

[Document Name] DESCRIPTION

[Title of Invention] CROSS-SECTION STRUCTURE OF PURE COPPER ALLOY WIRE FOR ULTRASONIC BONDING

[Technical Field]

[0001]

The present invention relates to a pure copper alloy wire for ultrasonic bonding, the wire being suitable for connecting an IC chip electrode to an external lead or the like on a substrate used in a semiconductor device, particularly a bonding wire for ultrasonic connection with a diameter of 100 to 700  $\mu\text{m}$ , a rectangular wire having the same cross-sectional area, or a copper bonding wire for forming free air ball (FAB) or for ultrasonic bonding to be used as an ultra-fine wire of 80  $\mu\text{m}$  or smaller, for use under high temperature environment such as on a vehicle, a power semiconductor, a high-speed device, and the like.

[Background Art]

[0002]

Conventionally, as a ball bonding wire for connecting an IC chip electrode to an external lead in a semiconductor device, pure gold wires composed of gold (Au) at purity of 99.99% by mass or higher and an additional metallic element at an amount lower than 100 ppm % by mass are extensively used for their excellent reliability in connectivity. One end of such a pure gold wire is formed with a molten ball and is then ball-bonded to an aluminum pad on an IC chip electrode by thermosonic bonding (first bonding), while the other end thereof is connected via sonication by an ultrasonic method (second bonding) to an external lead wire

or the like on a printed substrate. Subsequently, the connecting wire is sealed with a molding resin to give a semiconductor device. Alternatively, such a wire, as a heavy wire having no ball formed, is directly subjected to first bonding and second bonding by ultrasonic bonding. The aluminum pad is composed of pure aluminum (Al) or an Al alloy containing 0.2 to 2% by mass of Si, Cu, Ni, and/or the like, usually formed by dry plating such as vacuum deposition and magnetron sputtering.

[0003]

As an alternative to such a pure gold wire, use of a pure copper alloy wire to which a trace base metal element such as titanium (Ti) and zirconium (Zr) is added has been conventionally considered. For example, a claim of Japanese Patent Application Publication No. S61-99646 (JP S61-99646 A) ("Patent Document 1" to be listed below) discloses "a copper bonding wire for a semiconductor device characterized by comprising highly pure copper (Cu) at purity of 99.99% or higher and 5 to 150 ppm of one, two, or more fifth-row elements such as 5 to 50 ppm of zirconium (Zr), 10 to 100 ppm of silver (Ag), and 10 to 100 ppm of tin (Sn)", a claim of Japanese Patent Application Publication No. S64-3903 (JP S64-3903 A) discloses "a fine copper wire for electronic equipment characterized by comprising 0.05 to 10 ppm in total of one, two, or more kinds of Ti, Zr, and the like, 1 to 30 ppm of oxygen, and the balance Cu", claim 1 of Japanese Patent Application Publication No. H6-168974 (JP H6-168974 A) discloses "a connecting wire characterized by comprising 20 to 560 ppm by wt of one, two, or more elements selected from Zr, Hf, Ti, Cr, and Mn, . . . . ., and practically the balance Cu", claim 3 of Japanese Patent Application Publication No.

2008-85320 (JP 2008-85320 A) ("Patent Document 2" to be listed below) discloses "a copper alloy connecting wire for semiconductor devices characterized by comprising 10 to 700 ppm by mass of P, 6 to 300 ppm by mass of Ti, and 6 to 30 ppm by mass of oxygen", claim 2 of Japanese Patent Application Publication No. 2012-89685 (JP 2012-89685 A) ("Patent Document 3" to be listed below) discloses "a copper connecting wire comprising not lower than 2 ppm by mass and not higher than 12 ppm by mass of sulfur, higher than 2 ppm by mass and not higher than 30 ppm by mass of oxygen, not lower than 4 ppm by mass and not higher than 55 ppm by mass of titanium, and inevitable impurities as the balance, wherein the copper connecting wire has a surface layer having a crystal structure with an average crystal grain size of not greater than 20  $\mu\text{m}$  from the surface to a depth of 50  $\mu\text{m}$  before processing", and claim 2 of Japanese Patent Application Publication No. 2013-26475 (JP 2013-26475 A) ("Patent Document 4" to be listed below) discloses "a copper connecting wire comprising oxygen at an amount of higher than 2 ppm by mass, sulfur at an amount of not lower than 2 ppm by mass and not higher than 12 ppm by mass, and a soft dilute copper alloy material that contains an element selected from the group consisting of Ti, Zr, and the like and the balance copper, characterized in that the average crystal grain size of the crystal structure from the surface to a depth of at least 20% the wire diameter is not greater than 20  $\mu\text{m}$ ". Such pure copper alloy wires are less expensive compared to a pure gold wire and therefore have been considered to be used as a bonding wire for ultrasonic connection with a relatively great diameter for

use under high temperature environment such as on a vehicle, a power semiconductor, a high-speed device, and the like.

[0004]

These copper alloy wires are devised for immobilizing a gas component such as dissolved oxygen (O) and sulfur (S) by a base metal element such as titanium (Ti) because the gas component such as dissolved oxygen (O) and sulfur (S) in a pure copper matrix is believed to impair bonding properties. This is specifically mentioned in description “a copper connecting wire comprises 2 to 12 ppm by mass of sulfur, 2 to 30 ppm by mass of oxygen ....., titanium (Ti) as TiO, TiO<sub>2</sub>, TiS, a compound having a Ti-O-S bond, or an aggregate of TiO, TiO<sub>2</sub>, TiS, or a compound having a Ti-O-S bond, and the balance Ti and S as a solid solution (paragraph 0022 of “Patent Document 3” to be listed below)” and in description “based on the assumption that all the oxygen is present in the oxide film (Cu<sub>2</sub>O) on the surface ..... 30 ppm by mass of oxygen makes 4.8 nm (when the wire diameter is 25 μm). However, oxygen forming a solid solution with copper must be taken into consideration, and therefore the practical thickness of the copper oxide (Cu-oxide) film via calculation from the oxygen concentration is estimated to be smaller than above (paragraph 0042 of Japanese Patent Application Publication No. 2008-85320 (JP 2008-85320 A))”. Thus, by using an alloy containing a trace base metal element, it is now possible to lower the softening temperature to the same level as that of a pure copper alloy wire at purity of 99.9999% by mass while avoiding hardening of a molten ball at the time of first bonding so as to maintain bonding properties at the time of FAB bonding and to further perform second bonding by sonication.

The FAB herein refers to a molten ball formed at the tip of a wire extending from the tip of a bonding tool by spark discharge with a non-oxidizing gas and/or a reducing gas such as nitrogen being sprayed to the tip of the wire. Use of FAB has an advantage that such gas atmosphere is maintained until the time of first bonding of a molten ball formed on a connecting wire and therefore the pure copper alloy wire is not oxidized nor does an oxide film form at the bonding interface between the wire and a pad.

[0005]

Even though satisfactory bonding conditions for FAB bonding are possibly given at the prototyping phase, such a pure copper alloy connecting wire in mass production exhibits a wide range of variation in bonding properties in second bonding by ultrasonic bonding, and therefore practical use of such a pure copper alloy connecting wire has been limited. Such a wide range of variation in bonding properties in second bonding is also caused in the case of ultrasonic bonding of a heavy wire by relatively high energy where a substrate to be bonded does not undergo heating.

[0006]

A pure copper connecting wire composed of a pure copper alloy at purity of 99.9999% by mass or higher and no trace element and containing dissolved oxygen at an amount of not higher than several ppm by mass, when prototyped as a bonding wire, forms a hard molten ball at the time of first bonding to cause aluminum splash.

[0007]

As an alternative method, a bonding wire comprising "one of Au, Al, and Cu as a primary element and drawn into an ultra-fine wire of about 10 to 50  $\mu\text{m}$ , a certain length of

which would be wound onto a spool for installation on a wire bonder for use (paragraph 0002 of Japanese Patent Application Publication No. H6-151497 (JP H6-151497 A) ("Patent Document 5" to be listed below))", is subjected to melting and casting and then to acid washing and/or the like of the ingot to fabricate "a bonding wire for semiconductor devices characterized in that total organic carbon on the surface is 50 to 1500  $\mu\text{g}/\text{m}^2$  (claim 1 of the same publication)". This method is described as follows; "As a method for fabricating a wire having total organic carbon on the surface of 50 to 1500  $\mu\text{g}/\text{m}^2$ , a wire that is produced by ordinary steps, namely, steps of melting, casting, drawing, annealing, and winding and having total organic carbon on the surface of higher than 1500  $\mu\text{g}/\text{m}^2$  is washed by a method such as ... acid washing ... to give total organic carbon on the surface of within the range of 50 to 1500  $\mu\text{g}/\text{m}^2$  (claim 2 of the same publication). This method is characterized in that the method has only to have a washing step added before or after an annealing step of the ordinary steps and is therefore easily implemented (paragraph 0010 of the same publication)", and "Examples of a lubricant component include mineral oil-based lubricants such as paraffin hydrocarbons, naphthene hydrocarbons, and aromatic hydrocarbons, synthetic oil-based lubricants such as polyolefins, alkylbenzenes, fatty acids, higher alcohols, fatty acid soaps, polyglycols, polyphenyl ethers, fatty acid diesters, polyol esters, polyoxyethylene alkyl ethers, sulfonic acid salts, amines, amine salts, silicones, phosphoric acid esters, fluorocarbons, fluoropolyethers, and fluoroglycols, and natural oil/fat-based lubricants such as beef tallow, lard, palm oil, soybean oil, rape oil,

castor oil, and pine root oil, and any of these may be used. A mixture of several of these components may also be used. (paragraph 0012 of the same publication)".

[0008]

When applied to a pure copper wire, however, this method results in a wide range of variation in bonding conditions at the time of second bonding by ultrasonic bonding and therefore not always forms secure bonding. Particularly in the case of use in a power semiconductor and the like to be used at high temperatures, lack of heating process performed on a substrate to be bonded (subject material to be bonded) as mentioned above makes the surface state of the bonding wire, even as a heavy wire, more influential, which inevitably results in a wide range of variation in bonding conditions. This presents a problem that, when a bond formed by second bonding is weak, growth of an oxide film formed on the bonding interface at the time of second bonding is promoted and the bond becomes even weaker at the bonding interface.

[Citation List]

[Patent Literature]

[0009]

[Patent Document 1] Japanese Patent Application Publication No. S61-99646 (JP S61-99646 A)

[Patent Document 2] Japanese Patent Application Publication No. 2008-85320 (JP 2008-85320 A)

[Patent Document 3] Japanese Patent Application Publication No. 2012-89685 (JP 2012-89685 A)

[Patent Document 4] Japanese Patent Application Publication No. 2013-26475 (JP 2013-26475 A)

[Patent Document 5] Japanese Patent Application Publication No. H6-151497 (JP H6-151497 A)

[Summary of Invention]

[Technical Problem]

[0010]

The present invention is devised to solve the problem above and has an object to provide a cross-sectional structure of a pure copper alloy connecting wire, the cross-sectional structure being capable of preventing atmospheric oxygen from promoting the growth of copper oxide on the wire surface for a certain period of time, making FAB ball bonding be performed in a consistent fashion, and making the process window wide for ultrasonic bonding that is difficult to control compared to FAB bonding.

[Solution to Problem]

[0011]

It is known that, compared to a pure gold wire, a pure copper alloy connecting wire tends to react with atmospheric oxygen at the wire surface to form a stable oxide ( $\text{Cu}_2\text{O}$ ) film. The inventors of the present invention analyzed the process of formation of this oxide ( $\text{Cu}_2\text{O}$ ) in detail, as follows. First, a solid-gas phase reaction is allowed to proceed to bind atmospheric oxygen to the surface of a pure copper alloy wire to form unstable copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) as the outermost layer of the wire cross section. Subsequently, after being left for some time in the atmosphere at room temperature, the unstable copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) grows into stable copper oxide ( $\text{Cu}_2\text{O}$ ) to make the wire surface altered to assume a patchy pattern (the cross section of the wire to assume a ripple pattern) after a while. The inventors of the present invention noticed that such a copper oxide ( $\text{Cu}_2\text{O}$ ) layer assuming a patchy

pattern induced inconsistency in bonding properties at the time of ultrasonic bonding.

[0012]

When this copper oxide ( $\text{Cu}_2\text{O}$ ) layer on the wire surface is removed by acid washing and the drawn surface is made devoid of an oxide layer, a fresh active surface forms on the surface of the copper alloy wire. It is found that such a fresh active surface on the copper alloy wire is highly reactive unlike one on a pure gold wire, and therefore when a bonding wire is simply left in the atmosphere right after fabrication, another copper oxide ( $\text{Cu}_2\text{O}$ ) film assuming a patchy pattern forms on the bonding wire even though the composition of the copper alloy gives excellent bonding properties, resulting in the loss of bonding properties thus derived from the composition of the copper alloy and eventually in a variation in bonding conditions at the time of ultrasonic bonding. The same phenomenon occurs on either a solid pure copper alloy wire at purity of 99.9999% by mass or higher or a pure copper alloy connecting wire containing not higher than 0.02% by mass of a metal component other than copper (Cu).

[0013]

In comparison to a pure gold wire, a pure copper alloy connecting wire when being left in the atmosphere characteristically causes internal oxidation of a trace base metal element due to the nature of a pure copper (Cu) matrix to allow oxygen to permeate therethrough. Because of this, in an attempt to prevent copper oxide on the surface of a pure copper alloy wire from being altered to assume a patchy pattern, the inventors of the present invention incorporated a readily-oxidized base metal element into a pure copper (Cu) matrix so as to make the

base metal element in the pure copper (Cu) matrix preferentially react with oxygen at the wire surface. In other words, by making a readily-oxidized base metal element present in a pure copper (Cu) matrix, they tried to make oxygen atoms in the atmosphere cause internal oxidation of a base metal element in a pure copper (Cu) matrix rather than to make oxygen atoms in the atmosphere form a stable copper oxide ( $\text{Cu}_2\text{O}$ ) layer from unstable copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) on the wire surface. In addition, they devised to form an organic carbon layer that was thin enough not to reduce the oxide layer while most of the copper oxide layer on the wire surface remains as unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) so as to achieve a balance between oxidation and reduction of the copper oxide layer and prevent the copper oxide ( $\text{Cu}_2\text{O}$ ) layer assuming a patchy pattern from growing on the wire surface. As a result, the process window at the time of ultrasonic bonding was made wider, consistent ultrasonic bonding of an ultra-fine wire having a diameter of not greater than  $15\text{ }\mu\text{m}$  was achieved, and excellent bonding properties derived from the composition of the copper alloy were successfully exhibited.

[0014]

As the cross-sectional structure of a pure copper alloy connecting wire for ball bonding capable of solving problems of the present invention, the cross-sectional structure of a pure copper alloy wire composed of not higher than 0.02% by mass of a metal component other than copper (Cu) and the balance copper (Cu) is characterized in that:

the composition of the wire includes not lower than 40 ppm by mass and lower than 100 ppm by mass (hereinafter, abbreviated as "40 to 100 ppm by mass") of at least one

base metal of titanium (Ti), zirconium (Zr), zinc (Zn), and tin (Sn) and the balance copper (Cu) at purity of 99.990 to 99.996% by mass,

the cross-sectional structure of the wire has a drawn surface with the diameter reduced through a diamond die and, on all over the wire surface, an organic carbon layer with total organic carbon (TOC value) of (about 200 to 2,000 or 20 to 200)  $\mu\text{g}/\text{m}^2$ , and

a copper oxide layer of 2 to 20 nm thick formed of copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) containing unsaturated oxygen forms as the outermost layer of the wire, and base metal underneath the copper oxide layer remains without receiving internal oxidation.

[0015]

As for the cross-sectional structure of a pure copper alloy connecting wire of the present invention, a reason for forming a drawn surface with the diameter reduced through a diamond die on the wire surface is that the diamond die slides on the surface of the pure copper alloy wire well and therefore can prevent a fresh active surface from forming on the wire surface in the processing step of continuous drawing. Diameter reduction through a diamond die is usually performed by wet continuous drawing in water or in a shower, and such a diameter reduction process forms no fresh active surface on the wire surface nor a fresh oxide film on the wire surface.

[0016]

As for the cross-sectional structure of a pure copper alloy connecting wire of the present invention, copper (Cu) at purity of 99.990 to 99.996% by mass is selected as the balance in the composition of the pure copper alloy wire in an attempt to use an oxidizing metal component other than

copper (Cu) for preventing an ultra-thin oxide layer from growing as the outermost layer on the wire surface. In other words, the selection is made based on the ability of a pure copper alloy at purity of about 99.99% by mass, namely at purity of 99.990 to 99.996% by mass, to make a trace element preferentially react with atmospheric oxygen to cause internal oxidation. Another reason for the selection is that the trace base metal component added in the present invention can give the pure copper alloy connecting wire with bonding properties derived from the composition of the copper alloy. In other words, appropriate selection of such a trace element allows to take advantage of the property of a pure copper alloy connecting wire to become less hard and perform ultrasonic connection before an ultra-thin oxide layer grows as the outermost layer. The selection can also prevent aluminum splash from occurring at the time of bonding a molten ball in FAB process to, for example, a pure aluminum (Al) pad and/or an Al alloy pad containing 0.2 to 2% by mass of Si, Cu, Ni, and/or the like.

[0017]

Herein, in the composition of the pure copper alloy wire, the ratio of an oxidizing base metal component other than copper (Cu) is determined as 40 to 100 ppm by mass. The lower limit is set as 40 ppm by mass in order to allow the base metal to be capable of immobilizing all the dissolved oxygen and dissolved sulfur when dissolved oxygen and sulfur are initially present in a pure copper matrix, and also allow part of the base metal to be bonded, inside a pure copper matrix, to oxygen atoms entering from the atmosphere through the wire surface while the rest of the base metal remains unoxidized and available for internal

oxidation. By leaving a pure copper matrix lack of oxygen in this way, alteration of an unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface into a saturated copper oxide ( $\text{Cu}_2\text{O}$ ) layer can be delayed.

On the other hand, the upper limit is set to be lower than 100 ppm by mass because the ratio exceeding 100 ppm by mass results in hardening of a copper (Cu) matrix even in the presence of silver (Ag) and phosphorus (P) and when no silver (Ag) nor phosphorus (P) is contained, qualification for "four nines copper wire (i.e. copper wire at purity of 99.99% by mass or higher)" as of a pure gold alloy connecting wire is provided. The composition of the bonding wire is selected, as needed, depending on the specification of a semiconductor on which the bonding wire is installed. When the ratio of the base metal is lower than 100 ppm by mass, no segregation of the base metal element as an alloy element occurs in the vicinity of the surface layer of the pure copper alloy connecting wire.

[0018]

The specific composition of the pure copper alloy wire of the present invention is selected by an ultrasonic bonding test on appropriate combinations of the compositions of known pure copper alloys, the results of the test being greatly affected by a copper oxide ( $\text{Cu}_2\text{O}$ ) layer assuming a patchy pattern on the wire surface. In the pure copper alloy of the present invention, the outermost layer on the wire surface is a copper oxide ( $\text{Cu}_2\text{O}$ ) layer of about several nanometers (nm) grown by a solid-gas phase reaction, and a pure copper matrix immediately therebelow has an unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer and a base metal other than copper (Cu). Because of this, if the carbon layer of the present invention is absent, a copper oxide

(Cu<sub>2</sub>O) layer assuming a patchy pattern forms as the outermost layer on the wire surface from the unsaturated copper oxide (Cu<sub>2-x</sub>O) layer. The mechanism of this is as follows.

[0019]

An oxygen atom captured into a copper (Cu) matrix is preferentially bonded to a trace base metal in the pure copper matrix to form a base metal oxide immediately below the surface layer. Due to the formation of the base metal oxide, the volume of the copper (Cu) matrix increases by the increment of the volume of the oxygen added to the base metal. This results in the grid of the copper (Cu) matrix strained by the increment of the volume to assume a wedge-like shape, whereby another oxygen atom easily advances into the copper (Cu) matrix. Such another oxygen atom that has reached inside forms a base metal oxide, which allows even more oxygen to advance inside. In this way, a base metal other than copper (Cu) undergoes internal oxidation. As the internal oxidation of the base metal proceeds to some extent, atmospheric oxygen allows the unsaturated copper oxide (Cu<sub>2-x</sub>O) layer on the wire surface to be altered into a saturated copper oxide (Cu<sub>2</sub>O) layer, and then the copper oxide (Cu<sub>2</sub>O) layer readily grows inside the copper (Cu) matrix. As a result, a saturated copper oxide (Cu<sub>2</sub>O) layer assuming a patchy pattern forms on the wire surface.

The inventors of the present invention noticed that such a copper oxide (Cu<sub>2</sub>O) layer assuming a patchy pattern made bonding properties poor in ultrasonic bonding.

[0020]

In the present invention, the base metal refers to at least one base metal of titanium (Ti), zirconium (Zr), zinc (Zn),

and tin (Sn). Each of these elements is a metal that is readily oxidized and therefore the presence of these elements makes the alteration of an unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface into a saturated copper oxide ( $\text{Cu}_2\text{O}$ ) layer less likely to occur. Titanium (Ti) or zirconium (Zr) is more preferable. Titanium (Ti) is particularly preferable. As described in Patent Document 3, titanium (Ti) forms a stable compound in a copper (Cu) matrix not only with oxygen but also with sulfur (S).

[0021]

The metal component of the present invention can include 1 to 30 ppm by mass of silver (Ag) or 1 to 100 ppm by mass of phosphorus (P). Silver (Ag) acts to delay aggregation of the base metal in the copper (Cu) matrix. Phosphorus (P) has action to reduce the base metal oxide on a molten ball in a nitrogen atmosphere in FAB process. Neither of silver (Ag) nor phosphorus (P) interacts with the base metal element in the copper (Cu) matrix. Silver (Ag) or phosphorus (P) thus has different action on the base metal in the copper (Cu) matrix and therefore is preferably used in combination with the base metal element above. More preferably, the total content of silver (Ag) and phosphorus (P) is greater than the total content of titanium (Ti), zirconium (Zr), zinc (Zn), and tin (Sn). Particularly, the total content of silver (Ag) or phosphorus (P) is most preferably greater than the total content of titanium (Ti) or zirconium (Zr).

[0022]

Total organic carbon (TOC value) all over the oxide layer is set as 50 to 3,000  $\mu\text{g}/\text{m}^2$  because an ultra-thin carbon layer cannot be directly measured. A carbon layer, when

present, can contaminate a bonding tool such as a capillary to cause a malfunction, and therefore the carbon layer is preferably as thin as possible. For this reason, the upper limit is set as 3,000  $\mu\text{g}/\text{m}^2$ . More preferably, the upper limit is lower than 1,000  $\mu\text{g}/\text{m}^2$ . On the other hand, the lower limit is set as about 500  $\mu\text{g}/\text{m}^2$  because a too-thin carbon layer allows the unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface to react with atmospheric oxygen. More preferably, the lower limit is not lower than 200  $\mu\text{g}/\text{m}^2$ .

[0023]

As the organic carbon layer, an ultra-thin organic carbon layer is provided on all over the surface of the pure copper alloy connecting wire. A reason for this is to make atmospheric oxygen less prone to adhere to the unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface and to prevent the unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface, the layer naturally forming as an ultra-thin oxide layer on the surface of the pure copper alloy connecting wire, from growing. Controlling so as to achieve the range of 50 to 3,000  $\mu\text{g}/\text{m}^2$  can be carried out by washing with hot deionized water, ultrasonic cleaning, or immersion in an ultra-dilute solution of an organic macromolecular compound, preferably by immersion in a dilute solution. This is because fluctuation caused to total organic carbon (TOC value) on the surface of the bonding wire is small.

[0024]

As the organic carbon layer, lubricant oil components in paragraph 0012 of Patent Document 5 can be used and an organic carbon layer based on a water-soluble alcohol that

has reducing action on a pure copper alloy is preferable. The organic carbon layer is extremely thin and therefore an organic carbon layer based on a surfactant may also be used. A reason for selecting an organic carbon layer based on a water-soluble alcohol is that an alcohol has gentle reducing action on a pure copper alloy. Another reason for this is that an organic carbon layer based on a water-soluble alcohol is completely decomposed by subsequent heat treatment. Thus, by immersing the pure copper alloy connecting wire in an aqueous alcohol solution of an extremely low concentration, an ultra-thin organic carbon layer can form on all over the unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) that is left as the outermost layer on the wire surface. Forming an organic carbon layer in the absence of an unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface is unpreferable because this induces activation of the surface of the wire to allow copper (Cu) on the wire surface to directly react with atmospheric oxygen and eventually form a saturated copper oxide ( $\text{Cu}_2\text{O}$ ) layer.

[0025]

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, and glycerol. One based on ethanol, methanol, or isopropyl alcohol is more preferable.

[0026]

Both of the unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer and the organic carbon layer on the wire surface in the present invention are extremely thin, and therefore the copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer and the organic carbon layer that are weakly bonded to the surface of the pure copper alloy connecting wire are thermally decomposed by ultrasonic

energy at the time of ultrasonic bonding and disappear. In an application as a ball bonding wire, the copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer and the organic carbon layer evaporate in the course of molten ball formation by thermal energy, that is more intense than ultrasonic energy, of a molten ball at the time of FAB bonding as first bonding, or disperse to the interior of the ball and disappear.

[0027]

A reason for forming the organic carbon layer on all over the drawn surface of the present invention is that atmospheric oxygen (O) is bonded to an area, if any, on which no organic carbon layer forms and this results in formation of a saturated copper oxide ( $\text{Cu}_2\text{O}$ ) layer assuming a patchy pattern.

The thickness of the organic carbon layer is set as 50 to 3,000  $\mu\text{g}/\text{m}^2$  in terms of total organic carbon (TOC value) because the theoretical thickness of the organic carbon layer can be easily determined by calculation using total organic carbon (TOC value) based on the diameter, 15 to 50  $\mu\text{m}$ , of a common ball bonding wire.

[Advantageous Effects of Invention]

[0028]

The cross-sectional structure of a pure copper alloy connecting wire for ultrasonic bonding of the present invention has an organic carbon layer formed on an inert drawn surface that has a reduced diameter and therefore can delay the alteration of an unsaturated copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) layer on the wire surface into a saturated copper oxide ( $\text{CuO}$ ) layer. With the cross-sectional structure of a pure copper alloy connecting wire for ultrasonic bonding of the present invention, no saturated copper oxide ( $\text{CuO}$ ) layer assuming a patchy pattern forms as a saturated oxide film

and settings of sonication (the width of process window) can be set wide. This makes formation of a fine wire possible. An oxidizing metal component in the pure copper alloy connecting wire for ball bonding of the present invention has excellent bonding properties as conventionally known. The pure copper alloy connecting wire for ball bonding of the present invention can ensure the product lifetime as a connecting wire until use. The cross-sectional structure of a pure copper alloy connecting wire of the present invention causes no contamination of a capillary after repeated bonding.

[Examples]

[0029]

A pure copper alloy wire (copper (Cu) at purity of 99.9999% by mass or higher, and the other alloy components at purity of 99.99% by mass or higher) having the composition shown in Table 1 was subjected to uniform melting and casting and then continuous drawing to give a heavy wire with a diameter of 2 mm. Without undergoing heat treatment, the resultant heavy wire in a wet state was continuously drawn through a diamond die to give a wire with a diameter of 20  $\mu\text{m}$ . Subsequently, the resultant was continuously immersed in an organic compound solution at each concentration shown in Table 1 and was then subjected to tempering heat treatment to give a pure copper alloy connecting wire for ball bonding of the present invention (example product 1 to example product 19).

[0030]

[Table 1]

| Composition of pure copper alloy                    |            |    |     |     |    |    |     |    |       | TOC value<br>( $\mu\text{g}/\text{m}^2$ ) | Alcohol etc.                     |
|-----------------------------------------------------|------------|----|-----|-----|----|----|-----|----|-------|-------------------------------------------|----------------------------------|
|                                                     | Cu         | Ti | Zr  | Sn  | Zn | Ag | P   | Cr | of Mn |                                           |                                  |
| E<br>x<br>a<br>m<br>p<br>l<br>e                     | 1 Balance  | 50 |     |     |    |    |     |    |       | 700                                       | Ethanol                          |
|                                                     | 2 Balance  |    | 70  |     |    |    |     |    |       | 550                                       | Methanol                         |
|                                                     | 3 Balance  |    |     | 90  |    |    |     |    |       | 1500                                      | Isopropyl alcohol                |
|                                                     | 4 Balance  |    |     |     | 42 |    |     |    |       | 310                                       | 1-Propanol                       |
|                                                     | 5 Balance  | 48 |     |     |    |    |     |    |       | 460                                       | 2-Methyl-2-propanol              |
|                                                     | 6 Balance  |    | 82  |     |    |    |     |    |       | 970                                       | Ethylene glycol                  |
|                                                     | 7 Balance  |    |     | 58  |    |    |     |    |       | 220                                       | Glycerol                         |
|                                                     | 8 Balance  |    |     |     | 66 |    |     |    |       | 940                                       | Cationic surfactant              |
|                                                     | 9 Balance  | 18 |     |     |    |    | 25  |    |       | 700                                       | Nonionic surfactant              |
|                                                     | 10 Balance |    | 46  |     |    |    |     | 50 |       | 200                                       | Nonionic surfactant              |
|                                                     | 11 Balance |    |     | 32  |    | 11 |     |    |       | 1400                                      | Nonionic surfactant              |
|                                                     | 12 Balance |    |     |     | 83 |    | 35  |    |       | 340                                       | Methanol                         |
|                                                     | 13 Balance | 28 |     |     |    | 5  | 25  |    |       | 520                                       | Ethanol                          |
|                                                     | 14 Balance |    | 28  |     |    | 26 | 10  |    |       | 760                                       | Methanol                         |
|                                                     | 15 Balance |    |     | 32  |    | 17 | 45  |    |       | 60                                        | Isopropyl alcohol                |
| E<br>x<br>a<br>m<br>p<br>l<br>e                     | 16 Balance |    |     |     | 54 |    |     |    |       | 490                                       | 1-Propanol                       |
|                                                     | 17 Balance | 20 | 20  | 20  | 10 | 20 |     |    |       | 580                                       | 2-Methyl-2-propanol              |
|                                                     | 18 Balance | 15 | 15  | 15  | 15 |    | 55  |    |       | 1900                                      | Ethylene glycol                  |
|                                                     | 19 Balance | 5  | 5   | 5   | 5  | 12 | 40  |    |       | 820                                       | Glycerol                         |
|                                                     | 20 Balance |    |     |     |    |    |     |    |       | Not detectable                            | Deionized water                  |
| C<br>o<br>m<br>p<br>a<br>r<br>a<br>t<br>i<br>v<br>e | 2 Balance  |    | 190 |     |    |    |     |    |       | 521                                       | Ethanol                          |
|                                                     | 3 Balance  |    |     | 190 |    |    |     |    |       | 3200                                      | Nonionic surfactant              |
|                                                     | 4 Balance  |    |     |     | 90 |    |     |    |       | Not detectable                            | Ultra-dilute 1-propanol          |
|                                                     | 5 Balance  | 30 | 30  |     |    | 80 | 100 |    |       | 60                                        | Not detectable                   |
|                                                     |            |    |     |     |    |    |     |    |       | 60                                        | Not detectable                   |
|                                                     |            |    |     |     |    |    |     |    |       |                                           | Ultra-dilute nonionic surfactant |

[0031]

(Measurement of total organic carbon (TOC))

Total organic carbon (TOC) was measured as follows.

Total organic carbon was measured in the following procedure. A pure copper alloy connecting wire of 10,000 m was weighed and thereto 200 g of a 0.1-N aqueous NaOH solution was added, followed by boiling in a water bath for 30 minutes for extraction. After cooling, 2.5 ml of 8 N-HCl was added, followed by gentle shaking and bubbling with highly pure air for 15 minutes. The resultant was fed to TOC-5000 organic carbon analyzer manufactured by Shimadzu Corporation to measure the concentration of organic carbon, and the concentration was then used to calculate the total weight of organic carbon. The resultant value was divided by the surface area of the pure copper alloy connecting wire with a diameter of 20  $\mu\text{m}$  to give total organic carbon

contained in an alcohol and a nonionic surfactant present on the surface.

[0032]

After stored in a clean room at 20°C at humidity of 30% for 48 hours, the pure copper alloy connecting wire for ball bonding of the present invention (example product 1 to example product 19) was subjected to a second window test as shown in Table 2 to give results shown in Table 3.

[0033]

(Second window test)

The second window test on an ultrasonic device was a test in which an X axis indicating an ultrasonic current on a scale of 10 mA to 130 mA in increments of 10 mA (13 scales in total) and a Y axis indicating applied pressure on a scale of 10 gf to 100 gf in increments of 10 gf (10 scales in total) were used to determine the total number of boxes indicating successful bonding among 130 boxes in total. Table 2 shows, as an example, results of a second window test on a bonding wire having the composition of Example 1 with a diameter of 30  $\mu\text{m}$  right after fabrication. The test was repeated 1,000 times per window on an Ag-plated lead frame (QFP-200) using ICONN fully-automatic ultrasonic ribbon bonder manufactured by K&S at a frequency of 120 kHz. In the example shown in Table 2, the number of boxes indicating successful bonding (white boxes) is 65, while the number of boxes indicating failed bonding or the case where the bonder stopped operating (meshed boxes) is also 65. The test results show that in the case of using a bonding wire with a great wire diameter and applying great ultrasonic power thereto, appropriate deformation of grooves in a ripple pattern in terms of the pitch, the

depth, and the like before diameter reduction may be performed.

[0034]

[Table 2]

Results of second window test on ultrasonic device

|                       |     | Ultrasonic current (mA) |    |    |    |    |    |    |    |    |     |     |     |     |
|-----------------------|-----|-------------------------|----|----|----|----|----|----|----|----|-----|-----|-----|-----|
|                       |     | 10                      | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 | 130 |
| Pressure applied (gf) | 10  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 20  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 30  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 40  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 50  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 60  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 70  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 80  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 90  |                         |    |    |    |    |    |    |    |    |     |     |     |     |
|                       | 100 |                         |    |    |    |    |    |    |    |    |     |     |     |     |

Number of bonding samples: 1000 wires per window

Evaluation

|  |                                                       |
|--|-------------------------------------------------------|
|  | Failed bonding or case where bonder stopped operating |
|  | Successful bonding                                    |

[0035]

(Second window test on example products)

Each pure copper alloy connecting wire for ball bonding of the present invention (example product 1 to example product 19) was evaluated by rating the case where the number of process windows for successful ultrasonic bonding was 20 or more among 130 windows in total as Excellent, the case where the number was 10 to 20 as Fair, the case where the number was 5 to 9 as Poor, and the case where the number was 4 or less as Very poor.

The power output by the ultrasonic device was selected, as needed, as the optimum frequency (about 40 to 120 kHz) and

the optimum power (about 0.1 to 5 W) depending on the diameter of a bonding wire.

[0036]

[Table 3]

| Results of second window test on ultrasonic device |                   |            |                                                                                          |            |           |
|----------------------------------------------------|-------------------|------------|------------------------------------------------------------------------------------------|------------|-----------|
| Wire right after fabrication                       |                   |            | Wire stored in clean room at 20° C at humidity of 30% for 48 hours following fabrication |            |           |
| Number                                             | Number of windows | Evaluation | Number of windows                                                                        | Evaluation |           |
| Example                                            | 1                 | 20         | Excellent                                                                                | 20         | Excellent |
|                                                    | 2                 | 21         | Excellent                                                                                | 19         | Fair      |
|                                                    | 3                 | 19         | Fair                                                                                     | 18         | Fair      |
|                                                    | 4                 | 11         | Fair                                                                                     | 10         | Fair      |
|                                                    | 5                 | 13         | Fair                                                                                     | 12         | Fair      |
|                                                    | 6                 | 14         | Fair                                                                                     | 12         | Fair      |
|                                                    | 7                 | 16         | Fair                                                                                     | 13         | Fair      |
|                                                    | 8                 | 15         | Fair                                                                                     | 13         | Fair      |
|                                                    | 9                 | 21         | Excellent                                                                                | 18         | Fair      |
|                                                    | 10                | 20         | Excellent                                                                                | 20         | Excellent |
|                                                    | 11                | 18         | Fair                                                                                     | 16         | Fair      |
|                                                    | 12                | 18         | Fair                                                                                     | 18         | Fair      |
|                                                    | 13                | 20         | Excellent                                                                                | 20         | Excellent |
|                                                    | 14                | 20         | Excellent                                                                                | 19         | Fair      |
|                                                    | 15                | 18         | Fair                                                                                     | 19         | Fair      |
|                                                    | 16                | 23         | Excellent                                                                                | 20         | Excellent |
|                                                    | 17                | 21         | Excellent                                                                                | 20         | Excellent |
|                                                    | 18                | 14         | Fair                                                                                     | 13         | Fair      |
|                                                    | 19                | 20         | Excellent                                                                                | 16         | Fair      |
| Comparative Example                                | 1                 | 4          | Very poor                                                                                | 2          | Very poor |
|                                                    | 2                 | 5          | Poor                                                                                     | 4          | Very poor |
|                                                    | 3                 | 3          | Very poor                                                                                | 3          | Very poor |
|                                                    | 4                 | 4          | Very poor                                                                                | 2          | Very poor |
|                                                    | 5                 | 4          | Very poor                                                                                | 3          | Very poor |

[Comparative Examples]

[0037]

A heavy wire with a diameter of 1 mm was obtained and was

then continuously immersed in an organic compound solution at each concentration shown in Table 1 in the same manner as in the examples (except that deionized water was used for comparable product 1, dilute nitric acid was used for acid washing of the surface and continuous immersion was performed in an ethanol solution for comparable product 2, a nonionic surfactant at a high concentration was used for comparable product 3, and ultra-dilute 1-propanol and an ultra-dilute nonionic surfactant were used for comparable products 4 and 5) to give a pure copper alloy connecting wire for ball bonding of an comparative example (comparable product 1 to comparable product 5).

[0038]

The pure copper alloy connecting wire as well as the pure copper alloy connecting wire after storage in a clean room at 20°C at humidity of 30% for 48 hours were subjected to a second window test as shown in Table 2 to give results shown in Table 3.

[0039]

As is evident from the second window test with sonication, each of the pure copper alloy connecting wires for ball bonding (example product 1 to example product 19) yielded 11 or more process windows for successful bonding of a wire right after fabrication and 10 or more process windows for successful bonding of a wire after storage in a clean room at 20°C at humidity of 30% for 48 hours following fabrication, proving that ultrasonic bonding was performed consistently regardless of some differences made in bonding conditions. On the other hand, each of the pure copper alloy connecting wires for ball bonding in the comparative examples (comparable product 1 to comparable product 5) yielded mere 5 or less process windows for successful

bonding of a bonding wire even right after fabrication. Each of the ones after storage in a clean room at 20°C at humidity of 30% for 48 hours following fabrication yielded mere 3 or less process windows for successful bonding, proving that minimal differences made in bonding conditions ended in a failed fit to process windows for successful bonding and failed to yield adequate bonding.

[0040]

It was also found that each of the pure copper alloy connecting wires for ball bonding of the present invention (example product 1 to example product 19) that were subjected to wire bonding at a length greater than 5000 m yielded excellent FAB bonding as first bonding accompanied by no clogging of a capillary, proving that they were excellent as a ball bonding wire as well.

[Industrial Applicability]

[0041]

The pure copper alloy connecting wire for ball bonding of the present invention has applications in semiconductors such as in general-purpose ICs, discrete ICs, memory ICs, and IC packages for LEDs and IC packages for automobile semiconductors where low cost fabrication is sought after despite the possible use under high temperature and highly humid environment.

[Document Name] CLAIMS

[Claim 1]

A cross-sectional structure of a pure copper alloy connecting wire composed of not higher than 0.02% by mass of a metal component other than copper (Cu) and the balance copper (Cu), characterized in that:

the composition of the pure copper alloy connecting wire includes not lower than 40 ppm by mass and lower than 100 ppm by mass (hereinafter, abbreviated as "40 to 100 ppm by mass") of at least one base metal of titanium (Ti), zirconium (Zr), zinc (Zn), and tin (Sn) and the balance copper (Cu) at purity of 99.990 to 99.996% by mass,

the cross-sectional structure of the pure copper alloy connecting wire has a drawn surface with the diameter reduced through a diamond die and, on all over the pure copper alloy connecting wire surface, an organic carbon layer with total organic carbon (TOC value) of 50 to 3,000  $\mu\text{g}/\text{m}^2$ , and a copper oxide layer of 2 to 20 nm thick formed of copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) containing unsaturated oxygen forms as the outermost layer of the pure copper alloy connecting wire, and base metal underneath the copper oxide layer remains without receiving internal oxidation.

[Claim 2]

The cross-sectional structure of a pure copper alloy connecting wire according to claim 1, characterized in that the metal component other than copper (Cu) contains 1 to 30 ppm by mass of silver (Ag) or 1 to 100 ppm by mass of phosphorus (P), and the said pure copper alloy connecting wire is a bonding wire for ball bonding.

[Claim 3]

The cross-sectional structure of a pure copper alloy connecting wire according to claim 1, characterized in that, regarding the metal component other than copper (Cu), the total content of silver (Ag) and phosphorus (P) is greater than the total content of titanium (Ti), zirconium (Zr), zinc (Zn), and tin (Sn), and the said pure copper alloy connecting wire is a bonding wire for ultrasonic bonding.

[Claim 4]

The cross-sectional structure of a pure copper alloy connecting wire according to claim 1, characterized in that the base metal is titanium (Ti) or zirconium (Zr), and the said pure copper alloy connecting wire is a bonding wire for ultrasonic bonding.

[Claim 5]

The cross-sectional structure of a pure copper alloy connecting wire according to claim 1, characterized in that, regarding the metal component other than copper (Cu), the total content of silver (Ag) or phosphorus (P) is greater than the total content of titanium (Ti) or zirconium (Zr), and the said pure copper alloy connecting wire is a bonding wire for ultrasonic bonding.

[Claim 6]

The cross-sectional structure of a pure copper alloy connecting wire according to claim 1, characterized in that the said pure copper alloy connecting wire is a bonding wire for ultrasonic bonding.

[Claim 7]

The cross-sectional structure of a pure copper alloy connecting wire according to claim 1, characterized in that the said pure copper alloy connecting wire is a bonding wire for forming free air ball.