Pd-Coated Copper Ball Bonding Wire

[Technical Field]

[0001]

The present invention relates to a Pd-coated copper wire useful for connecting electrodes on semiconductor devices to leads of circuit wiring substrate by ball boding.

[Background of the Invention]

[0002]

Nowadays, gold wires having a wire diameter of 15 – 30 micrometers or so are commonly used as the bonding wires to connect electrodes on the semiconductor devices to external terminals by ball bonding. However, on account of the price hikes of the gold bullions of late, the gold wires of high purities as good as four nines (purities of 99.99 mass % or higher) are losing ground to copper wires of diameters 10 – 25 micrometers or so.

[0003]

The copper wires are considered to be used in applications where gold wires have been used, for example, in the field of packaging such as QFP (Quad Flat Packaging) where the current lead frame is used, and in addition to this, BGA (Ball Grid Array) where substrate, polyimide tape, etc. are used, and new variations such as CSP (Chip Scale Packaging), and accordingly better bonding wires improved in loop formation, bonding strength, sustainability in mass-production, at the time of ball bonding operation are called for.

[0004]

On the other end, the materials which are to be coupled with the copper bonding wire can be similar to those used with gold wires, such that in the case of the wiring and electrodes on silicon substrates, they may be embodied by high purity copper (Cu) suitable for extra thin wires as well as conventional aluminum (Al) alloy pad. Also, lead frames are coated with silver (Ag) plating or gold (Au) plating or nickel (Ni) plating with palladium plating on top of it, and copper (Cu) wiring is installed on resin substrates, tapes, etc., and over them

is often laid a film of a noble metal element such as gold (Au) or its alloy. Corresponding to each of these various items with which the copper (Cu) wire is coupled, the bonding strength and bonding reliability of the copper wire are hoped to be improved.

[0005]
In the beginning a use of a copper (Cu) wire having a purity as high as three to six nines (purities of 99.9 mass % to 99.9999 mass %) was conceived. However, copper wire was too easy to be oxidized. For this reason a proposal was made to improve the corrosion resistance and strength of the wire by coating a core wire of Cu or Cu-Sn or the like with a layer of Pd, Pd-Ni, Pd-Co or the like having a thickness of 0.00 2 – 0.5 micrometer (see IP Publication 1). Furthermore, bonding wires are proposed in which a noble metal such as gold (Au) is coated over this palladium (Pd) coating layer (IP Publications 2 through 4). However, when a copper wire as proposed in these publications was used in a semiconductor device which was used in environments of temperatures 80 – 200 degrees C, it happened that an oxide of aluminum (Al) grew in the bonding interface between a pad of aluminum (Al) etc. and the wire even though the ball bonding operation on the pad had been done well, and consequently a detachment occurred at the bonding interface.

[0006]
On the other hand, it is known that growth of an oxide of aluminum (Al) can be restricted if palladium (Pd) could be dispersed in the bonding interface between the pad and wire (Non-IP Publication 1).

[Prior art publications]
[IP publications]
[0007]

[IP Publication 1]
Japanese Published Utility Model Application S60-160554
[IP Publication 2]
Japanese Published Patent Application S62-97360
[IP Publication 3]
Japanese Published Patent Application 2005-167020

[IP Publication 4]
WO2011013527(A1)
[IP Publication 5]
Japanese Patent 3024584
[Non-IP Publications]
[0008]
[Non-IP Publication 1]
2006 July SEI Technical Review No. 169 P47-51; "Development of Hybrid Bonding Wire" by Shingo Kaimori and two others

[Summary of the Invention]
[Problems the invention seeks to solve]
[0009]
A copper wire clad with palladium coat has itself been known conventionally; but it is chiefly adopted for the purpose of preventing the susceptible copper core from oxidizing or to effect wedge bonding against a palladium-clad lead frame, and it has been experienced that even if palladium coat is provided the palladium is taken into the copper core during the formation of molten ball and thus a dispersion of palladium in the ball surface does not occur sufficiently to provide a required concentration thereof.

In general, the palladium coating layers in these uses are made relatively thin due to the high price of the element, and the amount of the expensive palladium to make the coating layer over the copper (Cu) core is one twentieth or smaller of the amount of copper constituting the core, so that simultaneously as the cupper (Cu) ball is formed the palladium (Pd) disperses into the cupper (Cu), and as such the palladium (Pd) does not form a uniformly dispersed extra thin layer to cover the molten ball.

The palladium-coated copper wire described in IP Publication 4 is a wire for creation of a wedge bonding between itself and the palladium-coated lead frame, and for this a 3 – 80 nm thick alloy layer containing gold and palladium is formed on the surface of the palladium coating layer.

However, palladium even after being made into an alloy is apt to disperse into the core copper and thus it has not been possible to form a palladium dispersion layer around the molten ball surface.

[Means to solve the problems]
[0010]
The present inventors attempted to create a structure whereby palladium (Pd) is caused to uniformly and finely disperse around the molten ball of high melting point and this they did by designing to place gold (Au) having a melting point lower than the core copper (Cu) over the core copper (Cu) to thereby allow the gold (Au) to function as a prime to stimulate the core copper (Cu) to melt in the first place and then the melting of the palladium (Pd) takes place which has a melting point higher than copper (Cu). For this purpose, a coating of gold (Au) is formed over palladium, and to this a mild heat treatment is given to an extent that there is caused no alloying between the gold (Au) and the palladium (Pd), in other words, occasioning Stranski-Krastanov growth, whereby the palladium (Pd) is spatially grown into the gold (Au) coating layer to create a layer wherein gold (Au) and palladium (Pd) are mixed pell-mell. It is known that the tissue that is formed as the result of this Stranski-Krastanov growth shapes a very thin metal layer and this forms an island structure grown from the underlying metal, and deteriorates the flatness of the surface layer (IP Publication 5); however, in the system of the present invention, the tissue created by the Stranski-Krastanov growth would have a construction such that the gold layer formed over the palladium coating layer becomes extremely thin, and the palladium is spatially grown into this gold layer of a thickness of several nanometers where fine palladium phase and gold phase are intermixed with each other.

Gold (Au) and palladium (Pd) fundamentally mix with each other at any ratio, and as the difference in crystal lattice is as small as about 4.9 % between them so that the adhesion between the gold (Au) layer and the palladium (Pd) layer is good and when the gold (Au) layer is extremely thin it is possible to educe the palladium (Pd) underlying layer into the gold (Au)

layer surface by means of Stranski-Krastanov growth.

[0011]
Now, the mixture layer wherein the gold (Au) and palladium (Pd) are intermixed is not stable, and the higher the purities of the gold (Au) and the palladium (Pd) are, the greater the tendency of their forming an alloy becomes. Thus, the present inventors thought to stabilize this mixture layer by causing the palladium (Pd) to absorb hydrogen atoms, which was effected by exposing the surface of the palladium (Pd) to hydrogen gas at a high temperature, whereby the mixture layer was to be stabilized. After the thermal treatment, if the aqueous solution in which sudden cooling is effected is mixed with an alcohol such as ethanol, it is better because the surface layer of the suddenly cooled palladium (Pd) takes in hydrogen atoms which are released as the alcohol is thermally decomposed.

[0012]
The present inventors decided to conduct the thermal treatment based on the Stranski-Krastanov growth simultaneously as the final annealing for controlling of the expansion/tensile strength of the copper (Cu) bonding wire through a proper controlling of the final thermal treatment after the continuous drawing operation, and then by liquid-cooling the wire as soon as it is passed through a brief and final thermal treatment, they tried to secure a stabilized structure of gold (Au) and palladium (Pd) intermixed layer.

[0013]
Furthermore, the present inventors decided to conduct the thermal treatment based on the Stranski-Krastanov growth simultaneously as the high temperature treatment for causing the palladium (Pd) to absorb the hydrogen atoms as well as the final annealing for controlling the expansion/tensile strength of the copper (Cu) bonding wire through a proper controlling of the final thermal treatment after the continuous drawing operation, and they by liquid –cooling the wire as soon as it is passed through a brief and final thermal treatment, they tried to secure a stabilized structure of gold (Au) and palladium (Pd) intermixed layer.

[0014]
It is an object of the present invention to solve the above-described problem and it is characteristic in having the following construction. (1) A coated copper wire for ball bonding of the present invention is a surface coated copper wire for ball bonding having a wire diameter of 10 – 25 micrometers which includes a core made of copper (Cu) or a copper alloy and an intermediate coating layer made of palladium (Pd), wherein the intermediate coating layer is made of a palladium of a purity of 99 mass % or higher, and an uppermost layer of gold is formed over the intermediate layer, and on that interface of the intermediate coating layer which is not the interface facing the core is formed a mixture layer having a mean thickness of 5 nm or smaller as measured from the cross section observed by scanning electron microscopy in which the palladium (Pd) and gold (Au) of a purity of 99.9 mass % or higher are intermixed by thermal growth and the palladium surface of this mixture layer is treated with hydrogen diffusion.

[0015]
A concrete embodiment of the coated copper wire for ball bonding of the present invention is as follows. (2) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the mean (average) thickness of the cross section of the mixture layer is 3 nm or smaller.

(3) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the mean thickness of the cross section of the mixture layer is 1 nm or smaller.

(4) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the wire is coated with palladium (Pd) by means of wet plating.

(5) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the palladium (Pd) is spatially grown into the gold (Au) coating layer, by means of Stranski-Krastanov growth, after the copper wire coated with gold (Au) and palladium (Pd) is strongly drawn, whereby the

mixture layer in which gold (Au) and palladium (Pd) are intermixed is created.

(6) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the copper wire coated with gold (Au) and palladium (Pd) having the mixture layer after being strongly drawn was caused to absorb hydrogen in a hydrogen-containing inert atmosphere at 450 – 700 degrees C.

(7) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the gold (Au) is put by magnetron sputtering at a room temperature.

(8) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the intermediate coating layer is palladium (Pd) put by means of wet plating.

(9) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the copper (Cu) constituting the core is a copper having a purity of 99.999 mass % or higher.

(10) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the copper (Cu) constituting the core is a copper having a purity of 99.9999 mass % or higher.

(11) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the copper alloy constituting the core is made of 0.1 – 500 mass ppm of phosphor (P) and the balance copper (Cu).

(12) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the copper alloy constituting the core is made of at least one of zirconium (Zr), tin (Sn), vanadium (V), boron (B) and titanium (Ti) in a collective amount of 0.5 – 99 mass ppm and the balance copper (Cu) with a purity of 99.9 mass % or higher.

(13) A coated copper wire for ball bonding as described in the sentence (1) above, wherein the copper alloy constituting the core is made of at least one of zirconium (Zr), tin (Sn),

vanadium (V), boron (B) and titanium (Ti) in a collective amount of 0.5 – 99 mass ppm and phosphor in an amount of 0.1 – 500 mass ppm and the balance copper (Cu) with a purity of 99.9 mass % or higher.

[Effects of the Invention]
[0016]
According to the present invention, at the time of creating a molten ball for the first bonding, the core copper (Cu) is melted by letting it be stimulated with the melting of more readily fusible gold (Au) as the prime, and then the palladium (Pd) in contact with the copper (Cu) is melted, and finally the surface palladium (Pd) impregnated with hydrogen atoms is melted, so that it has become possible to uniformly and finely disperse palladium (Pd) into the surface of the molten ball which is brought in contact with the aluminum (Al) interface on the pad.

Also, with the present invention, by properly controlling the thickness of the layer of gold (Au) having a purity of 99.9 mass % or higher and the final thermal treatment, it has become possible to form a mixture layer in which gold (Au) and palladium (Pd) are intermixed, in place of a layer of an alloy of gold (Au) and palladium (Pd).

Furthermore, by introducing hydrogen gas during the final thermal treatment to thereby allow the palladium surfacing beyond the gold surface layer to react with the hydrogen molecules and thus causing the palladium (Pd) to intake hydrogen atoms, it has become possible to stabilize more securely the mixture layer wherein gold (Au) and palladium (Pd) are intermixed.

By virtue of the wire construction of the present invention, at the time of the creation of a molten ball for the first bonding, gold (Au), which has the lowest melting point (1064 degrees C) among the elements in the outermost surface layer of the Stranski-Krastanov structure, starts melting and flows accompanied by palladium, which exists intermixed with gold in the same layer, from the palladium layer in the intermediate

layer to a wire end face where it covers up the exposed copper core.

Copper (Cu) has a higher melting point (1085 degrees C) than gold (Au) and palladium (Pd), but readily fuses at the wire end face where it is contacted by molten gold (Au) and forms a ball – the copper is stimulated to fuse by the molten gold working as a prime.

Palladium (Pd), which has the highest melting point (1555 degrees C) among the elements in the wire, remains solid in a shape of thin pipe sheathing the melting copper for a while, but starts melting as the copper forms a molten ball, in which it (Pd) is taken and diffuses; on the other hand, that palladium in the mixture layer which reached the wire end face accompanying the gold (Au), which had melted in the first place, is stabilized by the hydrogen atoms it had absorbed and finally melts without becoming an alloy, but would separate in the vicinity of the ball surface and thus is thought to retain its high concentration as palladium (Pd).

[0017]
The bonding wire according to the present invention has the construction as described above so that when it is let to sit for a long time at a high temperature, there occurs little separation of aluminum oxide or the like at the bonding interface between the wire and the pad, and thus it has an excellent and lasting high temperature stability.

[Examples to embody the Invention]
[0018]
In the coated copper wire of the present invention, an upper limit for a theoretical thickness of the ultra thin surface layer is 10 nm, and a preferable upper limit is 8 nm, and a more preferable upper limit is 7 nm or even thinner. Here, the “theoretical thickness” is a thickness obtained by proportion from the thickness of the surface layer as of the time of dry plating prior to the continuous wire drawing, and this is used since the direct measurement of the wholly clad ultra thin surface layer is very difficult.

A proportionality factor used to obtain this "theoretical thickness" is a quotient obtained by dividing the wire diameter after a continuous drawing of the bonding wire by the wire diameter before the continuous drawing. The actual thickness can be directly observed by means of a high magnification scanning electron microscope, but even so what is obtained is a rough mean film thickness since the value is on a nanometer order whether determined theoretically or by direct measurement. The smaller the thickness is, the easier it is for Stranski-Krastanov growth to take place involving gold (Au) and palladium (Pd). On the other hand, when the thickness becomes over large, the interaction between gold (Au) atoms themselves becomes speedier than that between gold (Au) and palladium (Pd) so that palladium (Pd) cannot surface beyond the gold (Au) surface, and thus palladium fails to absorb hydrogen atoms.

[0019]
The ultra thin gold (Au) surface layer is preferably put by means sputtering method from the viewpoints of throwing power and its conjugation with the intermediate coating layer. The gold (Au) and other metals that are put by sputtering method show good throwing power even if their purities are 99.9 mass % or higher for the reason that they turn harder as the result of the bombardment of the gaseous molecules. A surface layer such as of gold (Au) fills in infinitesimal conjugation interface recesses of the palladium (Pd) separation, which turns harder in comparison during the continuous drawing at cold temperatures, whereby the layer is strongly conjugated during the cold drawing.

Incidentally, the ultra thin surface layer of a metal such as gold (Au) which is laid by sputtering method does not assume a geometrically balanced circular ring of a uniform thickness when seen in cross section of the wire cut across a circumference, but it is readily absorbed into the copper (Cu) core by means of surface tension when a molten ball is created, and the unevenness of the surface layer is cancelled and a molten ball of a true sphericity is obtained.

[0020]
An especially preferable embodiment of wire core includes 1 – 80 mass ppm of phosphor (P) and the balance copper (Cu) with a purity of 99.999 mass % or higher. This is because even an infinitesimal amount of phosphor (P) can push up the recrystallization temperature of the copper wire and thus effectively increase the strength of the wire itself. Here, "with a purity of 99.999 mass % or higher" means that the metal impurities excluding phosphor (P) and copper (Cu) amount to less than 0.001 mass %, and the gaseous elements such as oxygen, nitrogen and carbon existing in the cupper (Cu) are not counted. When a predetermined amount of phosphor is contained in the core, it triggers deoxygenation of the copper (Cu) ball, which has been molten, as the molten copper ball solidifies in the first bonding. If the purity of the copper (Cu) is 99.999 mass % or higher, the phosphor in an amount of one mass ppm or more can trigger deoxygenation, and the same in an amount of 80 mass ppm or smaller, does not cause the copper (Cu) core to undergo work hardening during the wire drawing operation. By virtue of this deoxygenation effect of phosphor (P), even if there is a part where the core copper (Cu) is oxidized, the phosphor (P) in the vicinity of the surface layer of the molten ball undergoes enrichment to thereby divide and erase the oxidation of the copper (Cu) whereby this oxidized part of the core copper does not affect the molten ball formation.

[0021]
The intermediate layer is constituted by palladium (Pd). The melting point of palladium (Pd), which is 1554 degrees c, is higher than that of copper (Cu), which is about 1085 degrees C, and that of a copper alloy including trace element(s). For this reason, palladium (Pd) forms a thin skin to protect the molten ball from oxidation that proceeds from side face, at the first stage when the core of copper (Cu) or a copper alloy forms a spherical molten ball.

The purity of the palladium intermediate layer does not much affect the sphericity of the molten ball, and the magnitude of its thickness does not cause eccentricity in the ball; but in order to allow continuous wire drawing it is necessary to

use palladium (Pd) of a purity of 99 mass % or higher. The thickness of the intermediate layer is arbitrarily determined; however, the tendency is such that the thicker the palladium (Pd) intermediate layer becomes the slower the deterioration proceeds in the copper (Cu) or copper alloy core material.

[0022]
Method for forming the palladium (Pd) intermediate coating layer may be dry plating or wet plating. The dray plating can be a sputtering method, ion plating method, vacuum vapor deposition method or the like. From the viewpoint of avoiding entrance of impurities, dry plating is preferable, but when it is desired to obtain a cross section with uniform circular ring formation, wet plating is to be selected.

[0023]
In order to maintain the purity of copper (Cu), which is prepared at a high level, the galvanizing bath with regard to palladium (Pd) is preferably an ammoniacal aqueous solution or cyanide aqueous solution that does not contain halogen ion or sulphate ion. Also, gloss agents such as high polymer compound and metallic salt should not be contained in the layer lest they should ill-affect the sphericity of the molten ball. The film that is electroplated on a core made of copper (Cu), etc. is thereafter forcibly compressed by continuous drawing so that its film quality properties are not as important as the film components. If the film components include sulphur (S), it can enter into the copper (Cu) during the formation of the molten ball and there is a fear that it work-hardens the molten ball.

As the palladium (Pd) galvanizing bath, it is possible to adopt palladium P-salt ($Pd(NH_3)2(NO_2)_2$), ammonium nitrite and potassium nitrate, or palladium p-salt($Pd(NH_3)_2$ $(NO_2)_2$), alkalescent ammoniacal aqueous solution of ammonium nitrate and aqueous ammonia, neutral ammoniacal aqueous solution of $Pd(NH_3)_2(COO)_2$ and $(NH_4)_2HPO_4$ (United States Patent S4715935). In a case of a bath making use of palladium p-salt, the greater the pH value was, the larger the particle size of the deposit became. In a case in which palladium is plated in a wet manner,

the purity of the copper (Cu) is preferably 99.999 mass % or higher rather than 99.99 mass % in order that an abnormal deposition of sputter film is prevented from forming.

[0024]
Incidentally, it is possible to lay a strike plating (ultrathin plating) of palladium (Pd), platinum (Pt), nickel (Ni) or the like before the laying of the palladium (Pd) plating, for the purpose of controlling the timing at which the gold (Au) ultrathin surface layer dissolves into the copper (Cu) core at the time of the formation of the molten ball.

[0025]
With respect to the formation of a molten ball by means of arc discharge, the respective melting points of the metals within the coating layers are very important. A large part of a bonding wire is constituted by the core of high purity copper (Cu) so that the melting point of the copper (Cu) (about 1085 degrees C) is the key point. It is known that the core of a high purity copper (Cu) turns perfectly spherical when hit by an arc discharge in a reducing atmosphere.

Also is it known that a core of a high purity copper (Cu) coated with palladium (Pd) turns spherical when hit by an arc discharge in a non-oxidizing atmosphere. Although the melting point of palladium (Pd), which is about 1555 degrees C, is higher than that of copper (Cu), which is about 1085 degrees C, it is thought that palladium is forced to accompany the copper (Cu) as the latter turns spherical in the non-oxidizing atmosphere.

However, although in the case of a bonding wire of a high purity gold (Au), when it is hit by arc discharge it melts and forms a spherical molten ball irrespective of the atmosphere, a bonding wire in which the core of a high purity copper (Cu) is directly clad with a high purity gold (Au) would melt to form a spear-like body and a spherical ball is not obtainable. The melting point of gold (Au), which is about 1064 degrees C, is lower than that of copper (Cu), which is about 1085 degrees C, so that the surface layer consisting of the lower melting point gold (Au) melts earlier than the copper (Cu) does as the

copper (Cu) forms the spherical molten ball, and thus the molten gold immediately tries to wrap the wire end face but is prevented from doing so by the higher-melting point palladium (Pd). As a result, it is thought, diffusion of the low-melting point gold (Au) into the copper (Cu) occurs predominantly, and thus the gold is absorbed into the molten copper (Cu), and thereafter the palladium (Pd) melts. The trace additive elements in the copper (Cu) barely affect the melting phenomenon.

Thus, in the case of a general palladium-clad copper wire, the thickness of the outermost gold (Au) layer affects the sphericity of the molten ball, but in the present invention, as described above, the gold (Au) which has melted earlier promotes the melting of the copper (Cu) at the wire end face, but the thickness of the gold/palladium mixture layer is on an order of several nanometers so that the amount of gold (Au) is so small that its effect is limited, and as such the gold does not ill-affect the sphericity of the molten ball.

[0026]
The wet plating operation of the palladium (Pd) intermediate layer has a tendency of causing separation of irregular particles because leveling agent and gloss agent are not included. Also, the dry plating operation of the same has a tendency of causing separation in the form of a layer aligned with the crystal plane of the high-purity copper (Cu) core. In either case, the wire cross section would not exhibit a perfect circular ring, but so long as the thickness of the surface layer is 1 nm or greater it suffices.

[0027]
It is possible to form, over the intermediate coating layer, a surface layer consisting of a high purity gold (Au) or the like having a more uniform thickness by conducting an operation such as turning the wire about its axis during sputtering, reciprocating the wire axially during sputtering, sputtering upon the wire from both sides of the wire, instead of merely relying on the throwing power of sputtering. The surface layer consisting of a high purity gold (Au) or the like has a good

ductility so that it is possible to conduct upon it a continuous drawing down to the final wire diameter copying the die hole shape of the diamond die. During the continuous wire drawing, the clearance forming the interface between the surface later consisting of gold (Au) or the like and the intermediate coating layer is filled up, so that even if an abnormal separation or the like occurs during the wet plating of the palladium (Pd) intermediate layer, it does not mechanically penetrate the surface layer to form a separation, with a result that the surface of the bonding wire is coated entirely with gold (Au) or the like.

[0028]
As for the continuous wire drawing operation, a wet type wire drawing, which is conducted in cooling water, is better. This is because the outermost surface layer is constituted by the extremely thin coating layer, and thus it is feared that, if a dry type wire drawing is adopted, the heat created by the strengthened compression would cause the gold (Au) of the ultra thin surface layer to diffuse into the copper (Cu) core and thus be lost. In order to lower the frictional resistance between the diamond die and the gold (Au), it is advised to use a commercially available metal lubricant liquid solution to which a surfactant is added and which is thinned with a diluent such as water or alcohol, and also to conduct the continuous wire drawing in a solution such as an aqueous solution containing ethyl alcohol, methyl alcohol or isopropyl alcohol.

[Example 1]
[0029]
Hereinafter we will explain examples.

Copper wires having diameters of 500 micrometers were drawn respectively from such copper (Cu) ingots as detailed in Table 1 and they were used as the cores; in a usually practiced procedure a 2.0-micrometer-thick palladium (Pd) intermediate layer was deposited on the wire surface by electroplating. The palladium (Pd) plating bath used for the electroplating was prepared by adding 10 gW/l of phosphate to a neutral

dinitrodiamine palladium bath and the purity of the thus obtained palladium (Pd) was 99 %. Next, at the room temperature, gold (Au) of a purity of 99.99 mass % was sputtered by means of magnetron and a 0.08-micrometer-thick separation was obtained. The thickness of the plating was measured by means of Auger electron spectroscopy (AES).

Thereafter, this coated copper wire was drawn through a die to a final diameter of 17 micrometers. The theoretical film thickness of the gold (Au) was 0.0027 micrometer. Next, the deformation acquired during the wire drawing operation was removed and a predetermined final thermal treatment designed to control the extension ratio to about 10 % was performed. The conditions of this final thermal treatment were such that each wire was passed through a thermal treatment furnace with an effective treatment length of 50 cm and an atmosphere of nitrogen plus 5 % hydrogen at 700 degrees C, at a speed of 8 m/sec, and then the wire was cooled in a 10 % ethanol aqueous solution (at 20 degrees C).

[Table 1]

Composition of Copper Core

	composition of core (ppm)						
samples	Cu	P	Zr	Sn	V	B	Ti
1	balance	0	0	0	0	0	0
2	balance	10	0	0	0	0	0
3	balance	50	0	0	0	0	0
4	balance	0	5	0	0	0	0
5	balance	0	0	8	0	0	0
6	balance	0	0	0	4	0	0
7	balance	0	0	0	0	10	0
8	balance	0	0	0	0	0	6
9	balance	5	15	0	20	0	10
10	balance	60	0	45	15	5	0
11	balance	100	5	10	0	20	15
12	balance	200	20	15	15	30	5

[Example 2]
[0030]
A coated copper wire as obtained under the same conditions of Example 1 was passed through the thermal treatment furnace with an atmosphere of nitrogen plus 5 % hydrogen at 600 degrees C, at a speed of 5 m/sec, and then the wire was cooled in pure water (at 40 degrees C).

[Comparative Example 1]
[0031]
What were done in Example 1 were done herein except that a gold (Au) of a purity of 99 mass % with a thickness of 0.0027 micrometer (0.0027 micrometer thick theoretically) was separated in a pure gold plating bath (AUTRONEX series GVC-S manufactured by Electroplating Engineers of Japan Ltd.), and that each wire was passed through the thermal treatment furnace with an atmosphere of nitrogen at 550 degrees C, at a speed of 5 m/sec.

[Comparative Example 2]
[0032]
What were done in Example 2 were done herein except that the conditions of the final thermal treatment were modified such that each wire was passed through a thermal treatment furnace with an atmosphere of nitrogen plus 5 % hydrogen at 800 degrees C, at a speed of 8 m/sec.

[0033]
With regard to the respective wires of the above-described examples and comparative examples, manufacturing details are shown in Table 2.

[Table 2]

Manufacturing conditions for examples and comparative examples

	furnace temperature (degrees C)	speed (m/sec)	atmosphere	coolant	Pd coating method	Au coating method
Example 1	700	8	N_2 + 5%H_2	10% ethanol water (20 degrees C)	Pd plating	Au sputtering
Example 2	600	5	N_2 + 5%H_2	pure water (40 degrees C)	Pd plating	Au sputtering
Comparative Example 1	550	5	N_2	10% ethanol water (20 degrees C)	Pd plating	Au plating
Comparative Example 2	800	8	N_2 + 5%H_2	pure water (40 degrees C)	Pd plating	Au sputtering

[0034]
Each one of the wires prepared in these examples and comparative examples was bonded and stitched by welding on an aluminum electrode, and estimation was made with regard to high temperature reliability, bonding strength, and axial eccentricity.

The stitching conditions, test conditions and result of the estimation in each case are as follows.

[0035]
The ball bonding/stitching of the bonding wire was conducted using a commercially available automatic wire bonder (a ultrasonic thermo-compression wire bonder "MAX μ m Ultra" [a commercial name] manufactured by K&S Co., Ltd. A molten ball was made at a front end of each wire by an arc discharge using

Maxμm plus Copper Kit in a gas atmosphere where a mixture gas consisting of 4 volume % hydrogen and the balance nitrogen was passed at a flow rate of 0.5 (l/mm).

The ball-pointed end of the wire was stitched to a 0.8-μm-thick electrode film made of aluminum (Al plus 0.5% Cu) laid on a silicon substrate, and the other end of the wire was stitched to a lead frame (made of "alloy 42" and 150μm in thickness) heated to 200 degrees C and clad with a plating of 4-μm-thick silver (Ag). The capillary used was one made by SPT Corporation, and the wire bonder was set to operate at values, with respect to the molten ball, such that Ball Size would be of EFO Fire Mode and FAB Size would turn such that the actual diameter of the molten ball would become twice as large as the wire diameter. The stitching condition for the bonding was regulated such that the deformed ball diameter would be 2.5 times the wire diameter.

[0036]
Estimation of high temperature stability

Each wire bonded under the above-described conditions was used as respective sample, of which the first stitching end was bonded on the electrode film of aluminum (Al plus 0.5% Cu) and the second stitching end was bonded on the lead frame clad with a plating of silver (Ag). Pads for the first stitching of the sample were of a shape of 90μm square, and they were pitched at 100μm intervals. Also, some of neighboring pairs of the first stitched ends were so designed circuit-wise to electrically connect with each other. After the bonding, the circuitry was sealed up with a commercially available molding resin containing a halogen, and then superfluous parts of tie bars, etc. were cut away, and the samples were cured for two hours at a temperature of 175 degrees C, and finally they were let to sit for certain predetermined time periods in a high temperature heating furnace at a temperature of 220 degrees C. Measurement of the electric resistance was conducted using "Sourcemeter (type 2004)" (Product Name) manufactured by KEITHLEY INSTRUMENTS INC., in combination with a specially prepared IC sockets and a specially constructed automatic

measurement system. The procedure adopted for this measurement was so-called DC four terminal method. A certain constant electric current was let to run from probes for measurement between selected neighboring pairs of external leads (the pairs selected were those for which the pads on the IC chips were in short circuitry), and the voltage between the probes was measured. Such measurement of electric resistance was conducted with respect to 100 pairs (that is, 200 pins) of external leads before and after the sitting in the furnace, and ones whose electric resistance rose by 20 % or more were considered as defective. Also, we measured the time, with respect to each sample, that was required for the defective percentage of the wires of each sample to amount to 50 %, and the longer the time was the better the sample was rated. In particular, if such time was 200 hours or longer, it was judged that the sample would have no major problems in use so that we gave it a highest rating of ◎; if such time was no less than 150 hours but less than 200 hours, we gave it a second highest rating of ○; if such time was no less than 100 hours but less than 150 hours, we gave it a rating of △; if such time was shorter than 100 hours, we gave it a lowest rating of ×.

The results of these ratings are as shown in Table 3.

[Table 3]

High Temperature Stability Rating Result

	Example 1		Example 2		Comparative Example 1		Comparative Example 2	
Sample No.	rating	mixture layer (nm)	rating	mixture layer (nm)	rating	mixture layer (nm)	rating	mixture layer (nm)
1	◎	4	◎	5	△	3	×	12
2	◎	3	○	3	×	2	×	9
3	○	3	○	2	×	4	×	10
4	◎	5	○	4	×	3	×	11
5	◎	2	◎	5	×	2	×	13
6	◎	1	◎	1	△	5	×	10
7	◎	5	○	2	×	4	×	9
8	◎	3	◎	3	×	2	×	14
9	◎	2	○	2	×	1	×	15
10	○	4	○	4	×	2	×	11
11	○	4	○	5	×	4	×	13
12	○	5	○	1	×	3	×	16

[0037]
Estimation of bonding strength

For the estimation of bonding strength, the above-mentioned electrode film of aluminum (Al plus 0.5% Cu) was not used, but a ball bonding/stitching of the bonding wire was conducted upon a lead frame (made of "alloy 42" and 150 μm in thickness) heated to 200 degrees C and clad with a plating of 4-μm-thick silver (Ag) at both ends of the wire. Three thousand nine hundred twenty wires were bonded in each case, and when the number of bonding failure was no more than one we gave a rating of ◎, when 2 to 3 ○, when 4 to 20 ○, and when 21 or more ×.

The result is shown in Table 4.

[Table 4]

Bonding Strength Rating Result

	Example 1		Example 2		Comparative Example 1		Comparative Example 2	
Sample No.	rating	mixture layer (nm)	rating	mixture layer (nm)	rating	mixture layer (nm)	rating	mixture layer (nm)
1	○	4	○	5	×	3	×	12
2	◎	3	○	3	×	2	×	9
3	◎	3	○	2	×	4	×	10
4	○	5	○	4	△	3	×	11
5	◎	2	○	5	×	2	×	13
6	◎	1	◎	1	×	5	×	10
7	○	5	○	2	×	4	×	9
8	○	3	○	3	×	2	×	14
9	◎	2	○	2	△	1	×	15
10	◎	4	○	4	×	2	×	11
11	◎	4	○	5	×	4	×	13
12	○	5	○	1	×	3	×	16

[0038]

Estimation of Axial Eccentricity

In order to estimate the axial eccentricity, a ultrasonic thermo-compression wire bonder "MAXμm Ultra" [a commercial name] manufactured by K&S Co., Ltd. was used to continuously make FAB with the Loop Parameter set to assume a FAB Mode whereby estimation was effected. Bonding was continuously conducted upon a lead frame heated to 200 degrees C and clad with a plating of 4-μm-thick silver (Ag), and the electrode film of aluminum (Al plus 0.5% Cu) was not used. Incidentally, the other parameters regarding the wire bonding operation were the same as those adopted in the damage estimation of the above-mentioned electrode film of aluminum (Al plus 0.5% Cu). The estimation was conducted by first observing the shapes of 200 molten balls before the stitching, in particular the quality of axial eccentricity and dimension accuracy. The number of cases wherein the axial eccentricity between the wire and ball was more than 5 nm was counted, and when the count

was no more than one, the ball formation was considered good and the highest rating of ◎ was given, and when the count was 2 – 4, the situation was considered problem-free in practical use so that the relatively good rating of ○ was given, but when the count was 5 – 9 the lower rating of △ was given, and when 10 or more the worst rating of × was given.

The result of s5.uch estimation is shown in Table 5.

[Table 5]

Result of Axial Eccentricity Estimation

	Example 1		Example 2		Comparative Example 1		Comparative Example 2	
Sample No.	rating	mixture layer (nm)	rating	mixture layer (nm)	rating	mixture layer (nm)	rating	mixture layer (nm)
1	◎	4	◎	5	×	3	×	12
2	◎	3	◎	3	△	2	×	9
3	◎	3	○	2	×	4	×	10
4	◎	5	◎	4	×	3	×	11
5	◎	2	◎	5	×	2	×	13
6	◎	1	◎	1	×	5	×	10
7	◎	5	○	2	×	4	×	9
8	◎	3	◎	3	×	2	×	14
9	◎	2	◎	2	△	1	×	15
10	◎	4	◎	4	×	2	×	11
11	◎	4	○	5	×	4	×	13
12	◎	5	◎	1	×	3	×	16

[0039]
As is shown in Table 2, Example 1 and Example 2 differ from each other in the heat treatment conditions and the cooling conditions, but from the results of the estimations shown in the tables, one can see that there is no major difference between the two in terms of the thickness of the mixture layer, while their estimation results lowered somewhat. In contrast to these, Comparative Example 1 does not show much difference

in the mixture layer thickness but the result of its estimation is not good on account of the fact that hydrogen was not added to the atmosphere for the heat treatment. Also, since Au plating was adopted as the method for applying the Au coating, the adhesiveness and the densification of the coated layer would become lower compared to the one obtained by wet-type plating, so that there would exist local unevenness in the film thickness and also due to no small amounts of impurities from the additives and pH control agents, good estimation result was not obtained.

Also, on account of the fact that the heat-treatment temperature was too high in the case of Comparative Example 2, the thickness of the mixture layer got way larger than what is claimed in the present application, and accordingly the effect of the invention was not enjoyed.

It is recognized from this that the thickness of the mixture layer is a determinant factor and that the effect of the hydrogen addition is not small.

[Industrial applicability]

[0040]

The coated copper wire for ball bonding of the present invention exhibits a high bonding reliability when stitched to an aluminum electrode in a high temperature atmosphere, and this without trading off its characteristics of low electric resistance inherent to a high purity copper, of which the wire core is made, and its low price, so that it recommends itself to various types of applications.

[Document name]
Scope of what is claimed

[Claim 1]
A surface coated copper wire for ball bonding having a wire diameter of 10 – 25 micrometers comprising a core made of copper (Cu) or a copper alloy, an intermediate coating layer made of palladium (Pd) of a purity of 99 mass % or higher, and an uppermost mixture layer consisting of gold (Au) and palladium (Pd) and having a cross-sectional average thickness of 5 nm or smaller when measured by scanning electron microscopy; said surface coated copper wire being characterized by that said gold (Au) of said uppermost mixture layer has a purity of 99.9 mass % or higher and had originally formed a single surface layer but was penetrated and broken into pieces by palladium (Pd) which has thermally grown from said intermediate layer to penetrate through the gold layer to thereby be locally exposed adjacent to the broken gold pieces as a result of a heat treatment conducted in a hydrogen containing atmosphere, said palladium (Pd) being diffused with hydrogen as a result of said heat treatment.

[Claim 2]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the mean thickness of the cross section of the mixture layer is 3 nm or smaller.

[Claim 3]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the mean thickness of the cross section of the mixture layer is 1 nm or smaller.

[Claim 4]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the wire is coated with palladium (Pd) by means of wet plating.

[Claim 5]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that said palladium (Pd) is spatially

grown into the gold (Au) coating layer, by means of Stranski-Krastanov growth, after the copper wire coated with gold (Au) and palladium (Pd) is strongly drawn, whereby the mixture layer in which gold (Au) and palladium (Pd) are intermixed is created.

[Claim 6]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that said copper wire coated with gold (Au) and palladium (Pd) having the mixture layer after being strongly drawn was caused to absorb hydrogen in a hydrogen-containing inert atmosphere at 450 – 700 degrees C.

[Claim 7]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that said gold (Au) is laid by magnetron sputtering at a room temperature.

[Claim 8]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that said intermediate coating layer is of palladium (Pd) put by means of wet plating.

[Claim 9]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the copper (Cu) constituting the core is a copper having a purity of 99.999 mass % or higher.

[Claim 10]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the copper (Cu) constituting the core is a copper having a purity of 99.9999 mass % or higher.

[Claim 11]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the copper alloy constituting the core is made of 0.1 – 500 mass ppm of phosphor (P) and the balance copper (Cu).

[Claim 12]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the copper alloy constituting the core is made of at least one of zirconium (Zr), tin (Sn), vanadium (V), boron (B) and titanium (Ti) in a collective amount of 0.5 – 99 mass ppm and the balance copper (Cu) with a purity of 99.9 mass % or higher.

[Claim 13]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the copper alloy constituting the core is made of at least one of zirconium (Zr), tin (Sn), vanadium (V), boron (B) and titanium (Ti) in a collective amount of 0.5 – 99 mass ppm and phosphor in an amount of 0.1 – 500 mass ppm and the balance copper (Cu) with a purity of 99.9 mass % or higher.

[Claim 14]
The surface coated copper wire for ball bonding as claimed in Claim 1, characterized by that the copper alloy constituting the core is made of at least one of zirconium (Zr), tin (Sn), vanadium (V), boron (B) and titanium (Ti) in a collective amount of 0.5 – 99 mass ppm and phosphor in an amount of 1 – 80 mass ppm and the balance copper (Cu) with a purity of 99.9 mass % or higher.