of the invention is to provide a bonding wire which has improved resistance to corrosion and/or oxidation.

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Another object of the invention is to provide a system for bonding an electronic device, which can be used with standard chip and bonding technology, which system shows reduced failure rate at least with respect to a second bonding.

15 Another object of the invention is to provide a method for manufacturing an inventive bonding wire, whereby the method basically shows no increase in manufacturing costs compared with known methods.

20 The wires of the present invention have been found to solve at least one of the objects mentioned above. Further, a process for manufacturing these wires has been found which overcomes at least one of the challenges of manufacturing wires. Further, electric devices comprising the wires of the invention were found to be more reliable, both at the interface between the wire according to the invention and other electrical elements, e.g., the printed circuit board, the pad/pin etc., as well at interfaces within the electric devices, where bonding wires are connected to other electric or electronic parts thus constituting the electric device.

25 A contribution to the solution of at least one of the above objects 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 which also makes a contribution to solving at least one of the objects mentioned above.

A first aspect of the invention is a wire, comprising of at least a core with a surface, a first coating layer with a layer surface and a further coating layer, wherein

- A) the core comprises copper and elemental phosphorus;
- B) the first coating layer is composed of at least one element selected from the group comprising of palladium, platinum and silver, wherein the first coating layer is superimposed over the surface of the core;
- 5 C) the further coating layer is superimposed over the layer surface of the first coating layer of core; wherein the further coating layer is composed of at least one element selected from silver and gold and wherein the composition of the further coating layer is different from the composition of the first coating layer;

10 wherein the wire has an average diameter in the range of from 8 to 80 μm ;

characterized in that at least one, two, three or all of the following conditions are met:

- A1) the ratio of the average grain size of the crystal grains in the core, measured in longitudinal direction, and the diameter of the wire is in the range of from 0.14 to 0.28 ($\mu\text{m}/\mu\text{m}$), more preferred in the range of from 0.17 to 0.24, or in the range
- 15 from 0.17 to 0.20, and the relative standard deviation (RSD) of the average grain size is less than 0.9; or
- A2) the degree of recrystallization of the crystal grains in the core, measured in longitudinal direction, is in the range of from 50 to 95 %, more preferred in the range of from 80 to 90%; or
- 20 A3) the fraction of twin boundaries, measured in longitudinal direction, is in the range of from 2 to 25 %, more preferred in the range of from 15 to 20 %; or
- A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each % with respect to the total number of crystals with orientation parallel to the drawing direction of the wire. Yet more preferred are 35 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 30 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction. Grains of the wire are oriented in the specified direction if the direction of the crystal grains deviates less than from -15° to $+15^\circ$, whereby drawing direction of the wire was used as reference orientation. The $\langle 100 \rangle$ and
- 25 $\langle 111 \rangle$ texture percentages were calculated by counting the number of crystals with $\langle 100 \rangle$ and the number of crystals with $\langle 111 \rangle$ orientation. These numbers were divided by the sum of both $\langle 100 \rangle$ and $\langle 111 \rangle$, since usually no crystal grains with orientation $\langle 010 \rangle$ were identified.
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The wire is preferably a bonding wire for bonding in microelectronics. The wire is preferably a one-piece object. Numerous shapes are known and appear useful for wires of the present invention. Preferred shapes are – in cross-sectional view – round, ellipsoid and rectangular shapes.

In the context of the present invention, all values referring to a diameter of the wire and crystal grain sizes in the core are expressed in μm . The relative standard deviation RSD of a size x is calculated according to

$$RSD = \text{standard deviation}(x) / \text{arithmetic mean}(x).$$

A “twin boundary” in the context of the present invention separates the two crystals grains or a domain with sheared lattice within a grain in the wire core, where, a 60° rotation about $\langle 111 \rangle$ plane of orientation between the neighboring crystallographic domains or grains.

“Recrystallization” in the context of the present invention describes a modification of the crystals’ arrangement in the copper wire during annealing. In this stage of annealing, new strain-free grains nucleate and grow to replace those deformed grains by residual stresses.

“The degree of recrystallization” refers to the amount of recrystallized grains with respect to the total number of grains.

The term “superimposed” in the context of the present invention is used to describe the relative position of a first item, e.g. a copper core, with respect to a second item, e.g. a coating layer. “Superimposed” characterizes, that further items, such as an intermediate layer, can – but no need to be arranged between the first and the second item. Preferably, the second item is at least partially superimposed over the first item, e.g. for at least 30 %, 50 %, 70 % or for at least 90 %, each with respect to the total surface of the first item. Most preferably, the second item is completely superimposed over the first item.

The term “intermediate layer” in the context of this invention refers to a region of the wire between the copper core and the coating layer. In this region, a combination of materials of both, the core and the coating layer, is present.

- 5 The term “thickness” in the context of this invention is used to define the size of a layer in perpendicular direction to the longitudinal axis of the copper core, which layer is at least partially superimposed over the surface of copper core.

10 The average diameter is obtained 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 the wire is calculated using the density of the wire material (density of copper: $\rho_{Cu} = 8.92 \text{ g/cm}^3$). The average diameter is calculated as arithmetic mean of five measurements on five cuts of a particular copper wire.

- 15 For the present invention, the term bonding wire comprises all shapes of cross-sections and all usual wire diameters, though bonding wires with circular cross-section and thin diameters are preferred.

20 Such thin wires mostly, but not necessarily have a cross-sectional view essentially in the shape of a circle. The term “a cross-sectional view” in the present context refers to a view of a cut through the wire, wherein the plane of the cut is perpendicular to the longitudinal extension of the wire. The cross-sectional view can be found at any position on the longitudinal extension of the wire. A “longest path” through the wire in a cross-section is the longest chord which can be laid through the cross-section of the wire within the plane of the cross-sectional view. A
25 “shortest path” through the wire in a cross-section is the longest chord perpendicular to the longest path within the plane of the cross-sectional view defined above. If the wire has a perfect circular cross-section, then the longest path and the shortest path become indistinguishable and share the same value. The term “diameter” is the arithmetic mean of all geometric diameters of any plane and in any direction, wherein all planes are perpendicular to the longitudinal
30 extension of the wire.

The core of the wire in the present context is defined as a homogenous 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. oxygen content) and other features. The surface can be an outer surface of the inventive wire in preferred embodiments. In further embodiments, the surface of the wire core can be an interface region between the wire core and a coating layer superimposed on the wire core.

A preferred embodiment of the invention is a wire as described above, wherein at least one, two or all of the following conditions is met:

- 2.1) the amount of copper in core is at least 99.95 wt.%; or in the range of from 99.98 to 99.95 wt.%, or in the range of from 99.98 to 99.99 wt.%; usually, the amount of copper in the core is not more than 99.995 wt.%. A copper content as defined in this section allows for using common supplies of copper material for wire bonding without exceedingly high costs due to high purity specifications.
- 2.2) the amount of elemental phosphorus in core is in the range of from 20 to 300 ppm, yet more preferred in the range of from 20 to 100 ppm, or from 40 to 80 ppm, each based on the total weight of the core; or
- 2.3) the amount of elemental silver in core is in the range of from 2 to 250 ppm, yet more preferred in the range of from 2 to 50 ppm, or in the range of from 2 to 15 ppm,

wherein all the wt.-% and ppm values are based on the total weight of the core.

In a preferred embodiment, the core of the wire of the invention comprises in total in the range of from 0 to 100 ppm, preferably less than 30 ppm, of further components. The low amount of these further components ensures a good reproducibility of the wire properties. In the present context, 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 manufacturing process which produced the wire. Examples of such further components are: Ni, Mn, Pt, Cr, Ca, La, Al, B, Zr, Ti, Fe. Further components present in the core are usually not added separately. The presence of the further components originates from impurities present in one or more of components a), b) and c).

In a preferred embodiment, the core of the wire of the invention comprises less than the following amounts of further components:

- a) Any one of Ni, Mn in <15 ppm each;
- b) Any one of: Pt, Cr, Ca, La, Al, B, Zr, Ti in <2 ppm each;
- 5 c) Any one of S, Fe in <10 ppm each;

Yet more preferred at least two of the aforementioned limits are met by the material forming the core, most preferred all limits are met by the material forming the core.

- 10 A further preferred embodiment of the invention is a wire, wherein the first coating layer has a thickness in the range of from 40 nm to less than 0.5 μm , preferably in the range of from 40nm to 200nm, or in the range of from 40 nm to 80 nm.

- 15 In the event, the first coating layer is composed of palladium, a further embodiment of the invention has first a coating layer which has a thickness of less than 0.5 μm . Yet more preferred, further coating layer has a thickness of less than 0.05 μm . A sufficiently thin further coating layer causes only little changes to most properties of the overall wire. However, some properties are remarkably improved, in particular regarding the bonding process.

- 20 Concerning the composition of the first coating layer, the palladium content of the layer is at least 50 wt.%, more preferably at least 95 wt.%, each wt.% based on the total weight of the first coating layer. Particularly preferred, the coating layer consists of pure palladium. Pure palladium usually has less than 1 wt.% of further components, with regard to the total amount of palladium in the first coating layer. In a further preferred embodiment, the further components present in the first coating layer are noble metals.
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In another preferred embodiment of the invention, the further coating layer of the wire has a thickness in the range of from 1.0 nm to less than 50 nm, preferably in the range of from 1.0 nm to 40 nm, or from 1.0 nm to 25 nm.

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In a further preferred embodiment of the invention the core of the wire has a content of silver or gold in the range of 5 ppm to 10000 ppm, preferably in the range of 5 ppm to 1000 ppm, yet more preferred in the range of 200 ppm to 250 ppm. It was observed that the presence of at

least small amounts of silver improves the mechanical properties, e.g. awards some softness to the wire.

In a further preferred embodiment of the invention the content of the at least one element in the further coating layer on the wire is at least 50 wt.%, more preferably at least 95 wt.%, each based on the total amount wt.% of the further coating layer. Particularly preferred, the further coating layer consists of pure gold or pure silver. Pure gold usually has less than 1 wt.% of further components, with regard to the total amount of gold in the further coating layer.

A second aspect of the invention is a method for manufacturing a wire, comprising at least the steps of

- i. Providing a precursor item comprising at least copper and elemental phosphorus;
- ii. drawing the precursor item to a core precursor;
- iii. coating the core precursor with at least one element selected from the group consisting of palladium, platinum or silver whereby a first coating layer on the core precursor is formed;
- iv. further coating with at least one element selected from silver and gold on the first coating layer of the core precursor obtained in step iii.;
whereby the composition of the further coating layer is different from the composition of the first coating layer,
whereby a further coating layer is formed;
- v. drawing the coated core precursor obtained from step iv. to a final diameter of 8-80 μm ;
- vi. annealing the product prepared in step v.;
whereby the wire (1) is obtained,
wherein the wire (1) has an average diameter in the range of from 8 to 80 μm ,

characterized in that at least one, two, three or all of the following conditions are met:

- A1) the ratio of the average grain size of the crystal grains in the core, measured in longitudinal direction, and the diameter of the wire is in the range of from 0.14 – 0.28 ($\mu\text{m}/\mu\text{m}$), more preferred in the range of from 0.17 to 0.24, or in

the range from 0.17 to 0.20, and the relative standard deviation RSD of the average grain size is less than 0.9; or

A2) the degree of recrystallization of the crystal grains in the core, measured in longitudinal direction, is in the range of from 50 to 95 %%, more preferred in the range of from 80 to 90%; or

A3) the fraction of twin boundaries, measured in longitudinal direction, is in the range of from 2 to 25 %, more preferred in the range of from 15 to 20 %; or

A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each % with respect to the total number of crystals with orientation parallel to the drawing direction of the wire (1). Yet more preferred are 35 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 30 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction. Grains of the wire are oriented in the specified direction if the direction of the crystal grains deviates less than from -15° to $+15^\circ$, whereby drawing direction of the wire was used as reference orientation. The $\langle 100 \rangle$ and $\langle 111 \rangle$ texture percentages were calculated by counting the number of crystals with $\langle 100 \rangle$ and the number of crystals with $\langle 111 \rangle$ orientation. These numbers were divided by the sum of both $\langle 100 \rangle$ and $\langle 111 \rangle$, since usually no crystal grains with orientation $\langle 010 \rangle$ were identified.

Preferred embodiments of the second aspect of the invention are those, which have been described for the first aspect of the invention in the above. A precursor item as in step i. can be obtained by doping copper with an amount of elemental phosphorus, optionally by doping with further elements. Doping can be realized by producing a melt of said components and copper and cooling the melt to form a homogeneous piece of copper based precursor item.

In first preferred embodiment to the second aspect of the invention the annealing of the product in step vi. of the method is performed at a temperature of at least 400°C , preferably of at least 430°C , or of at least 540°C . Higher annealing temperatures can provide for higher values for the elongation of the wire.

Concerning further parameters for annealing, in particular thin wires need not be exposed to the annealing temperature for long. In most cases annealing is done by pulling the wire through an annealing oven of a given length and with a defined temperature profile at a given speed. An exposure time of a thin wire to the annealing temperature is typically in the range of
5 0.1 second to 10 seconds.

A third aspect of the invention is a method for connecting an electrical device, comprising the steps of

- I. providing a wire as described for the first aspect of the invention or one of the em-
10 bodiments thereto, or a wire obtained by a method according the second aspect of the invention or one of the embodiments thereto;
- II. bonding the wire provided in step I. to a first bond pad of the device by either ball bonding or wedge bonding; and
- III. bonding the wire of step I. which is bonded to a first bond pad to a second bond pad
15 of the device by wedge bonding;
wherein step III. is performed without the use of a forming gas; and
wherein step II. is performed in presence of an inert gas or forming gas.

In a first embodiment to the third aspect of the invention, the wire is bonded in step II. by ball
20 bonding and in step III. by wedge bonding.

Wires according to the third aspect of the invention or to the embodiment thereto have excellent properties with respect to oxidation effects. Even better protection against oxidation of the copper core is achieved by complete encapsulation of the core with thin gold over palladium
25 coating layers are present in combination with a certain amount of silver and/or phosphorous in the core material. The resulting properties allow for processing the wire by purging forming gas and hence lead to clean, axi-symmetrical free air ball form. Forming gas is known in the art as a mixture of an inert gas like nitrogen with hydrogen, wherein the hydrogen content may provide for reduction reactions of oxidized wire material. In the sense of the invention, omit-
30 ting of forming gas means that no reactive compounds like hydrogen is used. Nevertheless, use of an inert gas like nitrogen can still be advantageous.

A fourth aspect of the invention is a method for manufacturing a wire according to the invention, comprising the steps;

- a. providing a copper core precursor item as in the second aspect of the invention;
- b. drawing the precursor until a final diameter of the wire core is reached;
- 5 c. coating the copper core with the material of the first and further coating layer, either before or after step b - drawing the precursor;
- d. annealing the coated and drawn wire at a defined temperature for a minimum time.

Concerning steps b to c, the manufacturing method is generally known in the art. It is pointed
10 out that the coating layer might be applied by any known or suitable method like mechanical coating, electrolytic plating, electroless plating, physical vapor deposition (PVD), chemical vapor deposition (CVD) and more. The coating can be done before or after the drawing of the wire, which may be dependent on properties of the respective coating and coating method. In particular, the coating might be performed at an intermediate step, with a drawing of the wire
15 or precursor occurring before as well as after the coating step.

As to step d, annealing is performed in a controlled way as known in the art in order to achieve a softening of the wire and/or optimizing the crystal structure of the wire according to the respective demands. Preferably, the annealing is done dynamically while the wire is moved
20 through an annealing oven and wound onto a spool after having left the oven.

A fifth aspect of the invention is an electrical device comprising a first and a second bonding pad, and a wire according to the first aspect of the invention or an embodiment thereto, or a wire obtained by a method according the second aspect of the invention or one of the embodi-
25 ments thereto, wherein the wire is connected to at least one of the bonding pads using ball-wedge bonding. An electric device in the present context includes electronic devices. Electronic devices are those which comprise semiconducting elements.

An embodiment of the fifth aspect is an electrical device, wherein the wire is connected to both
30 pads by ball-wedge bonding.

A sixth aspect of the invention is a system for bonding an electronic device, comprising a first bond pad, a second bond pad and a wire according to the invention, wherein the wire is con-

nected to at least one of the bonding pads by means of stitch-bonding. This combination of an inventive wire in a system is preferred due to the fact that the wire has especially beneficial properties with respect to stitch bonding.

- 5 In an embodiment of the fifth and sixth aspect of the invention is a method, wherein the process window for the at least one stitch bond to a gold bond pad has a value of at least 10450 mA*g for a wire which has a diameter of 18 μ m.

10 The definition of a process window area for bonding wires is known in the art and is widely used to compare different wires. In principle, it is the product of a bonding window of an ultrasonic energy used in the bonding and a bonding window of a force used in the bonding, wherein the resulting bond has to meet certain pull test specifications, e.g. a pull force of 2.5 grams, no non-stick on lead etc.. The actual value of the process window area of a given wire further depends on the wire diameter as well as the bond pad material. In order to give a specific definition of the properties of an inventive wire, the claimed process window value is based on a
15 wire diameter of 18 μ m = 0.7 mil, wherein the bond pad consists of gold. The scope an inventive system is not limited to wires of this diameter and bond pads made of gold, but names this data only for definition purpose.

20 DESCRIPTION OF THE FIGURES

The subject matter of the invention is exemplified in the figures. The figures, however, are not intended to limit the scope of the invention or the claims in any way.

- 25 In Figure 1, a wire 1 is depicted.

Figure 2 shows a cross sectional view of wire 1. In the cross sectional view, a copper core 2 is in the middle of the cross sectional view. The copper core 2 is encompassed by a palladium coating layer 3. The palladium coating layer 3 is encompassed by a thin gold coating layer 41.
30 On the limit of copper wire 2, a surface 15 of the copper core is located. On the limit of palladium coating 3, a surface 42 of the palladium coating is located. On a line L through the centre 23 of wire 1 the diameter of copper core 2 is shown as the end to end distance between the intersections of line L with the surface 15. The diameter of wire 1 is the end-to-end distance

between the intersections of line L through the centre 23 and the outer limit of wire 1. In addition, thickness of coating layer 3 and 41 are depicted.

Figure 3 shows a process for manufacturing a wire according to the invention.

Figure 4 depicts an electric device 10 comprising two elements 11 and a wire 1. The wire 1 electrically connects the two elements 11. The dashed lines mean further connections or circuitry which connects the elements 11 with external wiring of a packaging device surrounding the elements 11. The elements 11 can comprise bond pads, lead fingers, integrated circuits, LEDs or the like.

Figure 5 depicts an annealing curve of a 0.7 mil wire. Pieces of this wire were annealed at different annealing temperatures. The value of elongation in %, based on the length of the wire before annealing, was recorded as a function of annealing temperature. Region A denotes starting of recrystallization; region B denotes starting of grain growth; region C denotes starting of over annealing.

Figure 6 depicts four items: item (a) is an inverse pole figure map. This map illustrates orientation of the grains to certain plane by the color contrast defined by color key, whereby angles are determined in longitudinal direction of the wire core. The copper wire is expected to be oriented to three main plane of direction $[111]$, $[101]$, $[100]$. Low-angle grain boundaries (LAGBs) have angles in the range of from $2^\circ < \Theta \leq 10^\circ$, High-angle grain boundaries (HAGBs) have angles in the range of from $10^\circ < \Theta$. Twin boundaries (TBs) are present when $\langle 111 \rangle$ is $> 60^\circ$.

Item (b) is a grain boundary map. This map illustrates the presence of grain boundaries. Boundaries in grey lines are low-angle grain boundaries and boundaries in light grey lines are twin boundaries. Dark grey lines represent high-angle grain boundaries.

Item (c) is an inverse pole figure. This figure illustrates orientation of the grains to certain plane as dots, more the number of dots, more the grains are highly oriented to the plane of direction, whereby angles are determined in longitudinal direction of the wire core. The copper wire is expected to be oriented mainly by the three plane of direction $\langle 111 \rangle$, $\langle 101 \rangle$, $\langle 100 \rangle$.

Item (d) is a color key of a 0.7mil finished Cu wire. Color key defines the color for each plane of orientation (the three main direction $\langle 111 \rangle$, $\langle 101 \rangle$, $\langle 100 \rangle$ which and to be reflected by each grain color and its orientation in the cross-sectioned wire core along the longitudinal di-
5 rection.

Figure 7 shows a chart reflecting the grain size distribution of a 0-7 mil Cu wire.

Figure 8 consists of three items. Item (a) is a recrystallization map. Dark areas represent re-
10 crystallized grains, light areas are sub-structured and deformed crystal grains. Black lines are boundaries between crystal grains. Item (b) is recrystallization a chart providing quantitative data on fractions of a 0.7mil finished Cu wire. "Finished" means that the final wire was drawn and annealed. Measurements were recorded in respect of the wire longitudinal direction. According to the chart, about 85 % of the crystal grains investigated by the measurement were
15 recrystallized and about 15 % of the crystal grains were sub-structured. About 1 % of the crystal grains was deformed.

Deformed crystal grains describe a situation usually found in an un-annealed drawn wire (without high temperature annealing), in which highly oriented crystals are present along the
20 deformation direction (wire axis). Some "deformed" crystal grains may remain after annealing.

Upon annealing the drawn wire, some grains nucleate inside recrystallized grains. This effect might depend on the extend of deformation, the time and the temperature of annealing. Grains which nucleate inside recrystallized grains are termed as "sub-grains". The microstructure is
25 referred to as "sub-structure".

Figure 9 consists of 2 items. Item (a) is a grain boundary map (*see* figure 6 (a)). Item (b) is chart showing the mis-orientation angle distribution of a 0.7mil finished (final wire drawn and annealed) Cu wire. According to the chart, the degree of mis-orientation is for most angles
30 between 1 and 3 %. The mis-orientation is 20 % for an angle of 2° and about 16 % for an angle of 60° . Measurements were recorded in respect of the wire longitudinal direction.

The invention is further exemplified by examples. 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.

TEST METHODS

1. Electron Backscattered Diffraction Pattern Analysis

- 5 The main steps adopted to measure wire texture were sample preparation, getting good Kikuchi pattern and component calculation;
- (a) The bonding wires were first potted using epoxy and polished as per standard metallographic technique. Ion milling was applied in the final sample preparation step to remove any mechanical deformation of the wire surface, contamination and oxidation layer. The ion-milled cross-sectioned sample surface was sputtered with gold. Then ion milling and gold sputtering were carried out for two further rounds. No chemical etching or ion-etching was carried out.
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- (b) The sample was loaded in a FESEM (field emission scanning electron microscope) with a 70° angled holder to the normal FESEM sample holding table surface. The FESEM was further equipped with an electron back-scattering diffraction (EBSD) detector. The electron back-scattering patterns (EBSP) which contain the wire crystallographic information were obtained.
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- (c) These patterns were further analyzed for grain orientation fraction, grain size, etc. (using a software called EBSD program developed by and available from Oxford Instruments). Points of similar orientation were grouped together to form texture component. To distinguish different texture component, maximum tolerance angle of 15° was used. The wire drawing direction was set as a reference orientation. The <100> and <111> texture percentages were calculated by measurement of the percentage of crystals with <100> and <111> orientation parallel to the reference orientation. Commonly <010> component was absent.
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- 30 Grain sizes were analyzed defining the crystallographic orientation between neighboring grid points of greater than a minimum, herein 10°, to determine the position of grain boundaries. The EBSD software calculated the area of each grain and converted it to equivalent circle diameter, which is defined as “crystal grain size”. All the grains along the longitudinal direction

of the wire within a length of $\sim 100\mu\text{m}$ were counted to determine mean and standard deviation of the crystal grain size.

Twin boundaries (also called $\Sigma 3$ CSL twin boundaries) were excluded in the grain size calculation. The twin boundary was described by a 60° rotation about $\langle 111 \rangle$ plane of orientation between the neighboring crystallographic domains.

In addition, points of similar orientation were grouped together to form texture component. To distinguish different texture component, maximum tolerance angle of 15° was used. The $\langle 100 \rangle$, $\langle 101 \rangle$ and $\langle 111 \rangle$ texture percentages were calculated by measurement of the percentage of crystals with these ($\langle 100 \rangle$, $\langle 101 \rangle$ and $\langle 111 \rangle$) orientation parallel to the reference orientation. The wire drawing direction (wire axis) was set as a reference orientation.

The degree of recrystallization of the annealed wire was also measured using the EBSD software. The software measured the maximum mis-orientation between any two points in a grain and then weights the grain according to the mis-orientation value. The average mis-orientation was defined as Θ . This was a pixel-based measurement that computed the average of the mis-orientation between a given point/pixel and its first nearest neighbor points. The number of points depends on the step size, which was less than $1/5$ of the average crystal grain size.

Based on the EBSD software analysis the wire micro-structure was classified into three types: 1) deformed, 2) sub-structured and 3) recrystallized grain. When there were no sub-grains and the average mis-orientation within the grain was $> 2^\circ$, the grain was defined as deformed. In addition when there were sub-grains existed in the grain, and within the sub-grain, the average mis-orientation was $< 2^\circ$, and the mis-orientation between every sub-grain was $> 2^\circ$, the grain-structure was defined as sub-structure. Besides the deformed and sub-structured grain structure, rest of the wire grain structure was defined as recrystallized grain. The deformed regions were strongly mis-oriented. The recrystallized regions were strain free, and the majority revealed high angle recrystallization boundaries.

2. Wire Processing

Copper of 4N purity was used to prepare the alloys and was melted in a vacuum induction furnace. Phosphorus was added into the melt using Cu-0.5wt%P master alloy (composition of Cu-0.5 wt%P alloy: 99.5 wt.% Cu and 0.5 wt.% P). The melt was held for few minutes to allow a thorough dissolution. The alloy was continuously cast into 2 to 25mm rods at slow speed. No significant loss in dopant addition was observed. These rods were wire drawn at room temperature (25°C). Tungsten carbide die was used to draw heavy wire and a diamond die was used for further reduction. It was drawn in two stages at a drawing speed of 15m/s or less. The die reduction ratio was around 14 to 18% for thick wires and 4 to 12% for thin size. During cold drawing, the wires were lubricated.

The thin wires with a diameter of 6 to 15mil were in-line degreased, palladium electroplated and then gold electroplated, finally washed and spooled for finishing wire drawing. During electro-plating the wire speed was maintained at 5 to 25m/min., voltage applied was between 1V and 8V and the current applied was from 0.05 to 5 A. The pH of palladium plating bath was maintained between 7 to 10 and gold plating was maintained at pH in the range from 4 to 6. The plating was processed at 40 to 60°C.

The electroplated wires were drawn to final size 0.5 to 2mil. Finally, the drawn wires were strand annealed, spooled on clean anodized (plated) aluminum spools, vacuum packed and stored.

The ratio of the average grain size of the crystal grains in the core and the diameter of the wire was in the range of 0.14 to 0.28 and with standard deviation of ~0.9. This was achieved by annealing the wire in the temperature range of 470 to 520°C (example: *see* Figure 5 for a 0.7 mil wire). The average crystal grain size ratio in the outer range of the above mentioned values was achieved by annealing the wire in the range of 420 to 470°C.

3. Ball-wedge Bonding Parameter Definition

Wires were bonded using a KNS-iConn bonder. Bonding of a wire to a plated surface was performed at 20°C. First the free air ball was formed by electric flame off firing for varying cur-

rent in the range 3 to 5V. Further, the free air ball was bonded to bond pad on the ICs (integrated chips). Most of the bond pads were metallized with the composition Al-0.5Cu (99.5 wt.% Al and 0.5 wt.% Cu). Some bond pads were metallized with gold surface. After forming a first ball bond between the wire and the bond pad, the wire was stitched (wedged) with its second end to the substrate lead fingers wherein the bonding was applied to the gold finger surface in BGA substrate, silver finger surface in lead frame. Some lead finger surface was plated with palladium or nickel, too. The distance of the bonds between the two ends of the wire was in the range of from 5 mm to 20 mm. This distance was selected in order to assure the angle of 45° between the wire and the substrate in wedge. During stitch bonding, ultrasonic sound of a frequency in the range of 60 – 140 kHz was applied to the bond tool for 40 to 500 milliseconds. The bonded wires were observed in LEO-1450VP scanning electron microscope (SEM) for good looping, first bond neck area, second bond heel and stitch, tool mark, etc.

4. Free air ball

The electric flame off (EFO) current and time defines the specification of the FAB. On EFO firing, the tip of the fractured Cu wire melts and form axi-symmetrical spherical FAB, further stitch the wire on lead frame such that FAB stand on air. This mode of bonding was referred to as cherry pits. The procedures are described in the KNS Process User Guide for Free Air Ball (Kulicke & Soffa Industries Inc, Fort Washington, PA, USA, 2002, 31 May 2009). The FAB diameter was measured using optical microscope at 200X to 500X magnification in micron scale. Morphology of the FAB was observed using scanning electron microscope (SEM).

5. Process window area

Measurements of ball-bonding process window area were done by standard procedure. The test wires were bonded using a KNS-iConn bonder tool (Kulicke & Soffa Industries Inc, Fort Washington, PA, USA). The definition of a 2nd bond process window area for bonding wires was known in the art and was widely used to compare different wires. In principle, it is the product of scrub amplitude and force used in the bonding, wherein the resulting bond has to meet certain pull test specifications, e.g. a pull force of 2.5 grams, no non-stick on lead etc.. The actual value of the 2nd bond process window area of a given wire further depends on the

wire diameter as well as the lead finger plated material. In order to give a specific definition of the properties of an inventive wire, the process window value were based on a wire diameter of $18\text{ }\mu\text{m} = 0.7\text{ mil}$, wherein the lead finger consists of silver.

5 The four corners of the process window were derived by overcoming the two main failure modes:

(1) supply of too low force and scrub amplitude lead to non-stick on lead (NSOL) of the wire, and

(2) supply of too high force and scrub amplitude lead to short tail (SHTL).

10

The scope of the inventive system was not limited to wires of this diameter and lead fingers made of silver, but names this data only for definition purpose.

15 **EXAMPLES**

The invention is further exemplified by examples. 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.

20

Example 1

A typical ICP analysis of sample1 and a comparative sample wires are provided in the Table.1. Sample1 core material is doped with "P". Predicted thickness of Au flash of the wire is close
25 to about 3nm. Predicted thickness of Pd coating of the wire is about 63nm. The inventive wire sample1 revealed wide 2nd bond window of 10450mA*g which is quite high (Table.1) compared to bare 4N Cu of about 8100mA*g. A competitor wire with composition close to sample1 has also showed wide 2nd bond window (comparative sample).

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35

5 **Table 1: ICP analysis and second bond process window of 0.7mil wires**

	ICP Analysis, wt.ppm			Predicted coating thickness from ICP data, nm		2 nd Bond Process Window		
Wire	Core Ma-terial - “P” dopant	Coating						
	P	Au	Pd	Au	Pd	USG, mA	Force, g	Area, mA.g
compar-ative sample	50	988	20540	2.1	69.4	10-110	70-180	11000
Sample1	78	1400	18570	2.9	63.1	10-120	65-160	10450

From the inverse pole figure, the texture of fine drawn and annealed wire of sample1 is shown in Figure 6, measured in the longitudinal direction. Two fiber components $\langle 111 \rangle + \langle 100 \rangle$ were observed. It is evident that the $\langle 100 \rangle$ is relatively stronger than $\langle 111 \rangle$ (Figure 6c). Generally, grains with $\langle 101 \rangle$ orientation was absent.

From the grain boundary map of low and high angle grain boundaries the wire grain morphology and size were calculated. The CSL $\Sigma 3$ boundaries (also referred to as: twin boundaries) were not included for grain size measurement. The crystal grain size has a normal distribution (Figure 7). The average crystal grain size is around $3.49\mu\text{m}$, and the standard deviation is around $3.05\mu\text{m}$. Ratio of the average grain size of the crystal grains in the core and the diameter of the wire is in the range of $0.14 - 0.28$, preferably $0.17 - 0.24$, and wherein the relative standard deviation RSD is less than 0.9. (see Figure 7, measured in the longitudinal direction).

Example2

A typical recrystallization map of sample1 drawn and annealed wire is shown in Figure 8, measured in the longitudinal direction. The recrystallization fraction of the crystal grains in the core is more than 50 % (Figure 8b).

Example3

10 A typical fraction of CSL $\Sigma 3$ twin boundaries $<111> 60^\circ$ calculated for sample1 is lower than 25%. This is shown for a 0.7mil wire in Figure 9b.

EMBODIMENTS OF THE INVENTION

I) A wire (1), comprising of at least a core (2) with a surface (21), a first coating layer (3) with a layer surface (31) and a further coating layer (4), wherein

A) the core (2) comprises copper and elemental phosphorus;

B) the first coating layer (3) is composed of at least one element selected from the group comprising of palladium, platinum and silver,

wherein the first coating layer (3) is superimposed over the surface (21) of the core (2);

C) the further coating layer (4) is superimposed over the layer surface (31) of the first coating layer (3) of core (2);

wherein the further coating layer (4) is composed of at least one element selected from silver and gold and

wherein the composition of the further coating layer (4) is different from the composition of the first coating layer (3);

wherein the wire (1) has an average diameter in the range of from 8 to 80 μm ; characterized in that at least one, two, three or all of the following conditions are met:

A1) the ratio of the average grain size of the crystal grains in the core, measured in longitudinal direction, and the diameter of the wire is in the range of from 0.14 – 0.28 ($\mu\text{m}/\mu\text{m}$), and

the relative standard deviation of the average grain size is less than 0.9; or

A2) the degree of recrystallization of the crystal grains in the core, measured in longitudinal direction, is in the range of from 50 to 95 %; or

A3) the fraction of twin boundaries, measured in longitudinal direction, is in the range of from 2 to 25 %; or

A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each % with respect to the total number of crystals with orientation parallel to the drawing direction of the wire (1).

II) The wire (1) according to embodiment I), wherein at least one, two or all of the following conditions is met:

- 2.1) the amount of copper in core (2) is at least 99.95 wt.%; or
- 2.2) the amount of elemental phosphorus in core (2) is in the range of from 20 to 300 ppm, each based on the total weight of the core (2); or
- 2.3) the amount of elemental silver in core (2) is in the range of from 2 to 250 ppm;

wherein all wt.% and ppm values are given with respect to the total weight of core (2).

III) The wire (1) according to any one of the precedent embodiments, wherein the first coating layer (3) has a thickness in the range of from 40 nm to less than 0.5 μm .

IV) The wire (1) according to any one of the precedent embodiments, wherein the further coating layer (4) has a thickness in the range of from 1.0 nm to less than 50 nm.

V) A method for manufacturing a wire (1), comprising at least the steps of

- i. Providing a precursor item (5) comprising at least copper and elemental phosphorus;
- ii. drawing the precursor item (5) to a core precursor (2a);
- iii. coating the core precursor (2a) with at least one element selected from the group consisting of palladium, platinum or silver whereby a first coating layer (3) on the core precursor (2a) is formed;
- iv. further coating with at least one element selected from silver and gold on the first coating layer (3) of the core precursor (2a) obtained in step iii.; whereby the composition of the further coating layer (4) is different from the composition of the first coating layer (3), whereby a further coating layer (4) is formed;
- v. drawing the coated core precursor obtained from step iv. to a final diameter of 8-80 μm ;
- vi. annealing the product prepared in step v.; whereby the wire (1) is obtained,

wherein the wire (1) has an average diameter in the range of from 8 to 80 μm ,
characterized in that at least one, two, three or all of the following conditions are met:

5 A1) the ratio of the average grain size of the crystal grains in the core, measured in longitudinal direction, and the diameter of the wire is in the range of from 0.14 – 0.28 ($\mu\text{m}/\mu\text{m}$) and the standard deviation RSD of the average grain size is less than 0.9; or

10 A2) the degree of recrystallization of the crystal grains in the core, measured in longitudinal direction, is in the range of from 50 to 95 %; or

A3) the fraction of twin boundaries, measured in longitudinal direction, is in the range of from 2 to 25 %; or

15 A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each % with respect to the total number of crystals with orientation parallel to the drawing direction of the wire (1).

VI) The method of embodiment V), wherein the annealing of the product in step vi. is performed at a temperature of at least 400 °C.

20 VII) A method for connecting an electrical device (6), comprising the steps of

I. providing a wire (1) according to any one of embodiments I) to IV), or a wire obtained by a method according to any one of embodiments V) to VI),

25 II. bonding the wire (1) to a first bond pad (61) of the device by either ball bonding or wedge bonding; and

III. bonding the wire (1) to a second bond pad (62) of the device by wedge bonding;

wherein step III. is performed without the use of a forming gas; and

30 wherein step II. is performed in presence of an inert gas or forming gas.

VIII) An electrical device (10) comprising a first and a second bonding pad (11, 11), and a wire (1) according to any one of embodiments I) to IV), or a wire obtained by a method

according to any one of embodiments V) to VI), wherein the wire (1) is connected to at least one of the bonding pads (11, 11) using ball-wedge bonding.

- 5 IX) The electrical device (10) according to embodiment VIII), wherein the process window for the at least one stitch bond to a gold bond pad has a value of at least 10450 mA*g provided the wire (1) has a diameter of 18 μm .

REFERENCE NUMERALS

(1)	Wire
(2)	Core
(2a)	Core precursor
(21)	Surface
(3)	Coating layer
(31)	Layer surface
(32)	Center of wire
(41)	Further coating layer
(42)	Surface of further coating layer
(5)	Precursor item
(6)	Electrical device
(10)	Electric device
(11)	Bond pad
(15)	surface
L	Imaginary line through cross section of wire

CLAIMS

1. A wire (1), comprising of at least a core (2) with a surface (21), a first coating layer (3) with a layer surface (31) and a further coating layer (4), wherein
- 5 A) the core (2) comprises copper and elemental phosphorus;
- B) the first coating layer (3) is composed of at least one element selected from the group comprising of palladium, platinum and silver,
- wherein the first coating layer (3) is superimposed over the surface (21) of the core (2);
- 10 C) the further coating layer (4) is superimposed over the layer surface (31) of the first coating layer (3) of core (2);
- wherein the further coating layer (4) is composed of at least one element selected from silver and gold and
- wherein the composition of the further coating layer (4) is different from the
- 15 composition of the first coating layer (3);
- wherein the wire (1) has an average diameter in the range of from 8 to 80 μm ; characterized in that at least one, two, three or all of the following conditions are met:
- 20 A1) the ratio of the average grain size of the crystal grains in the core, measured in longitudinal direction, and the diameter of the wire is in the range of from 0.14 – 0.28 ($\mu\text{m}/\mu\text{m}$), and
- the relative standard deviation of the average grain size is less than 0.9; or
- A2) the degree of recrystallization of the crystal grains in the core, measured in longitudinal direction, is in the range of from 50 to 95 %; or
- 25 A3) the fraction of twin boundaries, measured in longitudinal direction, is in the range of from 2 to 25 %; or
- A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each % with respect to the total number of crystals with orientation parallel
- 30 to the drawing direction of the wire (1).

2. The wire (1) according to claim 1, wherein at least one, two or all of the following conditions is met:

2.1) the amount of copper in core (2) is at least 99.95 wt.%; or

2.2) the amount of elemental phosphorus in core (2) is in the range of from 20 to 300 ppm, each based on the total weight of the core (2); or

2.3) the amount of elemental silver in core (2) is in the range of from 2 to 250 ppm;

wherein all wt.% and ppm values are given with respect to the total weight of core (2).

3. The wire (1) according to any one of the precedent claims, wherein the first coating layer (3) has a thickness in the range of from 40 nm to less than 0.5 μm .

4. The wire (1) according to any one of the precedent claims, wherein the further coating layer (4) has a thickness in the range of from 1.0 nm to less than 50 nm.

5. A method for manufacturing a wire (1), comprising at least the steps of

i. Providing a precursor item (5) comprising at least copper and elemental phosphorus;

ii. drawing the precursor item (5) to a core precursor (2a);

iii. coating the core precursor (2a) with at least one element selected from the group consisting of palladium, platinum or silver whereby a first coating layer (3) on the core precursor (2a) is formed;

iv. further coating with at least one element selected from silver and gold on the first coating layer (3) of the core precursor (2a) obtained in step iii.;

whereby the composition of the further coating layer (4) is different from the composition of the first coating layer (3),

whereby a further coating layer (4) is formed;

v. drawing the coated core precursor obtained from step iv. to a final diameter of 8-80 μm ;

vi. annealing the product prepared in step v.;

whereby the wire (1) is obtained,

wherein the wire (1) has an average diameter in the range of from 8 to 80 μm ,
characterized in that at least one, two, three or all of the following conditions are met:

- 5 A1) the ratio of the average grain size of the crystal grains in the core, measured
 in longitudinal direction, and the diameter of the wire is in the range of
 from 0.14 – 0.28 ($\mu\text{m}/\mu\text{m}$) and the standard deviation RSD of the average
 grain size is less than 0.9; or
- 10 A2) the degree of recrystallization of the crystal grains in the core, measured in
 longitudinal direction, is in the range of from 50 to 95 %; or
- A3) the fraction of twin boundaries, measured in longitudinal direction, is in the
 range of from 2 to 25 %; or
- 15 A4) 18 to 42 % of the grains of the wire are oriented in $\langle 100 \rangle$ direction and 27
 to 38 % of the grains of the wire are oriented in $\langle 111 \rangle$ direction, each
 % with respect to the total number of crystals with orientation parallel
 to the drawing direction of the wire (1).
6. The method of claim 5, wherein the annealing of the product in step vi. is performed at
a temperature of at least 400 °C.
- 20 7. A method for connecting an electrical device (6), comprising the steps of
- I. providing a wire (1) according to any one of claims 1 to 4, or a wire ob-
 tained by a method according to any one of claims 5 to 6,
- 25 II. bonding the wire (1) to a first bond pad (61) of the device by either ball
 bonding or wedge bonding; and
- III. bonding the wire (1) to a second bond pad (62) of the device by wedge
 bonding;
 wherein step III. is performed without the use of a forming gas; and
 wherein step II. is performed in presence of an inert gas or forming gas.
- 30 8. An electrical device (10) comprising a first and a second bonding pad (11, 11), and a
 wire (1) according to any one of claims 1 to 4, or a wire obtained by a method accord-

ing to any one of claims 5 to 6, wherein the wire (1) is connected to at least one of the bonding pads (11, 11) using ball-wedge bonding.

- 5 9. The electrical device (10) according to claim 8, wherein the process window for the at least one stitch bond to a gold bond pad has a value of at least 10450 mA*g provided the wire (1) has a diameter of 18 μm .