

[Document Name] Description

[Title of Invention] STRUCTURE OF COATED COPPER WIRE FOR
ULTRASONIC BONDING

[Technical Field]

[0001]

The present invention relates to a coated copper alloy wire for ultrasonic bonding which is suitable for connecting an IC chip electrode and an external lead over a substrate or the like used for a semiconductor device to each other and, particularly, to a bonding/bump wire for ultrasonic bonding used under high temperature environments such as those used for vehicles, power semiconductors, high speed devices, or the like or to a coated copper bonding wire for free air ball (FAB) usable as a very thin wire of 15 μm or less.

[Background Art]

[0002]

As a copper wire for connecting an IC chip electrode and an external lead of a semiconductor to each other, various types of copper wires have heretofore been developed. For instance, as a pure copper alloy wire, there have been known the one obtained by adding titanium (Ti) or zirconium (Zr) (JP 62-102551 A), the one obtained by adding boron (B) (JP 62-102552 A), the one obtained by adding magnesium (Mg) (JP 62-130248), the one obtained by adding a rare earth element (including yttrium (Y)) (JP 62-193254 A), the one obtained by adding calcium (Ca) (JP 62-

102552), the one obtained by adding phosphorus (P) or the like (JP 01-291435 A), the one obtained by adding iridium (Ir) (JP 04-184946), the one obtained by adding paradigm (Pd) or the like (JP 2012-222194 A), or the like.

[0003]

Further, as the copper alloy wire, there have been known the one containing palladium (Pd) (JP 59-139663 A), the one containing magnesium (Mg) (JP 60-236253 A), the one containing silver (Ag) (JP 61-019158), the one containing nickel (Ni) or the like (JP 04-218632), the one containing platinum (Pt) or the like (JP 07-070673 A), the one containing gold (Au) (JP 2011-003745 A), or the like.

[0004]

Furthermore, as the coated copper alloy wire, there have been known the one obtained by coating a noble metal (JP 61-285743 A), the one obtained by coating palladium (Pd) (JP 2004-006740 A), the one obtained by coating gold (Au) and palladium (Pd) (JP 2010-225722 A), the one having an Au/Pd mixture layer and a palladium (Pd) coating layer (JP Pat. No. 5088981), or the like.

[0005]

As to a wire diameter of these coated copper wires, a wire diameter of the coated copper bonding wires for free air ball (FAB) is generally from more than 10 μm to several tens of micrometers, and a wire diameter of the thick wires for power semiconductors is generally from several tens of micrometers to several hundreds of micrometers.

[0006]

Further, as the coated copper wires from the viewpoint of composition, there has been considered practical use of a pure copper alloy wire or a wire obtained by coating a core material such as copper (Cu) having purity of 99.999 mass% or more, or a copper alloy with palladium (Pd) having a submicron thickness as the bonding wire for FAB since the wire is excellent in connection reliability to an aluminum pad on an IC chip electrode (JP 2004-006740 A ("Patent Literature 1" listed below)). At the outset, a ball bonding method comprising forming a molten ball on one end of the Pd-coated copper wire, performing ball bonding to an aluminum pad on an IC chip electrode by ultrasonic wave-aided thermocompression bonding (first bonding), and stitch bonding the other end to an external lead wire or the like on a printed substrate by ultrasonic bonding (second bonding) was experimentally employed.

[0007]

After that, various improvements have been made, and various coated copper wires each of which is coated with solid pure copper or a copper alloy and is excellent in first bonding property by free air ball (FAB) have been proposed.

As used herein, "FAB" means a molten ball which is formed on one end of a wire extended from one end of a bonding tool by generating a spark discharge while blowing

a non-oxidizing gas or a reducing gas such as nitrogen or nitrogen-hydrogen to the end of the wire. In the case of FAB, since an inert atmosphere or a reducing atmosphere is maintained until the first bonding of the molten ball of the boing wire is finished, the pure copper alloy wire per se is not oxidized in the first bonding.

[0008]

Meanwhile, for the above-described bonding wire, bonding methods such as wedge bonding in which the first bonding and the second bonding are performed by employing the ultrasonic method to attain the bonding by directly using ultrasonic wave without forming any molten ball and a stud bump method in which the coated copper wire obtained by the wedge bonding is torn off by clamping may be employed. Also, in order to further facilitate the ultrasonic bonding, a ribbon wire having a rectangular sectional shape which is flattened by pressing the coated copper wire may be subjected to the ultrasonic bonding. The wire which is subjected to the ultrasonic bonding by any one of these methods is then sealed with a molding resin to give a semiconductor device. For the aluminum pad, a pure aluminum (Al) metal or an alloy obtained by adding 0.3 to 2.0 mass% of copper (Cu), silicon (Si), nickel (Ni), or the like to the aluminum (Al) metal is generally used. The aluminum pad is typically formed by dry plating such as vacuum vapor deposition.

[0009]

However, the above-described Pd-coated copper wire has not been put into practical use on a large scale. The reasons why the Pd-coated copper wire has not been commercialized are as follows.

First of all, the solid high purity copper wire has the crucial drawback that a copper oxide film is formed due to oxidization of a surface before the bonding. Therefore, the formation of copper oxide film has been prevented by: using the various alloying elements as described above; increasing a thickness of a coating layer of a nobler metal or the like or forming a multilayer as the coating film; or providing a diffusion layer on a core material/coating layer interface. Nevertheless, it has been difficult to form stable FAB with the coated copper wire which is coated with the thick layer of palladium (Pd) or the like, and the coated copper wire has entailed problems of unknown causes, such as sudden formation of distorted or hardened molten ball and occurrence of chip damage. From the reasons explained above, the Pd-coated copper wire has not been used so widely as a bonding wire for FAB.

[0010]

Later on, a coated copper wire having a gold (Au) surface layer and a palladium (Pd) coating layer was developed (JP 2012-89685 A ("Patent Literature 2" listed below)), which enabled to maintain bonding properties in FAB formation by preventing the molten ball from being hardened during the first bonding while lowering a

softening temperature to that similar to a softening temperature of a pure copper wire having purity of 99.9999 mass% by alloying a very small amount of a base metal element, and thus the real commercialization of the coated copper wire started.

[0011]

In the case of the Pd-coated copper wire having the gold (Au) surface layer and the palladium (Pd) coating layer, a total thickness of the coating layers including the palladium (Pd) layer and the gold (Au) layer is a little less than 100 nm. Therefore, it has been difficult to keep a good balance between the layers, and adjustment for the balancing has been very difficult. For instance, it has been necessary to detect the optimum balance between the coating layers every time a composition of a core material is changed or a wire diameter is changed from 25 μm to 20 μm or further to 18 μm . Further, the cost has been increased since the Pd-coated copper wire requires formation of spherical FAB in the first bonding, and it has been necessary to detect an optimum balance between the coating layers again at the mass production stage.

[0012]

And yet, with the use of the Pd-coated copper wire, an ultrasonic bonding region required for the second bonding is reduced along with a reduction in diameter of the bonding wire from 20 μm to 18 μm and from 18 μm to 15 μm , and a bonding region usable for the bonding is not left

at all in some cases. Thus, there has been a problem of unstable ultrasonic second bonding. The problem is found also in the ultrasonic bonding in the first bonding using ultrasonic bonding and the stud bonding.

The problem occurred since conditions for bonding the bonding wire for thinner line by using an ultrasonic device are decided based on a frequency (about several tens to several hundreds of kilohertz), an output (about several watts at maximum), and a compression force (several to several tens of gram force), and therefore the optimum ultrasonic conditions hinge upon the thickness of the coating layers in addition to the composition of the core material.

[0013]

Meanwhile, in the case of a thick wiring line for the power semiconductors or the like used under high temperatures, the copper oxide film is formed on a wide area when the thickness of the coating layers is reduced by reducing the amount of the expensive noble metal to be used. Due to the influences of the copper oxide film, bonding strength of the second bonding is reduced, and development of an oxide film on a bonding interface in the second bonding is accelerated. Therefore, a problem that the bonding strength is further reduced at the bonding interface was left unsolved.

[0014]

On the other hand, it has been proposed to directly

coat the copper wire with a carbon layer for various purposes. For instance, there has been contemplated to provide "a wire for bonding semiconductor elements, characterized in that a total organic carbon amount on a surface is 50 to 1500 $\mu\text{g}/\text{m}^2$ " which is attained by subjecting an ingot to pickling or the like after melting and casting (Claim 1 of JP 6-151497 A ("Patent Literature 3" listed below)), wherein the bonding wire "comprises as a main element any one of Au, Al, and Cu; is formed into a very thin wire of about 10 to 50 μm ; and is used in a state where a predetermined length thereof is wound around a spool and mounted on a wire bonder" (paragraph 0002 of the publication). The method is described as "since a total organic carbon in an amount larger than 1500 $\mu\text{g}/\text{m}^2$ is observed on a surface of the wire produced by an ordinary process i.e. by melting, casting, drawing, annealing, and winding steps, one of the methods for producing the wire having the surface total organic carbon amount of 50 to 1500 $\mu\text{g}/\text{m}^2$ includes cleaning the wire by pickling or the like... to keep the surface organic carbon amount within the range of 50 to 1500 $\mu\text{g}/\text{m}^2$ (Claim 2 of the publication). Since it is only necessary to add the cleaning step before or after the annealing step in the ordinary process, the method is characterized by the easy implementation." (paragraph 0010 of the publication). Further, it is described that "examples of the lubricant component include a mineral oil-based lubricant component such as paraffin-

based hydrocarbon, naphthene-based hydrocarbon, and aromatic hydrocarbon; a synthetic oil-based lubricant component such as polyolefin, alkyl benzene, fatty acid, higher alcohol, fatty acid soap, polyglycol, polyphenyl ether, fatty acid diester, polyol ester, polyoxyethylene alkyl ether, sulfonate, amine, amine salt, silicone, phosphoric acid ester, fluorocarbon, fluoropolyether, and fluoroglycol; a natural oil-based lubricant component such as beef tallow, lard, palm oil, soybean oil, rapeseed oil, castor oil, and pine root oil, and any one of them may be used. Also, some of the lubricant components may be mixed to be used" (paragraph 0012 of the publication). Further, a surfactant may be used (JP 2002-241782 A).

[0015]

However, since the core material is completely shielded from the atmosphere by the sufficiently thick coating layers of micrometer order in many of the conventional coated copper wires, it has been unnecessary to additionally coat the carbon layer.

For example, there has been known a production process comprising "forming an even and thin noble metal coating film on a base metal wire" by coating and heating a liquid composition comprising particles of the noble metal having a particle diameter of 100 nm or less, wherein "a thickness of the noble metal coating film may preferably be 1 μm or less for a cost reduction purpose" (paragraphs 0010 and 0011 of JP 2006-210642 A). Also, even with the

thickness of nanometer order, "it is difficult to improve reliability evaluation in the second bonding due to a bonding failure in the wedge bonding since the effect of suppressing oxidization is small when a thickness of an outer layer is less than 20 nm" (Claim 1 and paragraph 0053 of JP 2009-140953 A). Thus, it is apparent that the core material is completely shielded from the atmosphere by the coating layers in the case of the conventional coated copper wires.

[Prior Art Literature]

[Patent Literature]

[0016]

[Patent Literature 1]: JP 2004-006740 A

[Patent Literature 2]: JP 2012-89685 A

[Patent Literature 3]: JP 6-151497 A

[Summary of Invention]

[Problems to Be Solved by Invention]

[0017]

The present invention was accomplished in order to solve the above-described problem that a property of bonding using ultrasonic wave becomes unstable when a coated copper wire is thinned, and an object thereof is to provide a structure of a coated copper wire which enable to maintain a structure of a coating material when a composition or a wire diameter of a core material in a pure copper alloy or a copper alloy used for the bonding is changed. More specifically, it is intended to provide a

structure of an inexpensive coated copper wire having a wide process window width in the ultrasonic bonding, the coated copper wire enabling stable ultrasonic bonding without independently changing each bonding condition even when a type or a wire diameter of a coating material or a core material of the coated copper wire is changed.

[Means for Solving Problems]

[0018]

The inventors accomplished the present invention by completing a wire structure which enables to stabilize an ultrasonic bonding property in such a manner that a multiple of short streak-like grooves are formed at substantially equal intervals along a longitudinal direction of a wire to form groove pairs each consisting of a U-shaped groove and an inverted U-shaped groove which are adjacent to each other along a vertical direction when the wire is deformed during ultrasonic bonding. In other words, the present invention was accomplished by: reducing a thickness of a coating layer to be as thin as possible so that influences of a coating material surrounding a core material can be ignored even when forming FAB of first bonding; and utilizing the feature that the short streak-like grooves are substantially uniformly extended in a lateral direction along with deformation of the wire during the ultrasonic bonding for second bonding so that the multiple of grooves form a wedge structure in a pressing direction to contribute to the ultrasonic bonding.

[0019]

One of structures of a coated copper wire for ultrasonic bonding which solves the problem of the present invention is a structure of a coated copper wire comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a surface of the core material is provided with a multiple of short streak-like grooves which are formed along a longitudinal direction of the wire in such a manner as to form a ring in a lateral direction of the wire; and a surface form is such that a coating material comprising a nobler metal or an alloy of the nobler metal having higher oxidization resistance than the core material is coated on the core material.

[0020]

Another one of the structures of coated copper wire for ultrasonic bonding which solves the problem of the present invention is a structure of a coated copper wire comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a surface of the core material is provided with a multiple of short streak-like grooves in the form of rings along a longitudinal direction of the wire; a surface form is such that a coating material comprising a nobler metal or an alloy of the nobler metal (hereinafter referred to as "nobler metal or the like") is coated on the core material; and an organic carbon layer

having a total organic carbon amount (TOC value) of 50 to 3,000 $\mu\text{g}/\text{m}^2$ exists on the surface of the coated copper wire.

[0021]

A preferred mode of embodiment of the structure of coated copper wire for ultrasonic bonding of the present invention is as follows.

In the structure of coated copper wire for ultrasonic bonding of the present invention, it is preferable that a surface form of a coating material is formed along a crystal grain boundary of a core material.

[0022]

Further, in the structure of coated copper wire for ultrasonic bonding of the present invention, it is preferable that the surface form of the coating material is formed as spherical islands in a sea-island structure.

[0023]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the surface form of the coating material has a mosaic pattern comprising a part from which a metal color of the core material can be seen and a part from which a metal color of a nobler metal or the like of the coating material can be seen.

[0024]

In the structure of coated copper wire for ultrasonic bonding of the present invention, a total organic carbon amount (TOC value) may preferably be 200 to 1,000 $\mu\text{g}/\text{m}^2$.

[0025]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the coating material may preferably be a high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) having purity of 99.99 mass% or more or an alloy thereof. The high purity noble metal include a copper alloy comprising 1 to 40 mass% of the noble metal with the balance being copper (Cu) having purity of 99.99 mass% or more.

[0026]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the core material may preferably be a high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) having purity of 99.99 mass% or more or an alloy thereof with the balance being copper (Cu) having purity of 99.99 mass% or more.

[0027]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the core material may preferably be a copper alloy comprising 0.5 to 5 mass% of a high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) having purity of 99.99 mass% or more or an alloy thereof with the balance being copper (Cu) having purity of 99.99 mass% or more.

[0028]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the coated copper wire for ultrasonic bonding may preferably be a bonding wire for free air ball.

[0029]

In the structure of the pure copper alloy bonding wire of the present invention, the core material has the above-described composition comprising the pure copper alloy having purity of 99.99 mass% or more or the copper alloy in order to form a spherical ball in FAB formation during first bonding and in order to select a composition of a known pure copper alloy or a known copper alloy which enables to prevent aluminum splash when connecting a pure aluminum (Al) pad or a pad made from an Al-0.5 mass% Cu alloy or the like.

[0030]

In the case of the pure copper alloy wire, a lower limit of oxidizable metal components other than copper (Cu) may be 40 mass ppm. The lower limit is set to 40 mass ppm in order that the metal components immobilize entire oxygen and sulfur when oxygen and sulfur are molten in the pure copper alloy matrix and further to maintain a state in which the metal components combine with oxygen in the atmosphere to cause internal oxidization. By maintaining the pure copper alloy matrix to the above-described oxygen deficiency state, it is possible to delay a change from an

unsaturated copper oxide (Cu_{2-2x}O) layer on a nano-order layer on the surface of the wire to a saturated copper oxide (Cu_2O) layer.

On the other hand, an upper limit of the oxidizable metal components in the pure copper alloy wire may preferably be less than 100 mass ppm. The upper limit in the case of the pure copper alloy wire is set to less than 100 mass ppm to be in conformity with a pure gold alloy bonding wire represented by "four-nine gold". When an amount of the metal components is less than 100 mass ppm, metal impurities are not segregated in the vicinity of the surface layer of the pure copper alloy bonding wire.

[0031]

In the structure of coated copper wire of the present invention, a multiple of short streak-like grooves in the form of rings are formed along a longitudinal direction of a wire in order to form a multiple of structures each consisting of a pair of a U-shape and an inverted U-shape formed along a vertical direction at an arbitrary deformed portion of the wire when the wire is deformed at the portion due to a pressing force during the ultrasonic bonding. As a result, since each of the structures consisting of U-shape and inverted U-shape is continuous from the short streak-like grooves formed in such a manner as to form a ring in the lateral direction of the wire at a non-deformed portion, ultrasonic bonding strength of the coated copper wire is stabilized. Since it is possible to

form the multiple of short streak-like grooves irrespective of a wire diameter, the grooves are applicable not only to a thin wire diameter but also to a thick wire diameter.

[0032]

Further, in the case where a molten ball of the first bonding is formed by FAB in the coated copper wire of the present invention, it is considered that the molten ball of the coated copper wire has the spherical shape since the multiple of short streak-like grooves change into an onion-shaped structure.

[0033]

In order to form the multiple of short streak-like grooves along the longitudinal direction of the wire in the present invention: gentle wavy lines are formed on an outer periphery of the core material; the coating material of the nobler metal or the like is coated thereon; and a diameter of the laminate structure is reduced until a theoretical thickness reaches to several nanometers (nm). The groove formation is thus attained by differences in shape effect and contraction resistance at an interface between the core material and the coating material. When the outer shape of the core material is appropriately processed as described above, the rest of the production is easily performed by adjusting a wire drawing speed and a contraction ratio to ordinary values as required.

Preferred average roughness (Rz) of the short streak-like grooves detected by roughness measurement at 10 points

may preferably be 3% to 15%, more preferably 5% to 11%, of a final wire diameter. When the diameter of the core material is reduced solely, it is difficult to form the short streak-like grooves by the contraction. Further, the multiple of short streak-like grooves are formed when the theoretical thickness is several angstroms (0.1 nm) or larger, but the short streak-like grooves are not formed when the theoretical thickness is of a sub-angstrom order (<0.01 nm) due to the too thin coating material. As used herein, "theoretical thickness" means an estimated value of a thickness obtained by a proportional calculation based on an actually measured value of a thickness and a contraction ratio of a wire diameter.

[0034]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the surface form of the coating material is formed along the crystal grain boundary of the core material because the coating material becomes excessively thick when it is impossible to confirm the formation along the crystal grain boundary by microscopic observation, and the excessively thick coating material makes it difficult to form the spherical FAB in the case of forming the molten ball of the first bonding by FAB. Since the coating material which serves as the islands in the sea-island structure is coarsely distributed on the surface of the core material, it is considered that it is difficult to prevent oxidization which occurs inside the core

material.

[0035]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the surface form of the coating material has a mosaic pattern since it is easy to confirm that the coating material is excessively thin and that a process window width for the ultrasonic bonding is narrowed when the mosaic pattern cannot be seen.

[0036]

In the structure of coated copper wire for ultrasonic bonding of the present invention, a total organic carbon amount (TOC value) is set to 200 to 1,000 $\mu\text{g}/\text{m}^2$ since the thickness of the coating material surrounding the core material is kept as thin as possible. A larger total organic carbon amount is preferred for preventing oxidization of the copper wire, but a carbon powder which remains after formation of FAB is undesirable. Therefore, the range of 200 to 1,000 $\mu\text{g}/\text{m}^2$ is selected as the preferred range ranging from the optimum value in the case where the coating layer is thick (sea-island structure) to the optimum value in the case where the coating layer is thin (mosaic pattern).

[0037]

The total organic carbon amount (TOC value) on the surface of the coated copper wire is set to 50 to 3,000 $\mu\text{g}/\text{m}^2$ because it is difficult to directly measure a very thin carbon layer. Since the carbon layer contaminates a

bonding tool such as a capillary to be a cause of erroneous operation, the carbon layer may preferably be as thin as possible. Therefore, the TOC value may preferably be 200 to 1,000 $\mu\text{g}/\text{m}^2$. The TOC value may be selected depending on the types of the core material and the coating material and a usage of a semiconductor subjected to the ultrasonic bonding.

[0038]

As the organic carbon layer, a very thin organic carbon layer may preferably be provided on an entire surface of the pure copper alloy bonding wire in order to prevent adhesion of oxygen in the atmosphere to the unsaturated copper oxide (Cu_2O) layer of nanometer order on the surface of the wire and to prevent development to the saturated copper oxide (Cu_2O) layer while leaving a very thin oxide film of the unsaturated copper oxide (Cu_2O) layer spontaneously formed on the surface of the pure copper alloy bonding wire. It is possible to control the TOC value to be within the range of 200 to 1,000 $\mu\text{g}/\text{m}^2$ by way of cleaning with hot pure water, ultrasonic cleaning, or dipping into a very weak solution of an organic polymer component, and the dipping into the very weak solution is preferred since a fluctuation in the total organic carbon amount (TOC value) is suppressed.

[0039]

Lubricant oil components described in paragraph 0012 of Patent Literature 3 are usable for the organic carbon

layer. The lubricant oil components have a reducing action on the pure copper alloy, but a water-soluble alcohol-derived organic carbon layer is desirable. The water-soluble alcohol-derived organic carbon layer is selected because alcohol has a stronger reducing property on the pure copper alloy. Thus, it is possible to provide the very thin organic carbon layer on the entire surface of the wire while leaving the unsaturated copper oxide ($\text{Cu}_2\text{-}\cdot\text{O}$) layer on the wire surface by dipping the pure copper alloy bonding wire into the alcohol solution having very low concentration. If the organic carbon layer is formed after pickling the wire surface and without the unsaturated copper oxide ($\text{Cu}_2\text{-}\cdot\text{O}$) layer, the wire surface is activated to cause a direct reaction between oxygen in the atmosphere and copper (Cu) on the wire surface, thereby undesirably forming a saturated copper oxide (Cu_2O) layer. Therefore, it is preferable not to subject the wire surface to pickling.

[0040]

Examples of the water-soluble alcohol include ethanol, methanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, ethylene glycol, glycerin, or the like. Examples more preferred water-soluble alcohol include ethanol, methanol, and isopropyl alcohol-derived water soluble alcohols.

[0041]

Since the unsaturated copper oxide ($\text{Cu}_2\text{-}\cdot\text{O}$) layer and

the organic carbon layer on the wire surface and the coating material of the present invention are very thin, they disappear during the FAB bonding of the first bonding due to evaporation and dispersion into the ball. However, since the groove portions are relatively thick, they are considered to disappear after swelling in the form of an onion. Further, during the ultrasonic bonding of the second bonding, the unsaturated copper oxide ($\text{Cu}_2\text{-O}$) layer and the organic carbon layer which weakly combine with the pure copper alloy wire surface disappear due to heat decomposition by ultrasonic energy. However, since the groove portions are relatively resistant to deformation, they are considered to disappear after divergently extending in a direction orthogonal to the longitudinal direction of the wire.

[0042]

The organic carbon layer is formed on the entire surface of the wire drawing processing surface of the present invention since if there is a portion on which the organic carbon layer is not formed, there is a possibility that combination with oxygen (O) in the atmosphere can occur from the portion.

Further, the thickness of the organic carbon layer is set to 50 to 3,000 $\mu\text{g}/\text{m}^2$ as the total organic carbon amount (TOC value) because it is easy to calculate a theoretical thickness of the organic carbon layer from the total organic carbon amount (TOC value) in view of the fact that

a typical wire diameter of ball bonding wires is 15 to 25 μm .

[0043]

In the structure of coated copper wire for ultrasonic bonding of the present invention, the coating material is the predetermined high purity noble metal since it has a high oxidization suppression effect on the copper alloy of the core material.

[0044]

On the other hand, the core material comprises the copper alloy 0.5 to 5 mass % of the high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), iridium (Ir) having purity of 99.99 mass% or more or the alloy thereof with the balance being copper having purity of 99.99 mass% or more because these noble metal alloying elements delay oxidization of copper (Cu) and, in the case where the core material has a noble metal surface segregation layer, the property of bonding to the coating material of the nobler metal or the like is further improved.

In the structure of coated copper wire for ultrasonic bonding of the present invention, the nobler metal or the like may further preferably be a palladium alloy comprising 5 to 20 mass% of gold (Au), silver (Ag), or platinum (Pt) with the balance being palladium (Pd) having purity of 99.99 mass% or more.

[0045]

An upper limit of the thickness of the coating material may preferably be in a state of a sea-island structure in which spherical bodies of the coating material are aligned in the short streak-like grooves. When the thickness is larger than that described above, the short streak-like grooves are covered with the coating material to form a "coating layer", resulting in an expensive wire in the case of using the noble metal. Also, in the case of ball bonding, influences exerted by the material and the thickness of the "coating layer" are strong to make it difficult to form the spherical molten ball and to narrow the process window width in the ultrasonic bonding. The coating material may have a laminate structure comprising different noble metal layers, for example.

[0046]

A lower limit of the thickness of the coating material may preferably be such that the surface form of the coating material has a mosaic pattern having a portion from which a metal color of the core material can be seen and a portion of a metal color of the noble metal or the like of the coating material and from which the metal color of the core material cannot be seen. Since there is the crystal grain boundary under the mosaic pattern, combination of oxygen in the atmosphere with the core material is inhibited by the mosaic pattern. However, when the theoretical thickness is thinned to be less than the sub-angstrom order, the mosaic pattern disappears to make

it difficult to prevent the oxidization of the core material. Therefore, the presence of the mosaic pattern is preferred.

[Effects of Invention]

[0047]

According to the structure of coated copper wire for ultrasonic bonding of the present invention, since the multiple of short streak-like grooves are formed on the core material along the longitudinal direction of the wire, the structures each consisting of a pair of a U-shape and an inverted U-shape are formed during the ultrasonic bonding, thereby stabilizing the ultrasonic bonding property. More specifically, since the multiple of short streak-like grooves are formed on the core material along the longitudinal direction of the wire, it is possible to set a wide range of ultrasonic bonding conditions even when the wire is thinned, and thus the effect of attaining stable bonding strength at a low cost is attained. Therefore, thinning of the coated copper wire for ultrasonic bonding is realized. Further, since it is possible to inhibit the unsaturated copper oxide (Cu_2O) formed on the surface of the core material from spreading owing to the multiple of short streak-like grooves, it is possible to delay the formation of the copper oxide (Cu_2O) layer. In the case of the bonding wire forming the molten ball, too, it is possible to obtain relatively stable spherical balls without being influenced by the thickness

of the coating material irrespective of the type of the coating material. In the case of forming the organic carbon layer on the surface of the coated copper wire, it is possible to further delay the oxidization of the wire surface even on the portion from which the metal color of the core material can be seen. In other words, even when a certain period of time has passed after the production of the bonding wire until the wire is used for a product, it is possible to prevent the formation of the saturated copper oxide (Cu_2O) layer which is otherwise formed due to combination with oxygen (O) in the atmosphere on the surface of the pure copper alloy bonding wire. Further, with a sectional structure of the pure copper alloy connection wire of the present invention, the capillary is not contaminated when the bonding is performed repeatedly. Since the structure of coated copper wire of the present invention is not subject to influence of the coating material, the bonding properties such as first bonding and loop formation of the metal component of the favorable core material are improved. Therefore, the coated copper wire for ultrasonic bonding of the present invention ensures a product life as the bonding wire before the start of use thereof.

[Examples]

[0048]

Each of pure copper alloy wires having core material compositions and coating material compositions shown in

Table 1 (each of copper (Cu) and silver (Ag) has purity of 99.9999 mass% or more, and each of other alloying components has purity of 99.99 mass%) was uniformly molten and cast and then subjected to rolling with intermediate heat treatment to obtain a thick wire having a diameter of 1 mm. Grooves of a sub-micrometer order or having several micrometers were formed on an outer periphery of the thick wire, and then the coating material was coated. After that, wet continuous wire drawing was performed by using a diamond die, and a wire having a diameter of 15 μm was finally obtained. A theoretical thickness of each of Product 1 to Product 19 was 5 nm. An average contraction ratio was 6% to 20%, and a final linear velocity was 100 m/min.

Wires used for a second window test and photographing of surface forms of Products described below were separately prepared.

[0049]

[Table 1]

	Composition of core material														Coating material														Thick- ness (nm)	Carbon layer			
	Alloying element (mass%)							Additional trace element (mass ppm)							Composition of coating material															TOC value ($\mu\text{m}^2/\text{m}^2$)	Coating liquid		
	No.	Cu	Pd	Ag	Pt	Au	Ir	Rh	Ti	Zr	Sn	Zn	Ag	P	Pd	Ag	Pt	Au	Ir	Rh	Au60% Ag40%	Au70% Pd30%	Au90% Pt10%	Cu85% Pd15%	Cu70% Ag20% Pd10%	Cu95% Pt5%	Cu60% Au40%	Cu80% Ir20%				Cu99% Rh1%	
E x a m p l e	1	balance									1		5	○																	5	400	Nonionic surfactant
	2	balance											10	30		○															5	100	Cationic surfactant
	3	balance							1	2		4	15	100			○														5	200	1-propanol
	4	balance											20							○											5	0	Pure water
	5	balance							10	2	2	5	10								○										5	300	2-methyl-2-propanol
	6	balance											1					○													5	100	Nonionic surfactant
	7	balance											10	30				○													5	200	Cationic surfactant
	8	balance							1	2		4	15	100					○												5	2500	2-methyl-2-propanol
	9	balance											20										○								5	700	Nonionic surfactant
	10	balance							10		2	5	10										○								5	100	1-propanol
	11	balance				0.5							5					○						○							5	150	Ethanol
	12	balance	0.5	0.5			0.5	0.5					5											○							5	400	2-methyl-2-propanol
	13	balance				1							5		○																5	300	1-propanol
	14	balance	0.4			0.2	0.1		0.3				5													○					5	300	Cationic surfactant
	15	balance		0.5			0.5						5														○				5	0	Pure water
	16	balance											20			○															5	500	Nonionic surfactant
	17	balance											10	50															○		5	600	Nonionic surfactant
	18	balance									2	1	15																○		5	1100	Nonionic surfactant
	19	balance							10				5				○														5	60	Nonionic surfactant
C o m p a r a t i v e	1	balance									1	1	14		○																0.05	300	1-propanol
	2	balance									1	1	14					○													40	150	Ethanol
	3	balance									1	1	14				○														0	3	Nonionic surfactant
	4	balance									1	1	14															○			80	0	Pure water

[0050]

(Second Window Test)

The second window test with an ultrasonic device is the test for detecting the number of regions which are available for bonding among total 130 regions by setting 13 stages of ultrasonic currents on an X-axis from 10 mA to 130 mA at an interval of 10 mA and setting 10 stages of compression force on an Y-axis from 10 gf to 100 gf at an interval of 10 gf. In the example shown in Table 2, a bonding wire having the composition of Product 1 and a diameter of 30 μm immediately after the production was subjected to the second window test using Automatic Wire Bonder ICONN Ultrasonic Device produced by Kulicke & Soffa, in which the ultrasonic bonding was performed for 1,000 times on an Ag-plated lead frame (QFP-200) at a frequency of 120 kHz for each of the windows. The number of the bondable regions (white boxes) in the case of the example shown in Tale 2 was 65. The number of the regions (shaded boxes) where the bonding resulted in non-bonding or the bonder stopped was 65, too. From the test results, it should be understood that a pitch, a depth, or the like of the grooves of the wavy pattern before the contraction have only to be changed in the case of the bonding wire which has the large wire diameter and requires the large ultrasonic output.

[0051]

[Table 2]

		Results of second window test using ultrasonic device												
		Ultrasonic current (mA)												
		10	20	30	40	50	60	70	80	90	100	110	120	130
C o m p r e s s i o n (g f o r m i n g)	10													
	20													
	30													
	40													
	50													
	60													
	70													
	80													
	90													
	100													

[0052]

(Surface Forms of Products)

Photographs of surface forms of a portion which was not affected by thermal influence when FAB was formed and a portion which was crushed during the ultrasonic bonding using a bonding wire having the composition of Product 1 and a diameter of 18 μm immediately after the production were taken by a laser microscope (VK971 produced by Keyence Corporation). The photographs are shown in Fig. 1 and Fig. 2. As is apparent from Fig. 1, oval palladium (Pd) particles form lines along a longitudinal direction of the wire to form a sea-island structure in which the palladium (Pd) particles are dispersed on the pure copper alloy wire. Average roughness (Rz) obtained by the 10-point measurements based on JIS B0601 and B0031 was 1.4 μm .

A theoretical thickness of the palladium (Pd) coating material surrounding the core material shown in Fig. 1 and

Fig. 2 is 5 nm. The bonding wire was cut by using an FIB, and a section of the cut portion was observed with a scanning electron microscope at a magnification of $\times 20,000$. However, a film of the palladium (Pd) coating material was not observed.

[0053]

After that, coated copper wires for ultrasonic bonding of the present invention (Product 1 to Product 19) were obtained by subjecting each of the coated copper wires (Product 1 to Product 19) shown in Table 1 to continuous dipping into pure water or an organic compound solution having a predetermined concentration and then to a refining heat treatment at an optimum temperature.

[0054]

(Measurement of Total Organic Carbon Amount (TOC))

The total organic carbon amount was measured as follows.

10,000 m of each of the pure copper alloy connection wires was used. The pure copper alloy connection wire was subjected to extraction in a water bath by adding 200 g of a 0.1 N-NaOH solution and boiling for 30 minutes, followed by cooling. After that, 2.5 ml of 8N-HCl was added with gently shaking, and bubbling was performed with high purity air for 15 minutes. The pure copper alloy connection wire was fed to an organic carbon measurement device, TOC-5000, produced by Shimadzu Corporation to measure an organic carbon concentration, and a total organic carbon amount was

calculated from the organic carbon concentration. The obtained total organic carbon amount was divided by a surface area of the pure copper alloy connection wire of 20 μm diameter to detect a total organic carbon amount of an anionic surfactant on the surface.

[0055]

(Second Window Test of Products)

The pure copper alloy connection wires for ball bonding (Product 1 to Product 19) of the present invention were subjected to the second window test shown in Table 2 before and after storage in a clean room at $20^{\circ}\text{C} \times 30\%$ moisture for 72 hours to obtain the results shown in Table 3.

[0056]

[Table 3]

		Results of second window test using ultrasonic device			
		Wire immediately after production		Wire stored for 72 hours in clean room at 20°C×30% moisture after production	
	No.	Number of windows	Judgment	Number of windows	Judgment
E x a m p l e s	1	16	○	15	○
	2	15	○	16	○
	3	13	●	13	●
	4	11	●	11	●
	5	11	●	12	●
	6	14	●	14	●
	7	12	●	13	●
	8	13	●	13	●
	9	17	○	16	○
	10	15	○	15	○
	11	14	●	15	○
	12	13	●	13	●
	13	18	○	17	○
	14	13	●	12	●
	15	11	●	12	●
	16	15	○	15	○
	17	16	○	17	○
	18	14	●	13	●
	19	16	○	16	○
C o m p a r a t i v e E x a m p l e s	1	5	△	3	×
	2	3	×	2	×
	3	5	△	2	×
	4	5	△	2	×
	5	5	△	3	×

[0057]

As to the judgment of good or poor in the second window test: ○ indicates that the number of bondable regions was 15 or more; ● indicates that the number of bondable regions was 10 to 14; △ indicates that the number of bondable regions was 5 to 9; and × indicates that the

number of bondable regions was 4 or less, each among the total 130 regions. The output from the ultrasonic device was appropriately adjusted to an optimum frequency (about 40 to 120 kHz) and an optimum output (about 0.1 to 5 W) depending on the wire diameter of the bonding wire.

[Comparative Examples]

[0058]

Each of wires having a diameter of 15 μm was obtained from a thick wire having a diameter of 1 mm in the same manner as in Examples, and the wire was subjected to continuous dipping into an organic compound solution having a concentration shown in Table 1 to obtain the pure copper alloy connection wires for ball bonding of Comparative Products (Comparative Product 1 to Comparative Product 4). An average contraction ratio was 6% to 20%, and a final linear velocity was 150 m/min.

[0059]

A theoretical thickness of the palladium (Pd) coating layer surrounding the core material of the pure copper alloy having purity of 99.99 mass% of Comparative Product 1 is 0.05 nm. The coating material formed a uniform layer, and no mosaic pattern of the coating material was observed.

[0060]

A theoretical thickness of the palladium (Pd) coating layer surrounding the core material of the pure copper alloy having purity of 99.99 mass% of Comparative Product 2 is 20 nm. The coating material formed a uniform layer, and

no sea-island structure in which spherical bodies of the coating material are aligned was observed.

[0061]

A theoretical thickness of the palladium (Pd) coating layer surrounding the core material of the pure copper alloy having purity of 99.99 mass% of Comparative Product 3 is 5 nm. The sea-island structure disappeared due to the high temperature refining heat treatment at 700°C.

[0062]

A theoretical thickness of the palladium (Pd) coating layer (a surface layer is a mixture layer of gold (Au) and palladium (Pd)) surrounding the core material of the pure copper alloy having purity of 99.99 mass% of Comparative Product 4 is 80 nm, and a wire diameter thereof was smaller (15 μm) than the conventional wires (20 μm).

[0063]

Pure copper alloy connection wires of Comparative Product 1 to Comparative Product 4 were subjected to the second window test shown in Table 2 before and after storage in a clean room at 20°C $\times$ 30% moisture for 72 hours to obtain the results shown in Table 3.

[0064]

As is apparent from the ultrasonic second window test, the number of bondable regions of each of the pure copper alloy connection wires for ball bonding (Product 1 to Product 19) was 11 or more to show that the stable ultrasonic bonding was attained even when the bonding

conditions were somewhat changed. On the other hand, the number of bondable regions of each of the pure copper alloy connection wires of Comparative Examples (Comparative Product 1 to Comparative Product 4) is 5 or less even if they are bonding wires immediately after the production. What is worse, the number of bondable regions of each of Comparative Products stored in the clean room at 20°C × 30% moisture for 72 hours after the production is 3 or less to show that it is impossible to attain the favorable bonding since the bondable region is changed even with the slight change in bonding conditions.

[0065]

In addition, clogging of the capillary was not caused by any of the pure copper alloy connection wires for ball bonding of the present invention and Comparative Examples (Product 1 to Product 19 and Comparative Product 1 to 4) when the number of times of bondings exceeded 10,000 times to show that the pure copper alloy connection wires have the favorable sliding property in the capillary.

[Industrial Applicability]

[0066]

The coated copper wire for ultrasonic bonding of the present invention is usable for semiconductors such as general purpose ICs, discrete ICs, and memory ICs as well as for IC packages for LEDs and IC packages for in-vehicle semiconductors which are required to be produced at a low cost though used under high temperature high humidity

environments.

[Brief Description of Drawings]

[0067]

[Fig. 1] Fig. 1 is a photograph showing a surface form of a coated copper wire for ultrasonic bonding of the present invention.

[Fig. 2] Fig. 2 is a photograph showing a surface form of a portion which was crushed during ultrasonic bonding of the coated copper wire for ultrasonic bonding of the present invention.

[Document Name]Claims

[Claim 1]

A structure of a coated copper wire for ultrasonic bonding comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a multiple of short streak-like grooves are formed on a surface of the core material along a longitudinal direction of the wire in such a manner as to form rings; and a coating material comprising a nobler metal or an alloy of the nobler metal having higher oxidization resistance than the core material is coated on the core material along a crystal grain boundary of the core material to attain a coated surface form.

[Claim 2]

A structure of a coated copper wire for ultrasonic bonding comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a multiple of short streak-like grooves are formed on a surface of the core material along a longitudinal direction of the wire in such a manner as to form rings; a coating material comprising a nobler metal or an alloy of the nobler metal is coated on the core material along a crystal grain boundary of the core material to attain a coated surface form; and an organic carbon layer having a total organic carbon amount (TOC value) of 50 to 3,000 $\mu\text{g}/\text{m}^2$ exists on a surface of the

coated copper wire.

[Claim 3]

A structure of a coated copper wire for ultrasonic bonding comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a multiple of short streak-like grooves are formed on a surface of the core material along a longitudinal direction of the wire in such a manner as to form rings; and a coating material comprising a nobler metal having higher oxidization resistance than the core material or an alloy of the nobler metal is formed on the core material as spherical islands in a sea-island structure to attain a coated surface form.

[Claim 4]

A structure of a coated copper wire for ultrasonic bonding comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a multiple of short streak-like grooves are formed on a surface of the core material along a longitudinal direction of the wire in such a manner as to form rings; a coating material comprising a nobler metal having higher oxidization resistance than the core material or an alloy of the nobler metal is formed on the core material as spherical islands in a sea-island structure to attain a coated surface form; and an organic carbon layer having a total organic carbon amount (TOC value) of 50 to 3,000 $\mu\text{g}/\text{m}^2$ exists on a surface of the

coated copper wire.

[Claim 5]

A structure of a coated copper wire for ultrasonic bonding comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a multiple of short streak-like grooves are formed on a surface of the core material along a longitudinal direction of the wire in such a manner as to form rings; and a coating material comprising a nobler metal having higher oxidization resistance than the core material or an alloy of the nobler metal is coated on the core material as a mosaic pattern comprising a part from which a metal color of the core material can be seen and a part from which a metal color of the nobler metal having higher oxidization resistance or the alloy of the nobler metal of the coating material can be seen to attain a coated surface form.

[Claim 6]

A structure of a coated copper wire for ultrasonic bonding comprising a coating layer and a core material comprising a pure copper alloy having purity of 99.99 mass% or more or a copper alloy, characterized in that: a multiple of short streak-like grooves are formed on a surface of the core material along a longitudinal direction of the wire in such a manner as to form rings; a coating material comprising a nobler metal or an alloy of the nobler metal is coated on the core material as a mosaic pattern comprising a part

from which a metal color of the core material can be seen and a part from which a metal color of the nobler metal having higher oxidization resistance or the alloy of the nobler metal of the coating material can be seen to attain a coated surface form; and an organic carbon layer having a total organic carbon amount (TOC value) of 50 to 3,000 $\mu\text{g}/\text{m}^2$ exists on a surface of the coated copper wire.

[Claim 7]

The structure of the coated copper wire for ultrasonic bonding according to any one of claim 2, 4, or 6, characterized in that the total organic carbon amount (TOC value) is 200 to 1,000 $\mu\text{g}/\text{m}^2$.

[Claim 8]

The structure of the coated copper wire for ultrasonic bonding according to any one of claims 1 to 6, characterized in that the coating material is a high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) having purity of 99.99 mass% or more or an alloy thereof.

[Claim 9]

The structure of the coated copper wire for ultrasonic bonding according to any one of claims 1 to 6, characterized in that the core material is a copper alloy comprising a high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) having purity of 99.99 mass% or more or an alloy thereof with the balance being copper (Cu) having

purity of 99.99 mass% or more.

[Claim 10]

The structure of the coated copper wire for ultrasonic bonding according to any one of claims 1 to 6, characterized in that the core material is a copper alloy comprising 0.5 to 5 mass% of a high purity noble metal comprising gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), or iridium (Ir) having purity of 99.99 mass% or more or an alloy thereof with the balance being copper (Cu) having purity of 99.99 mass% or more.

[Claim 11]

The structure of the coated copper wire for ultrasonic bonding according to any one of claims 1 to 6, characterized in that the coated copper wire for ultrasonic bonding is a bonding wire for free air ball.