

ALLOYED SILVER WIRE

The invention relates to an 8 to 80 μm thick alloyed silver wire comprising a core comprising silver, palladium, gold, nickel and calcium in a specific weight ratio. The invention further relates to a process for manufacturing such wire.

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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.

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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.

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It is an object of the invention to provide an alloyed silver wire suitable for use in wire bonding applications, the alloyed silver wire being improved in particular in corrosion and moisture resistance but also exhibiting an overall well-balanced spectrum of properties which are relevant with regard to wire bonding applications including, for example, a wide stitch bonding window, formation of axi-symmetrical free air ball (FAB) with good reproducibility, low FAB hardness, high stitch pull strength, soft wire, low electrical resistivity, low electro-migration, etc.

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A contribution to the solution of said 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 which also makes a contribution to solving the objects mentioned above.

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In a first aspect, the invention relates to an alloyed silver wire comprising or consisting of a wire core (hereinafter also called "core" for short), the wire core itself consisting of:

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- (a) palladium in an amount in the range of from 0.1 to 3 wt.-% (weight-%, % by weight), preferably 0.5 to 1.5 wt.-%,
(b) gold in an amount in the range of from 0.1 to 3 wt.-%, preferably 0.2 to 1.5 wt.-%,
(c) nickel in an amount in the range of from 20 to 700 wt.-ppm (weight-ppm, ppm by
5 weight), preferably 275 to 325 wt.-ppm,
(d) calcium in an amount in the range of from 20 to 200 wt.-ppm, preferably 20 to 50 wt.-ppm,
(e) silver in an amount in the range of from 93.91 to 99.786 wt.-%, preferably 96.9625 to 99.2595 wt.-%, and

- 10 (f) 0 to 100 wt.-ppm of further components (components other than palladium, gold, nickel, calcium and silver),

wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the core, wherein the alloyed silver wire has an average diameter in the range of from 8 to 80 μm or even in the range of from 12 to 55 μm .

15 The alloyed silver wire is preferably a bonding wire for bonding in microelectronics. The alloyed silver wire is preferably a one-piece object. Numerous shapes are known and appear useful for alloyed silver wires of the invention. Preferred shapes are – in cross-sectional view – round, ellipsoid and rectangular shapes.

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

For the 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.

30 In line with the aforementioned, the wire core comprises (a) palladium, (b) gold, (c) nickel, (d) calcium, and (e) silver in the afore disclosed proportional ratio. However, the

core of the alloyed silver wire of the invention may comprise (f) further components in a total amount of 0 to 100 wt.-ppm. 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 wire manufacturing process, i.e., the presence of further components of the (f) type may for example originate from impurities present in one or more of the silver, palladium, gold, nickel and calcium. Examples of such further components are: Cu, Fe, Si, Mn, Cr, Ce, Mg, La, Al, B, Zr, Ti, S, etc. The low total amount of 0 to 100 wt.-ppm of the further components (f) ensures a good reproducibility of the wire properties. Further components (f) present in the core are usually not added separately.

In an embodiment, the core of the alloyed silver wire of the invention comprises less than the following amounts of further components (f):

- (i) Cu in < 30 wt.-ppm;
- (ii) any one of Cr, Ce, Mg, La, Al, Be, In, Mn, Ti in < 2 wt.-ppm each;
- (iii) any one of Si, Fe, S in < 15 wt.-ppm each.

The core of the alloyed silver 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. sulfur, chlorine and/or oxygen content) and other features. The surface can be an outer surface of the wire core; in such embodiment, the alloyed silver wire of the invention consists of the wire core. In an alternative, the surface can be an interface region between the wire core and a coating layer superimposed on the wire core.

The term "superimposed" in the context of the invention is used to describe the relative position of a first item, e.g. a wire 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.

5 The term "intermediate layer" in the context of this invention refers to a region of the alloyed silver wire between its core and coating layer superimposed thereon. In this region, a combination of materials of both, the core and the coating layer, is present.

10 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 core, which layer is at least partially superimposed over the surface of the core.

In an embodiment, the core has a surface, wherein a coating layer is superimposed over the surface of the core.

15 In an embodiment, the mass of the coating layer is not more than 5 wt.-%, preferably 2 wt.-% or less, each with respect to the total mass of the core. When a coating layer is present, it often has a minimum mass of 0.1 wt.-% or more or 0.5 wt.-% or more, each with respect to the total mass of the core. Applying a low amount of material as coating layer preserves the characteristics which are defined by the material of the core of the wire. On the other hand, the coating layer awards particular characteristics to the wire surface such as being inert against environment, resistance to corrosion, improved bondability, etc. For example, the thickness of the coating layer is in the range of from 20 to 120 nm for a wire of 18 μm in diameter. For a wire having a diameter of 25 μm , the coating layer may have a thickness in the range of from 30 to 150 nm, for example.

25 In an embodiment, the coating layer can be made of a precious metal element. The coating layer can be a single-layer of one of said elements. In another embodiment, the coating layer can be a multi-layer comprised of a number of super-positioned adjacent sub-layers, wherein each sub-layer is made of a different precious metal element.

30 Common techniques for deposition of such precious metal elements on the core 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.

In an embodiment, the alloyed silver wire of the invention or its core is characterized at least by one of the following intrinsic properties (see "Test method A" as described below):

(1) The average wire grain size (average grain size) is less than 10 μm , for example in the range of from 2 to 6 μm , preferably in the range of from 2 to 4 μm ,

(2) The wire grain [100] or [101] or [111] plane of orientation is less than 7 %, for example in the range of from 1 to 5 %, preferably in the range of from 2 to 3.5 %, 10

(3) The wire twin boundary fraction is less than 60 %, for example in the range of from 30 to 50 %, preferably in the range of from 40 % to 45 %, 15

(4) The FAB exhibits columnar grains (grains are elongated),

(5) The FAB average grain size is $\leq 18 \mu\text{m}$, for example in the range of from 6 to 14 μm , preferably in the range of from 8 to 12 μm , 20

(6) The FAB grain [101] plane of orientation is less than 45 %, for example in the range of from 30 to 40 %, preferably in the range of from 32 to 36 %, 25

(7) The FAB twin boundary fraction is less than 70 %, for example in the range of from 30 to 65 %, preferably in the range of from 60 % to 65 %, 30

and/or at least by one of the following extrinsic properties:

(α) The corrosion resistance has a value of not more than 5 % bonded ball lift, for example in the range of from 0 to 5 %, (see "Test method B" as described below),

(β) The moisture resistance has a value of not more than 5 % bonded ball lift, for example in the range of from 0 to 5 %, (see "Test method C" as described below),

(γ) The hardness of the wire core is not more than 85 HV, for example in the range of from 50 to 85 HV, preferably in the range of from 65 to 75 HV, (see "Test method D" as described below), 25

(δ) The process window area for stitch bonding has a value of at least 12000 mA·g, for example 13000 to 14400 mA·g for a wire of 18 μm in diameter, (see the detailed disclosure and "Test method E" as described below), 30

(ε) The resistivity of the wire is less than $2.5 \mu\Omega\cdot\text{cm}$, for example in the range of from 1.7 to $2.4 \mu\Omega\cdot\text{cm}$, preferably in the range of from 2.2 to $2.4 \mu\Omega\cdot\text{cm}$, (see "Test method F" as described below),

(ζ) The yield strength of the wire is not more than 170 MPa, for example in the range of from 140 to 170 MPa, (see "Test method G" as described below),

(η) The wire's silver dendritic growth is not more than $4 \mu\text{m/s}$, for example in the range of from 2 to $4 \mu\text{m/s}$, preferably in the range of from 2 to $3 \mu\text{m/s}$, (see "Test method H" as described below).

The terms "intrinsic property" and "extrinsic property" are used herein with regard to a wire core or a FAB. Intrinsic properties mean properties which a wire core or a FAB has of itself (independently of other factors), while extrinsic properties depend on the wire core's or FAB's relationship with other factors like a measuring method and/or measuring conditions employed.

In case of a preferred embodiment of the invention, the hardness of the wire core (i.e. hardness prior to bonding) is less than 85 HV, preferably in the range of from 65 to 75 HV. In addition, hardness of the FAB processed using a wire of the invention prior to bonding is less than 80 HV, preferably in the range of from 60 to 70 HV. Such hardness or, more precisely, softness of the wire core and FAB helps to prevent damage of a sensitive substrate in the course of bonding. Experiments have also shown that such soft wires according to the invention exhibit very soft FAB properties. Such limitation of FAB hardness is particularly helpful if mechanically sensitive structures are aligned below a bond pad. This is particularly true if a bond pad consists of a soft material like aluminum or gold. The sensitive structure can, for example, comprise one or several layers of porous silicon dioxide, in particular with a dielectric constant of less than 2.5. Such porous and hence weak material is becoming increasingly common as it can help to increase the device performance. Therefore, the mechanical properties of the bonding wire of the invention can be optimized to avoid cracking or other damaging of such weak layers.

In a particular embodiment, the alloyed silver wire of the invention exhibits a silver dendritic growth at a rate of less than $4\text{ }\mu\text{m/s}$, for example in the range of from 2 to less than $4\text{ }\mu\text{m/s}$, preferably in the range of from 2 to $3\text{ }\mu\text{m/s}$, which is about $1/10^{\text{th}}$ to $1/7^{\text{th}}$ of the about $25\text{ }\mu\text{m/s}$ growth rate of a 4N pure silver wire.

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In another advantageous embodiment, the resistivity of the wire is less than $3.2\text{ }\mu\Omega\cdot\text{cm}$, for example in the range of from 2.0 to $2.4\text{ }\mu\Omega\cdot\text{cm}$, preferably in the range of from 2.2 to $2.4\text{ }\mu\Omega\cdot\text{cm}$, i.e. meaning suitability for many applications.

10 In another aspect, the invention relates also to a process for the manufacture of the alloyed silver wire in any of its embodiments disclosed above. The process comprises at least the steps:

(1) providing a precursor item consisting of:

(a) palladium in an amount in the range of from 0.1 to 3 wt.-%, preferably 0.5 to 1.5 wt.-%,
15 %,

(b) gold in an amount in the range of from 0.1 to 3 wt.-%, preferably 0.2 to 1.5 wt.-%,

(c) nickel in an amount in the range of from 20 to 700 wt.-ppm, preferably 275 to 325 wt.-ppm,

(d) calcium in an amount in the range of from 20 to 200 wt.-ppm, preferably 20 to 50 wt.-ppm,
20 ppm,

(e) silver in an amount in the range of from 93.91 to 99.786 wt.-%, preferably 96.9625 to 99.2595 wt.-%, and

(f) 0 to 100 wt.-ppm of further components,

wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the precursor item,
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(2) elongating the precursor item to form a wire precursor, until the desired final diameter of the wire core is obtained; and

(3) finally strand annealing the wire precursor obtained after completion of process step (2) at an oven set temperature in the range of from 400 to 600 °C for an exposure time

30 in the range of from 0.4 to 0.8 seconds to form the alloyed silver wire,

wherein step (2) includes one or more sub-steps of intermediate batch annealing of the elongated precursor item at an oven set temperature of from 400 to 800 °C for an

exposure time in the range of from 50 to 150 minutes and/or one or more sub-steps of intermediate strand annealing of the elongated precursor item at an oven set temperature of from 400 to 800 °C for an exposure time in the range of from 0.4 seconds to 1.2 seconds.

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The term "strand annealing" is used herein. It is a continuous process allowing for a fast production of a wire with high reproducibility. Strand annealing means that the annealing is done dynamically while an elongated wire precursor item or wire precursor to be annealed is moved through an annealing oven and spooled onto a reel after having left the annealing oven.

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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).

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This disclosure distinguishes between precursor item, wire precursor and alloyed silver wire. The term "precursor item" is used for those wire pre-stages which have not reached the desired final diameter of the wire core, while the term "wire precursor" is used for a wire pre-stage at the desired final diameter. After completion of process step (3), i.e. after the final strand annealing of the wire precursor at the desired final diameter an alloyed silver wire in the sense of the invention is obtained.

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A precursor item as provided in process step (1) can be obtained by alloying/doping silver with the desired amount of palladium, gold, nickel and calcium. The silver alloy itself can be prepared by conventional processes known to the person skilled in the art of metal alloys, for example, by melting together the silver, the palladium, the gold, the nickel and the calcium in the desired 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 materials used can have a purity grade of, for example, 99.99 wt.-% and above. The melt so-produced can be cooled to form a homogeneous

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piece of silver 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, 5 to 100 m. Such rod can be made by casting said silver alloy melt in an appropriate mold of room temperature, followed by cooling and solidifying.

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If a coating layer in the form of a single- or multi-layer is present on the core of the alloyed silver wire as disclosed for some of the embodiments of the first aspect of the invention, this coating layer is preferably applied to the wire precursor item, which may not yet be elongated, not finally elongated or even fully elongated to the desired final diameter. The skilled person knows how to calculate the thickness of such coating layer on a precursor item to obtain the coating layer in the thickness disclosed for the
 10 embodiments of the wire, i.e. after elongating the precursor item with the coating layer to form the wire precursor. As already disclosed above, numerous techniques for forming a coating layer of a material according to the embodiments on a silver alloy
 15 surface are known. 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.

20 In order to superimpose a metal coating as single-layer or multi-layer to the wire core as disclosed for some of the embodiments of the first aspect of the invention, it is expedient to interrupt process step (2) once a desired diameter of the precursor item is reached. Such diameter may be in the range of, for example, 80 to 200 μm . Then the single- or multi-layer metal coating may be applied, for example, by one or more
 25 electroplating process steps. Thereafter process step (2) is continued until the desired final diameter of the wire core is obtained.

In process step (2) the precursor item is elongated to form a wire precursor, until the desired final diameter of the wire core is obtained. Techniques to elongate a precursor
 30 item to form a wire precursor are known and appear useful in the context of the invention. Preferred techniques are rolling, swaging, die drawing or the like, of which die

drawing is particularly preferred. In the latter case the precursor item is drawn in several process steps until the desired and final diameter of the wire core is reached.

The desired and final diameter of the wire core may be in the range of from 8 to 80 μm or, preferably, in the range of from 12 to 55 μm . 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.

Step (2) of the process of the invention includes one or more sub-steps of intermediate batch annealing of the elongated precursor item at an oven set temperature of from 400 to 800 °C for an exposure time in the range of from 50 to 150 minutes and/or one or more sub-steps of intermediate strand annealing of the elongated precursor item at an oven set temperature of from 400 to 800 °C for an exposure time in the range of from 0.4 seconds to 1.2 seconds. The one or more steps of intermediate annealing of the elongated precursor item may be performed between two or more of multiple elongation or drawing steps. To illustrate this by example, there may be performed three intermediate annealing steps at three different stages during drawing, for example, a first intermediate batch annealing of a rod drawn to a diameter of 2 mm and coiled on a drum at an oven set temperature in the range of from 400 to 800 °C for an exposure time of 50 to 150 minutes, a second intermediate strand annealing of the precursor item drawn to a diameter of 47 μm at an oven set temperature in the range of from 400 to 800 °C for an exposure time of 0.4 to 1.2 seconds and a third intermediate strand annealing of the precursor item further drawn to a diameter of 27 μm at an oven set temperature in the range of from 400 to 800 °C for an exposure time of 0.4 to 1.2 seconds.

In process step (3) the elongated wire precursor obtained after completion of process step (2), is finally strand annealed. The final strand annealing is performed at an oven set temperature in the range of, for example, 400 to 600 °C for an exposure time of 0.4 to 0.8 seconds, or, in a preferred embodiment, 400 to 500 °C for 0.5 to 0.7 seconds.

The final strand annealing is typically performed by pulling the elongated wire precursor through a conventional annealing oven, typically in the form of a cylindrical tube of a given length and with a defined temperature profile at a given annealing speed which may be chosen in the range of, for example, from 10 to 60 meters/minute. In so doing
 5 the annealing time/oven temperature parameters can be defined and set.

In a preferred embodiment, the finally strand annealed alloyed silver 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,
 10 i.e. within 0.2 to 0.6 seconds, cooling the finally strand annealed alloyed silver wire from the temperature it experienced in process step (3) down to room temperature, for example by dipping or dripping.

With respect to an embodiment of the invention, it was found that final strand annealing
 15 at a temperature below the temperature of maximum elongation can result in beneficial wire properties as the wire morphology can be influenced in a positive way. By this adjustment, other properties like e.g. wire hardness, ball-bonding behavior etc. can be influenced in a positive manner.

20 In an embodiment, the final strand annealing may be performed at a temperature which is at least 150 °C lower, for example 210 to 240 °C lower than a temperature at which the maximum elongation value is achieved by annealing; this may result in an elongation value of the wire after annealing being not more than 70 % of the maximum elongation value, for example 30 to 60 % of a maximum elongation value. For example,
 25 process step (3) may be performed at a temperature which is at least 150 °C, preferably at least 180 °C, or at least 200 °C lower than the temperature of maximum elongation $T_{\Delta L(max)}$. Often, the temperature in process step (3) is not more than 250 °C lower than $T_{\Delta L(max)}$. The temperature of maximum elongation $T_{\Delta L(max)}$ is determined by testing the elongation at break of a specimen (wire) at different temperatures. The data points are
 30 collected in a graph, showing the elongation (in %) as a function of temperature (°C). The resulting graph is often referred to as an "annealing curve". In the case of silver based wires, a temperature is observed where the elongation (in %) reaches a

maximum. This is the temperature of maximum elongation $T_{\Delta L(max)}$. An example is shown in Figure 1, which shows an exemplary annealing curve of an 18 μm alloyed silver wire according to sample 1 (Table 1). The annealing temperature is the variable parameter of the x-axis. The graph shows the measured values of the break load (BL, in grams) and the elongation (EL, in %) of the wire. The elongation was determined by tensile testing. Elongation measurements exhibited a typical local maximum value of about 19 % in the displayed example, which was achieved at an annealing temperature of around 700 °C. If the wire according to sample 1 was not final strand annealed at this temperature of maximum elongation, but at 480 °C, which was 220 °C below the temperature of the maximum elongation the result is an elongation value of about 8 % which is more than 40 % below the maximum elongation value.

The intermediate annealing of process step (2) as well as the final strand annealing of process step (3) may be performed in 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 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 93/7, 95/5 and 97/3 vol.-%/vol.-%, each based on the total volume of the mixture. Applying reducing atmospheres in annealing is particularly preferred, if some parts of the surface of the alloyed silver wire are sensitive to oxidation by oxygen of the air. Purging with said types of inert or reducing gas is preferably performed at a gas exchange rate (= gas flow rate [liter/min] : inner oven volume [liter]) lying in the range of 10 to 125 min^{-1} , more preferably 15 to 90 min^{-1} , most preferably 20 to 50 min^{-1} .

It is believed that the unique combination of the composition of the precursor item material (which is the same as that of the finished alloyed silver wire core) and the annealing parameters prevailing during process steps (2) and (3) is essential to obtain the wire of the invention exhibiting at least one of the above disclosed intrinsic and/or

extrinsic properties. The temperature/time conditions of the intermediate and the final strand annealing steps allow for achieving or adjusting intrinsic and extrinsic properties of the alloyed silver wire core.

5 After completion of process step (3) the alloyed silver wire of the invention 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 10 days after completion of process step (3). Alternatively, in order to keep the alloyed silver wire's wide wire bonding process window property and in order to prevent it from
10 oxidative or other chemical attack, the finished wire is typically spooled and vacuum sealed immediately after completion of process step (3), i.e. without delay, for example, within <1 to 5 hours after completion of process step (3) and then stored for further use as bonding wire. Storage in vacuum sealed condition should not exceed 6 months. After opening the vacuum seal the alloyed silver wire should be used for wire bonding within
15 no longer than 10 days.

It is preferred that all process steps (1) to (3) as well as spooling and vacuum sealing are carried out under clean room conditions (US FED STD 209E cleanroom standards, 1k standard).

20 A third aspect of the invention is an alloyed silver wire obtainable by the afore disclosed process according to the second aspect of the invention or of an embodiment thereof. It has been found that said alloyed silver wire is well suited for use as a bonding wire in wire bonding applications. Wire bonding technique is well known to the skilled person.
25 In the course of wire bonding it is typical that a ball bond (1st bond) and a stitch bond (2nd bond, wedge bond) are formed. During bond forming a certain force (typically 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
30 limits of the applied ultrasonic energy in a wire bonding process defines the wire bonding process window:

(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.

- 5 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.

- 10 In other words, the 1st bond (ball bond) process window area is the product of the difference between the upper and the lower limits of the force used in the bonding and the difference between the upper and the lower limits of the applied ultrasonic energy, wherein the resulting bond has to meet certain ball shear test specifications, e.g. a ball shear of 0.0085 grams/ μm^2 , no non-stick on bond pad, etc., while the 2nd bond (stitch
- 15 bond) process window area is the product of the difference between the upper and the lower limits of the force used in the 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 2.5 grams, no non-stick on lead, etc.

- 20 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. The wire of the invention exhibits a considerably wide wire bonding process window.

- 25 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

Preparation of FAB:

- 5 It was worked according to the procedures described in the KNS Process User Guide for Free Air Ball (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, EFO current of 18 mA, EFO time 455 μ s).

10 Test methods A. to J.

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

A. Electron Backscattered Diffraction (EBSD) Pattern Analysis of Wires and FAB:

- 15 The main steps adopted to measure wire and FAB texture were sample preparation, getting good Kikuchi pattern and component calculation:

The wires with or without FAB were first potted using epoxy resin and polished as per standard metallographic technique. Ion milling was applied in the final sample

- 20 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.

- 25 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 EBSD detector. The electron back-scattering patterns (EBSP) containing the wire crystallographic information were obtained.

- 30 These patterns were further analyzed for grain orientation fraction, average grain size, etc. (using a software called QUANTAX EBSD program developed by Bruker). Points of similar orientation were grouped together to form the texture component.

To distinguish different texture components, a maximum tolerance angle of 15° was used. The wire drawing direction was set as a reference orientation. The [100], [101] and [111] texture percentages were calculated by measurement of the percentage of crystals with [100], [101] and [111] plane of orientation parallel to the reference orientation.

Average 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 "average 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 average crystal grain size.

Twin boundaries (also called $\Sigma 3$ CSL twin boundaries) were excluded in the average grain size calculation. The twin boundary was described by a 60° rotation about $\langle 111 \rangle$ plane of orientation between the neighboring crystallographic domains. The number of points depends on the step size, which was less than $1/5$ of the average crystal grain size.

B. Salt-solution soaking test of bonded balls:

The wires were ball bonded to Al-0.5wt.-%Cu bond pads. The test devices with the so-bonded wires were soaked in salt-solution at 25°C for 10 minutes, washed with deionized (DI) water and later with acetone. The salt-solution contained 20 wt.-ppm NaCl in DI water. The number of lifted balls were examined under a low power microscope (Nikon MM-40) at 100X magnification. Observation of a higher number of lifted balls indicated severe interfacial galvanic corrosion.

C. Moisture resistance test of bonded balls:

The wires were ball bonded to Al-0.5wt.-%Cu bond pads. The test devices with the so-bonded wires were stored at 130°C temperature, 85 % relative humidity (RH) for 8 hours in a highly accelerated stress test (HAST) chamber and later examined for the

number of lifted balls under a low power microscope (Nikon MM-40) at 100X magnification. Observation of a higher number of lifted balls indicated severe interfacial galvanic corrosion.

5 D. Vickers Micro-hardness:

The hardness was measured using a Mitutoyo HM-200 testing equipment with a Vickers indenter. A force of 10 mN indentation load was applied to a test specimen of wire for a dwell time of 12 seconds. The testing was performed on the center of the wire core and the FAB.

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E. Stitch bonding process window area:

Measurements of the bonding process window area were done by a standard procedure. The test wires were bonded using a KNS-iConn bonder tool (Kulicke & Soffa Industries Inc., Fort Washington, PA, USA). The process window values were based on
15 a wire having an average diameter of 18 μm , wherein the lead finger to which the wire was bonded consisted of silver.

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

- 20 (1) supply of too low force and ultrasonic energy lead to non-stick on lead finger (NSOL) of the wire, and
(2) supply of too high force and ultrasonic energy lead to short wire tail (SHTL).

F. Electrical Resistivity:

- 25 Both ends of a test specimen, i.e. a wire of 1.0 meter in length, were connected to a power source providing a constant current/voltage. The resistance was recorded with a device for the supplied voltage. The measuring device was a HIOKI model 3280-10, and the test was repeated with at least 10 test specimens. The arithmetic mean of the measurements was used for the calculations given below.

30

The resistance R was calculated according to $R = V / I$.

The specific resistivity ρ was calculated according to $\rho = (R \times A) / L$, wherein A is the mean cross-sectional area of the wire and L the length of the wire between the two measuring points of the device for measuring the voltage.

- 5 The specific conductivity σ was calculated according to $\sigma = 1 / \rho$.

G. Elongation (EL):

The tensile properties of the wires were tested using an Instron-5564 instrument. The wires were tested at 2.54 cm/min speed, for 254 mm gauge length (L). The load and
10 elongation on fracture (break) were acquired as per ASTM standard F219-96. The elongation was the difference in the gauge length (ΔL) of the wire between start and end of the tensile test, usually reported in percentage as $(100 \cdot \Delta L / L)$, calculated from the recorded load versus extension tensile plot. The tensile strength and the yield strength were calculated from the break and yield load divided by the wire area. The
15 actual diameter of the wire was measured by the sizing method, weighing a standard length of the wire and using the density of it.

H. Electro-migration test of wires:

Two wires were kept parallel within a millimeter distance on a PTFE plate under the
20 objective lens of a low power microscope Nikon MM40 model at 50X magnification. A water drop was formed by a micropipette between the two wires to be connected electrically. One wire was connected to a positive and the other to a negative pole and 5 V was given to the wires. The two wires were biased with 5 V direct current in a closed circuit, connected in series with a 10 k Ω resistor. The circuit was closed by wetting the
25 two wires with a few drops of de-ionized water as an electrolyte. Silver electro-migrated from the cathode to the anode in the electrolyte forming silver dendrites, sometimes the two wires bridged. The rate of growth of silver dendrites strongly depended on the alloying additions. The tested wires' diameter was 75 μm .

Example 1

A quantity of silver (Ag), palladium (Pd) and gold (Au) of at least 99.99 % purity ("4N") in each case were melted in a crucible. Small amounts of silver-nickel and silver-calcium master alloy were added to the melt and uniform distribution of the added components was ascertained by stirring. The following silver-nickel and silver-platinum master alloys were used:

Name of Master Alloy	Composition	
Ag-0.5wt.-%Ni	99.5wt.-% Ag	0.5wt.-% Ni
Ag-0.5wt.-%Ca	99.5wt.-% Ag	0.5wt.-% Ca

For the alloys of Table 1 the corresponding combination of the master alloys Ag-0.5wt.-%Ni and Ag-0.5wt.-%Ca were added.

Then a wire core precursor item in the form of 8 mm rods was continuous cast from the melt. The wire core precursor item was then drawn in several drawing steps to form a wire core precursor with a specified diameter of $18 \pm 0.5 \mu\text{m}$. The cross section of the wire core was of essentially circular shape.

The rods drawn to a diameter of 2 mm and coiled on a drum were intermediate batch-annealed at an oven set temperature of 500 °C for an exposure time of 60 minutes. A second intermediate strand annealing of the precursor items drawn to a diameter of 47 μm at an oven set temperature of 600 °C for an exposure time of 0.8 seconds and a third intermediate strand annealing of the precursor items drawn to a diameter of 27 μm at an oven set temperature of 600 °C for an exposure time of 0.6 seconds were performed. A final strand annealing of the 18 μm wire core precursors at an oven set temperature of 480 °C for an exposure time of 0.6 seconds was performed followed by quenching the so-obtained wires in water containing 0.05 vol.-% of surfactant.

Intermediate batch annealing was performed using argon purging gas, while strand annealing was performed using a 95 vol.-% nitrogen : 5 vol.-% nitrogen purging gas mixture.

By means of this procedure, several different samples 1 to 5 of alloyed silver wires according to the invention and a comparative silver wire of 4N purity (Ref) were manufactured.

Sample	wt.-%		wt.-ppm			
	Au	Pd	Ni	Ca	Pt	Cu
4N Ag (Ref)	0.0002	0.0002	2	2	2	2
1	1.0	1.0	300	30	2	2
2	1.5	1.5	100	30	2	2
3	1.0	2.0	100	30	2	2
4	1.5	2.0	30	50	2	2
5	1.0	3.0	30	50	2	2

5 Table 1: Chemical composition of the silver alloys 1 to 5

Table 1 shows the composition of different wires according to the invention, samples 1 to 5. The palladium content was in the range of from 1 to 3 wt.-%. The gold content was in the range of from 1 to 1.5 wt.-%. The nickel addition was varied from 30 to 300 wt.-
 10 ppm. The calcium content was maintained at 30 and 50 wt.-ppm, respectively.

The grain sizes of wire samples 1 to 5 were measured and the average grain sizes were reported. The result was in the range of 2 to 5 μm in each case. For sample 1, the
 15 average grain size was 2.91 μm .

Table 2 below shows results of an evaluation on corrosion and moisture resistance of the bonded wires, behavior of 2nd bond process window and performance of FAB formation. The above defined wire samples 1 to 5 as well as the comparative wire of 4N pure silver were bonded to Al-0.5wt.-%Cu bond pads and tested according to the above
 20 disclosed test methods. All tests were carried out with 18 μm wires except for the electromigration test which was performed with 75 μm wires.

	Sample	4N Ag (Ref)	1	2	3	4	5
Mechanical properties	Elongation, %	7.51	7.50	7.49	7.53	7.52	7.57
	Tensile strength, MPa	185	264	262	262	263	262
	Yield strength, MPa	133	147	155	157	158	160
	Micro-hardness, HV (10 mN/12 s)	50	70	74	74	74	76
Electrical properties	Resistivity, $\mu\Omega\cdot\text{cm}$	1.6	2.3	2.3	2.3	2.4	2.4
Salt-solution soaking test of bonded balls	% bonded ball lift	85	2	5	5	5	5
Moisture resistance test	% bonded ball lift	50	2	5	5	5	5
Electro- migration test	Rate of growth of silver dendrites ($\mu\text{m/s}$)	25	2.4	2.5	2.5	2.6	2.7
FAB	Performance of FAB formation	+++	++++	++++	++++	++++	++++
Bonding process window	1st bond (ball bond), mA·g	650	1020	1020	1020	1020	1020
	2nd bond (stitch bond), mA·g	8100	14400	14400	14400	14400	14400

Table 2: Certain test results obtained with wire samples 1 to 5; Evaluation: +++++

Excellent, +++, Good, ++ Satisfactory, +Inferior

- 5 All of the wire samples resulted in process windows which were well suited for industrial application. A significant improvement of the corrosion and moisture resistance of the bonded balls was observed. In particular, wire sample 1 showed a value of near to zero, i.e. 2 ball lift, which is a particular improvement compared to the 4N pure silver wire (Ref).
- 10 In addition, the silver dendritic growth of the wire samples 1 to 5 was much lower than that of the 4N pure silver wire.

Table 3 shows the average grain size and texture component of wire sample 1 (wire, FAB and heat affected zone (HAZ)).

		4N Ag	Sample 1
[100] Orientation (area fraction, %)	FAB	0.9	9.2
	HAZ	6.2	4.8
	Wire	6.0	2.7
[101] Orientation (area fraction, %)	FAB	19.5	34.6
	HAZ	27.9	9.9
	Wire	38.7	3.2
[111] Orientation (area fraction, %)	FAB	6.1	4.0
	HAZ	4.5	1.2
	Wire	9.4	2.0
Average Grain size (μm)	FAB	11.6	10.7
	HAZ	4.28	2.53
	Wire	2.92	2.91
Fraction of twin boundaries (%)	FAB	73.6	61.8
	HAZ	76.2	51.1
	Wire	70.0	43.3

Table 3: Texture analysis of the annealed 18 μm wire sample 1

5

DESCRIPTION OF FIGURES

Fig.1 shows an exemplary annealing curve of a silver-palladium-gold-nickel-calcium alloy 18 μm wire, sample 1 (see Table 1). The annealing time was chosen to a constant value by adjusting the speed of the moving wire. The annealing temperature is the variable parameter of the x-axis. The graph shows the measured values of the break load (BL, in grams) and the elongation (EL, in %) of the wire. The elongation was determined by tensile testing. Elongation measurements exhibited a typical local maximum value of about 19 % in the displayed example, which was achieved at an annealing temperature of around 700 °C. Sample wire 1 was annealed at 480 °C, which was 220 °C below the temperature of the maximum elongation according to Figure 1.

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This resulted in an elongation value of about 8 %, which is more than 40 % below the maximum elongation value.

5 Fig.2 shows an exemplary ion-milled cross-section image of a silver-palladium-gold-nickel-calcium alloy 18 μm wire, sample 1 (Table 1). Grain morphology of the three different locations wire, HAZ and FAB are evident. The wire sample 1 was annealed at 480 °C, 7.5% EL. Ball to wire size ratio (BSR) of 1.8 and EFO current 18 mA and EFO time 455 μs were applied.

CLAIMS

1. An alloyed silver wire comprising or consisting of a wire core, the wire core itself consisting of:
 - 5 (a) palladium in an amount in the range of from 0.1 to 3 wt.-%,
 - (b) gold in an amount in the range of from 0.1 to 3 wt.-%,
 - (c) nickel in an amount in the range of from 20 to 700 wt.-ppm,
 - (d) calcium in an amount in the range of from 20 to 200 wt.-ppm,
 - (e) silver in an amount in the range of from 93.91 to 99.786 wt.-%, and
 - 10 (f) 0 to 100 wt.-ppm of further components,
 wherein all amounts in wt.-% and wt.-ppm are based on the total weight of the core, wherein the alloyed silver wire has an average diameter in the range of from 8 to 80 μm .

2. The alloyed silver wire of claim 1 having an average diameter in the range of
 - 15 from 12 to 55 μm .

3. The alloyed silver wire of claim 1 or 2, wherein the palladium amount is in the range of from 0.5 to 1.5 wt.-%.

- 20 4. The alloyed silver wire of any one of the preceding claims, wherein the gold amount is in the range of from 0.2 to 1.5 wt.-%.

5. The alloyed silver wire of any one of the preceding claims, wherein the nickel amount is in the range of from 275 to 325 wt.-ppm.
 - 25

6. The alloyed silver wire of any one of the preceding claims, wherein the calcium amount is in the range of from 20 to 50 wt.-ppm.

7. The alloyed silver wire of any one of the preceding claims, wherein the silver
 - 30 amount is in the range of from 96.9625 to 99.2595 wt.-%.

8. The alloyed silver wire of any one of the preceding claims having a round, ellipsoid or rectangular shape, in cross-sectional view.

9. The alloyed silver wire of any one of the preceding claims wherein the wire core has a surface, wherein the surface is an outer surface or an interface region between the wire core and a coating layer superimposed on the wire core.

10. The alloyed silver wire of claim 9 having a coating layer superimposed on the wire core, wherein the coating layer is a single-layer made of a precious metal element or a multi-layer comprised of a number of super-positioned adjacent sub-layers, wherein each sub-layer is made of a different precious metal element.

11. The alloyed silver wire of any one of the preceding claims wherein the wire core is characterized at least by one of the following intrinsic properties:

- (1) The average wire grain size is less than 10 μm ,
- (2) The wire grain [100] or [101] or [111] plane of orientation is less than 7 %,
- (3) The wire twin boundary fraction is less than 60 %,
- (4) The FAB exhibits columnar grains,
- (5) The FAB average grain size is $\leq 18 \mu\text{m}$,
- (6) The FAB grain [101] plane of orientation is less than 45 %,
- (7) The FAB twin boundary fraction is less than 70 %,

and/or at least by one of the following extrinsic properties:

- (α) The corrosion resistance has a value of not more than 5 % bonded ball lift,
- (β) The moisture resistance has a value of not more than 5 % bonded ball lift,
- (γ) The hardness of the wire core is not more than 85 HV,
- (δ) The process window area for stitch bonding has a value of at least 12000 mA·g,
- (ϵ) The resistivity of the wire is less than 2.5 $\mu\Omega\cdot\text{cm}$,
- (ζ) The yield strength of the wire is not more than 170 MPa,
- (η) The wire's silver dendritic growth is not more than 4 $\mu\text{m/s}$.

12. A process for the manufacture of an alloyed silver wire of any one of the preceding claims, wherein the process comprises at least the steps:

(1) providing a precursor item with the composition of the wire core of any one of claims 1 to 7,

(2) elongating the precursor item to form a wire precursor, until the desired final diameter of the wire core is obtained; and

- 5 (3) finally strand annealing the wire precursor obtained after completion of process step (2) at an oven set temperature in the range of from 400 to 600 °C for an exposure time in the range of from 0.4 to 0.8 seconds to form the alloyed silver wire, wherein step (2) includes one or more sub-steps of intermediate batch annealing of the elongated precursor item at an oven set temperature of from 400 to 800 °C for an
10 exposure time in the range of from 50 to 150 minutes and/or one or more sub-steps of intermediate strand annealing of the elongated precursor item at an oven set temperature of from 400 to 800 °C for an exposure time in the range of from 0.4 seconds to 1.2 seconds.

- 15 13. The process of claim 12, wherein the final strand annealing is performed at an oven set temperature in the range of 400 to 500 °C for an exposure time in the range of from 0.5 to 0.7 seconds.

14. The process of claim 12 or 13, wherein the finally strand annealed alloyed silver
20 wire is quenched in water which may contain one or more additives.

15. The process of any one of claims 12 to 14, wherein the intermediate annealing of process step (2) as well as the final strand annealing of process step (3) is performed in an inert or reducing atmosphere.

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16. An alloyed silver wire obtainable by the process of any one of claims 12 to 15.