

[Document Name] DESCRIPTION

[Title of Invention] WIRE STRUCTURE OF DILUTE ALLOYS OF  
NICKEL IN COPPER FOR BONDING SEMICONDUCTOR DEVICE

[Technical Field]

[0001]

The present invention relates to a structure of copper dilute-nickel alloy wire for bonding a semiconductor device and specifically relates to a structure of copper dilute-nickel alloy wire for ball bonding involving first bond to a pad electrode on a semiconductor element by free air ball (FAB) bonding and then second bond to an external electrode on a lead frame by stitch bonding.

[Background Art]

[0002]

A recent method for first bond to a pad electrode on a semiconductor element with a free air ball is as follows.

Copper alloy thin wire fed from a reel is introduced to a capillary as a bonding tool such that the end of the copper alloy thin wire is led from the outlet side of the tool by a certain length. The end of the copper alloy thin wire is then molten by micro-discharge between the end of the copper alloy thin wire and a spark rod while being blown with an inert gas such as a hydrogen-containing nitrogen gas to form an initial ball. This molten ball is then pressed with an ultra-hard tool onto an aluminum (Al)

or aluminum (Al) alloy pad electrode of a semiconductor element, such as an IC chip, heated within a range of 150°C to 300°C under ultrasonic vibration for thermocompression bonding (thermocompression bonding with ultrasound).

Here, the application of ultrasound has an effect of promoting the deformation of the copper alloy thin wire to widen the junction area and an effect of destroying and removing an oxide film of about several nanometers (nm) formed on the surface of the copper alloy thin wire to newly expose metal atoms, such as copper (Cu), at the underside and to thereby generate a plastic flow at the interface between the wire and the bonding pad opposing in contact with the wire to form interatomic bonds therebetween while gradually increasing the areas of faces adhering to each other.

[0003]

Subsequently, the capillary is moved in the XYZ directions (back and forth, right and left, and up and down directions) to form the copper alloy thin wire bonded onto the electrode of the IC chip into a predetermined loop shape. The copper alloy thin wire is bonded onto an external wiring lead frame by stitch bonding and is then cut to complete wire bonding. The stitch bonding is deemed as one type of wedge bonding of bonding wire with ultrasound.

[0004]

Since a high-purity copper alloy is too soft, the bonding wire generally contains a small amount of another

element. For example, Japanese Patent Laid-Open No. 2012-89685 (Patent Literature 1 described below) describes a method of producing copper bonding wire having a surface layer of which the crystalline structure before processing has an average crystal grain size of 20  $\mu\text{m}$  or less in a depth range of 50  $\mu\text{m}$  from the surface by using a soft dilute copper alloy material containing nine elements including titanium (Ti). The method improves the mechanical flexibility characteristics of bonding wire and the fatigue characteristics after bonding, while maintaining the electrical conductivity (the electrical conductivity at a resistivity of  $1.7241 \times 10^{-8} \Omega\text{m}$  based on the International Annealed Copper Standard is defined as 100%, the same shall apply hereinafter) to a relatively high value, 98% IACS or more.

[0005]

Japanese Patent Laid-Open No. S61-20693 (Patent Literature 2 described below) describes raw materials for copper alloy thin wire for bonding through formation of a relatively large molten ball under a completely reducing atmosphere, without using a free air ball (FAB) system.

It is disclosed that bonding wire contains 0.001% to 2% by mass of 24 elements such as magnesium (Mg), rare-earth elements, and tellurium (Te) (rare-earth elements are expediently counted as one element) and the remainder being substantially copper, in order to achieve a satisfactory bonding strength of the first bond while maintaining a high electrical conductivity of the bonding wire.

[0006]

Mass spectrometry of known high-purity copper alloy thin wire demonstrates that the wire contains, in addition to several mass ppm to several tens mass ppm of originally contained oxygen, several tens mass ppm to several hundred mass ppm, usually about 100 mass ppm, of oxygen penetrated through the surface layer and the grain boundary. That is, oxygen is present inside the copper alloy, in addition to the surface oxide film of copper oxide formed in the copper alloy thin wire.

If no easily oxidizable trace additive element is present in a high-purity copper alloy, the small amount of oxygen forms a metal deficient-type copper oxide (abbreviated to " $\text{Cu}_{2-x}\text{O}$ ") with Cu in the high-purity copper matrix to form a  $\text{Cu}_{2-x}\text{O}$  matrix. This  $\text{Cu}_{2-x}\text{O}$  matrix constantly attracts oxygen in the air through the surface layer at ambient temperature to provide the oxygen to the copper matrix. If  $\text{Cu}_{2-x}\text{O}$  molecules release oxygen atoms in the  $\text{Cu}_{2-x}\text{O}$  matrix on the surface layer side, copper atoms are newly generated, and the free oxygen atoms newly form metal deficient-type copper oxides ( $\text{Cu}_{2-x}\text{O}$ ) again with the copper matrix. Through this process,  $\text{Cu}_{2-x}\text{O}$  penetrates into the inside of the copper matrix. The newly generated free copper atoms can freely move in the metal deficient-type copper oxide matrix, and a part of the atoms binds to oxygen in the air to form a surface layer oxide (expediently abbreviated to " $\text{Cu}_2\text{O}$ ").

[0007]

High-purity copper alloy thin wire for bonding has a reduction in area of 99% or more by continuous wire drawing with a die, generally a diamond die. The surface of the wire is therefore highly affected by the wire drawing due to the compressive force of the die. In particular, in cold continuous wire drawing, microscopically, since the pressure force is not equally applied to the periphery of the thin wire, the damage of the thin wire by a strong drawing process significantly varies. Accordingly, even in copper dilute-nickel alloy thin wire having an oxygen content of 10 mass ppm or less subjected to cold wire drawing in water, internal oxidation occurs by oxygen in the air even at ambient temperature during leaving the bonding wire to stand after the continuous wire drawing process. As a result, even if the wire is thin wire having an oxygen content of 10 mass ppm or less and shows satisfactory bonding characteristics immediately after the production, after leaving to stand at ambient temperature for several ten days, as shown in Fig. 3, a  $\text{Cu}_2\text{O}$  film having a maximum thickness of about 10 nm that has been enlarged in an ununiformly hemispheric film is formed on the surface layer, in addition to a uniform  $\text{Cu}_2\text{O}$  coating film of several nanometers on the surface layer.

Even in the surface layer on which the thus-enlarged hemispheric  $\text{Cu}_2\text{O}$  film has been formed, the copper atoms newly derived from  $\text{Cu}_{2-x}\text{O}$  self diffuses via the  $\text{Cu}_2\text{O}$  film and can bind to oxygen in the air. Accordingly, the  $\text{Cu}_{2-x}\text{O}$  coating film gradually grows inwardly at ambient

temperature, and thereby the irregular hemispheric film inside the surface layer is also further oxidized into a thick  $\text{Cu}_2\text{O}$  coating film.

[0008]

When known high-purity copper alloy thin wire is used as bonding wire, since a molten ball is formed by blowing a reducing gas such as a hydrogen-containing nitrogen gas with a free air ball (FAB) system in first bond, the  $\text{Cu}_2\text{O}$  coating film of several to several ten nanometers (nm) and the irregular hemispheric  $\text{Cu}_2\text{O}$  film are thermally destroyed. However, since the bonding temperature in the stitch bonding of second bond is low, the oxide films are hardly broken, and the result of each bonding by the second bond varies depending on the conditions of the formed  $\text{Cu}_2\text{O}$  film. The influence of the surface layer becomes stronger to increase the variation of stitch bondability with an increase in the period of time for leaving the bonding wire to stand at ambient temperature and with a decrease in the diameter of the wire from 25  $\mu\text{m}$  to 20  $\mu\text{m}$  or further to 15  $\mu\text{m}$ .

[Citation List]

[Patent Literature]

[0009]

[Patent Literature 1] Japanese Patent Laid-Open No. 2012-89685

[Patent Literature 2] Japanese Patent Laid-Open No. S61-20693

[Non-Patent Literature]

[0010]

[Non-Patent Literature 1] Reidar Haugsrud, et al. "On the High-Temperature Oxidation of Cu-Rich Cu-Ni Alloys", Oxidation of Metals, Vol. 50, No. 314, 1998

[Non-Patent Literature 2] D.P. Whittle, et al. "TWO-PHASE SCALEFORMATION ON Cu-Ni ALLOYS", Corrosion Science, 1968, Vol. 295-308, Pergamon Press

[Summary of Invention]

[Technical Problem]

[0011]

It is a solution object of the present invention to provide copper alloy bonding wire that is prevented from forming an irregular hemispheric oxidation pattern on the surface layer of high-purity copper alloy thin wire, even if the wire is left to stand at ambient temperature for several days, and inhibits the variation in the stitch bondability of ultrasonic bonding, in particular, ball bonding.

[Solution to Problem]

[0012]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device of the present invention is characterized in that the copper dilute-nickel alloy wire for bonding a semiconductor device has a reduction in area of 99% or more by continuous wire drawing and is

constituted of a surface layer, an internal oxide layer in which nickel oxide particles formed by internal oxidation are finely dispersed, and a copper dilute-nickel alloy layer; the surface layer is composed of an oxide growth layer; the internal oxide layer is composed of a metal deficient-type copper oxide matrix and nickel oxide particles finely dispersed in the matrix; the copper dilute-nickel alloy layer is composed of an alloy layer of a copper (Cu) matrix having a purity of 99.995% by mass or more in which 0.1% to 1.5% by mass of nickel (Ni) is uniformly solid-soluted; and the internal oxide layer has a thickness at least 60 times larger than the thickness of the surface layer.

[0013]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device of the present invention is characterized in that the copper dilute-nickel alloy wire for bonding a semiconductor device has a reduction in area of 99% or more by continuous wire drawing and is constituted of a surface layer, an internal oxide layer, and a copper dilute-nickel alloy layer; the surface layer is composed of an oxide growth layer; the internal oxide layer is composed of a metal deficient-type copper oxide matrix and nickel oxide particles finely dispersed in the matrix; the copper dilute-nickel alloy layer is composed of an alloy layer of a copper (Cu) matrix having a purity of 99.995% by mass or more in which 0.1% to 1.5% by mass of nickel (Ni) and 1 to 5 mass ppm of phosphorus (P) are

uniformly solid-soluted; and the internal oxide layer has a thickness at least 60 times larger than the thickness of the surface layer.

[0014]

The copper dilute-nickel alloy in the present invention is a completely uniform solid solution. The microscopic state of the solid solution is therefore unclear. It is, however, known that when a copper-nickel alloy having a nickel (Ni) content of approximately 10% by mass is internally oxidized in an oxygen atmosphere, nickel oxide (abbreviated to "NiO") particles generated by internal oxidation are observed in a uniformly dispersed state ("On the High-Temperature Oxidation of Cu-Rich Cu-Ni Alloys" (Non-Patent Literature 1) and "TWO-PHASE SCALE FORMATION ON Cu-Ni ALLOYS" (Non-Patent Literature 2)).

Non-Patent Literatures 1 and 2 demonstrate that oxidation of Cu-5 wt% Ni or a copper-nickel alloy of 80%, 55%, or 10% Ni forms an external layer composed of a copper oxide and an internal layer composed of a  $\text{Cu}_2\text{O}$  matrix and NiO particles generated by internal oxidation dispersed in the matrix.

This suggests, though direct measurement is impossible, that nickel (Ni) is uniformly solid-soluted also in a copper dilute-nickel alloy as in above and that a reduction in the content of nickel (Ni) decreases the particle diameter of the NiO particles generated by internal oxidation and allows the NiO particles to be uniformly dispersed in the copper matrix in a dilute state.

In addition, the NiO particles generated by internal oxidation are thermodynamically stable, and NiO particles having a certain size or more do not move in a copper matrix, a  $\text{Cu}_{2-x}\text{O}$  matrix, and further a  $\text{Cu}_2\text{O}$  matrix at ambient temperature. The lower limit of the nickel (Ni) content is therefore determined to be 0.1% by mass. The formation of NiO particles by internal oxidation of the solid-soluted nickel (Ni) causes an increase in volume by the increased oxygen in the copper matrix, resulting in mechanical distortion of the copper matrix. This mechanical distortion is high in a surface layer to which oxygen is sufficiently supplied and becomes smaller toward the inside of the wire, leading to a microscopic wedge-shaped distortion. Consequently, free oxygen atoms released from the  $\text{Cu}_{2-x}\text{O}$  matrix or free oxygen atoms supplied from the surface layer penetrate in the  $\text{Cu}_{2-x}\text{O}$  matrix at a speed faster than the grain boundary diffusion (see Fig. 1). Therefore, a hemispheric  $\text{Cu}_2\text{O}$  film, which is observed in the high-purity copper alloy thin wire (see Fig. 3), is not formed on the surface layer (see Fig. 2).

[0015]

In Fig. 1, the graph at the left end of the drawing represents the results of a region near the surface layer at a depth of several nanometers or less and shows low oxygen concentrations due to influences such as noise specific to an apparatus and contamination of the surface of a sample. Although the precise conditions are therefore unclear, it is believed that in both the high-purity copper

alloy and the copper dilute-nickel alloy of the present invention, the region from the surface layer to a depth of several nanometers is a  $\text{Cu}_2\text{O}$  layer (for convenience of drawing the graph, the left end of the graph is not in contact with the vertical axis, and data in this range is blank).

As described below, when the region in which the counted number of oxygen atoms is one-tenth of that of the surface layer is defined as an internal oxide layer, in this region, a metal deficient-type copper oxide  $\text{Cu}_{2-x}\text{O}$  matrix in which nickel oxide microparticles are uniformly finely dispersed is formed accompanied by penetration of oxygen, and the irregularly enlarged hemispheric  $\text{Cu}_2\text{O}$  layer observed in Fig. 2 is not formed on the surface layer.

In contrast, in high-purity copper alloy, it is supposed that oxygen does not penetrate inwardly from the surface layer and that the oxygen forms an oxide with copper (Cu) diffused from the inside to form an enlarged hemispheric oxide layer directly below the surface layer.

These processes will now be described in detail.

[0016]

In the copper dilute-nickel alloy thin wire of the present invention, although nickel oxide ( $\text{NiO}_{1-y}$ ) is a metal deficient-type oxide like copper oxide ( $\text{Cu}_{2-x}\text{O}$ ), nickel in a  $\text{Cu}_{2-x}\text{O}$  matrix is preferentially oxidized into  $\text{NiO}$ . In addition, since  $\text{NiO}$  particles having a small particle diameter are uniformly dispersed in the  $\text{Cu}_{2-x}\text{O}$  matrix in a dilute state, oxygen is readily released from the  $\text{Cu}_{2-x}\text{O}$

matrix, and the internal oxidation rate of the released free oxygen in a certain range is accelerated. Accordingly, the upper and lower limits of the nickel (Ni) content in the copper dilute-nickel alloy thin wire are determined to be 1.5% by mass and 0.1% by mass, respectively. A nickel (Ni) content higher than the upper limit makes the size of the NiO particles too large to slow the internal oxidation rate, resulting in formation of a hemispheric pattern of copper oxide on the surface layer. In order to prevent the formation of the hemispheric pattern on the surface layer, the content of nickel (Ni) is preferably in a range of 0.8% to 1.2% by mass.

[0017]

In the copper dilute-nickel alloy thin wire of the present invention, 1 to 5 mass ppm of phosphorus (P) may be uniformly solid-soluted for preventing the formation of an oxide film on the surface of the molten ball during the first bond.

Since the content of phosphorus (P) is small compared to that of nickel (Ni), even if the bonding wire is left to stand at ambient temperature for several days, the phosphorus (P) does not adversely affect the mechanism of forming an internal oxide layer.

[0018]

In the copper dilute-nickel alloy thin wire of the present invention, the high-purity copper (Cu) as a raw material needs to have a purity of 99.995% by mass or more. Examples of the remainder in an amount less than 0.005% by

mass include silver (Ag), iron (Fe), nickel (Ni), lead (Pb), tin (Sn), antimony (Sb), arsenic (As), bismuth (Bi), chromium (Cr), tellurium (Te), selenium (Se), and silicon (Si). If the content of each of these impurity elements is 0.005% by mass or higher, surface segregation may occur on the copper dilute-nickel alloy thin wire or uniform dispersion of NiO particles in a dilute state in the  $\text{Cu}_{2-x}\text{O}$  matrix may be difficult. The purity of high-purity copper (Cu) is preferably 99.998% by mass or more for uniformly finely dispersing NiO particles.

[0019]

The copper dilute-nickel alloy thin wire of the present invention is oxidized by oxygen in the air immediately after melting casting the copper dilute-nickel alloy. For example, oxidation occurs during cooling after continuous casting, during the process of continuous cold wire drawing, and also in the thermal refining treatment after continuous wire drawing. In addition, oxidation progresses from the surface of the bonding wire even in the leaving state before shipping, and also oxidation gradually progresses after setting to a bonder in a state waiting for bonding.

However, even if the copper dilute-nickel alloy thin wire is left to stand for several to several ten days at ambient temperature, the  $\text{Cu}_2\text{O}$  film on the bonding wire surface barely changes the thickness as in conventionally known high-purity copper wire, and oxygen in the  $\text{Cu}_{2-x}\text{O}$

matrix rapidly penetrates. Consequently, no hemispheric film is formed on the surface layer.

As a result, the internal oxide layer formed by the thus-penetrated oxygen is enlarged. However, the oxygen concentration therein is significantly low and therefore hardly affects the physical and electrical properties of the bonding wire. In order to ensure these effects, the thickness of the internal oxide layer is at least 60 times, preferably 80 times, larger than that of the surface layer.

[0020]

This continuous drawing wire is cold-worked by 99% or more relative to the wire diameter before the continuous wire drawing. The continuous wire drawing process is preferably performed with a wire drawing die, in particular diamond die, which imparts a smooth surface to the copper dilute-nickel alloy thin wire. The smooth, uniform surface prevents the formation of a hemispheric film on the surface layer.

[0021]

In the present invention, the content of oxygen (O) in the bonding wire is preferably 10 to 150 mass ppm. Although the volume of an oxygen enriched layer is determined depending on the diameter of the bonding wire, if an excess amount of oxygen is contained in the copper dilute-nickel alloy thin wire, a hemispheric film is readily formed on the surface layer.

Furthermore, intermediate heat treatment allows the oxygen in the copper dilute-nickel alloy thin wire to

excessively readily move. The intermediate heat treatment is therefore preferably not applied. If the intermediate heat treatment is performed, it should be done in a non-oxidative atmosphere at a temperature as low as possible, 400°C to 700°C, for 60 to 180 minutes, which do not cause any problem.

[0022]

In the copper dilute-nickel alloy bonding wire of the present invention, an aluminum pad plated with a noble metal is preferably used for inhibiting penetration of oxygen from the bonding wire into the aluminum pad. The noble metal plating is preferably soft gold (Au), silver (Ag), or palladium (Pd) plating. If the plating hardness is similar to the static hardness of the copper dilute-nickel alloy bonding wire, the plastic flow

of the molten ball can be controlled, and chipping can be prevented. Specifically, the plating hardness is measured as Knoop hardness and is approximated to the Vickers hardness of the bonding wire.

[0023]

In the present invention, the lead frame is preferably made of a copper (Cu) alloy or iron (Fe) material coated with a copper (Cu) or copper (Cu) alloy by electroplating.

[Advantageous Effects of Invention]

[0024]

In the bonding wire of the present invention, free oxygen in the metal deficient-type copper oxide ( $\text{Cu}_{2-x}\text{O}$ )

matrix can much rapidly move in the  $\text{Cu}_{2-x}\text{O}$  matrix compared to the growth of the  $\text{Cu}_2\text{O}$  film of the surface layer at ambient temperature. Consequently, the metal deficient-type copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) matrix functions as a cushion layer to inhibit the formation of hemispheric oxide film pattern on the surface layer, resulting in stabilization of the  $\text{Cu}_2\text{O}$  film of the surface layer. As a result, the stitch bondability of the bonding wire in second bond is also improved.

In addition, the finely dispersed  $\text{NiO}$  particles do not move in the  $\text{Cu}_{2-x}\text{O}$  matrix. This internal penetration phenomenon is not changed even if the  $\text{Cu}_{2-x}\text{O}$  matrix is partially modified into a  $\text{Cu}_2\text{O}$  matrix by oxygen in the air. Accordingly, even if the bonding wire is left to stand at ambient temperature for several ten days, since oxygen in the air continues to penetrate into the inside of the copper matrix through the surface layer, a specific structure that the thickness of the copper oxide surface layer hardly changes as in a copper dilute-noble metal alloy fine wire is obtained.

[0025]

Furthermore, in the bonding wire of the present invention, the strength of the bonding fine wire itself is maintained by the copper dilute-nickel alloy, and the particle diameter of the  $\text{NiO}$  particles is controlled by adjusting the content of nickel ( $\text{Ni}$ ). As a result, no hemispheric copper oxide pattern is formed on the surface layer, and the finely dispersed  $\text{NiO}$  particles function as a

wedge to send oxygen to the Cu matrix to form an internal oxide layer several times faster than that in other copper dilute-noble metal alloy fine wire (see Fig. 1).

Accordingly, the stitch bondability of the bonding wire, even if it is left to stand for several ten days, is highly stabilized compared to conventionally known high-purity copper alloy bonding wire. In addition, since the content of nickel (Ni) is several percent by mass, even if the plastic flow of a molten ball is generated by a free air ball (FAB) system, no aluminum splash is caused by an increase in the dynamic strength of the bonding wire in first bond. In addition, even if heat is generated by an increase in the specific resistance compared to conventionally known high-purity copper alloys, since the mechanical strength is high, the high temperature stability is not inferior to those of the conventionally known high-purity copper alloy. Furthermore, since the wire strength is larger than those of the conventionally known high-purity copper alloys, the wire is hardly deformed during the bonding action, and the eccentricity of the free air ball is low.

[Brief Description of Drawings]

[0026]

[Fig. 1] Fig. 1 shows distribution curves of the relative secondary ion intensity of copper (Cu), nickel (Ni), and oxygen (O) in the depth direction of copper dilute-nickel alloy thin wire of the present invention after being left to stand at ambient temperature for 30

days from production. The vertical axis is a logarithmic scale.

[Fig. 2] Fig. 2 shows a bright-field transmission electron microscopic image (2200000 $\times$  magnification) of the surface layer and the metal deficient-type copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) matrix (lower side of the photograph) of copper dilute-nickel alloy thin wire of the present invention after being left to stand at ambient temperature for 30 days from production.

[Fig. 3] Fig. 3 shows a bright-field transmission electron microscopic image (2200000 $\times$  magnification) of the surface layer and the metal deficient-type copper oxide ( $\text{Cu}_{2-x}\text{O}$ ) matrix (lower side of the photograph) of high-purity copper alloy thin wire of a conventional example after being left to stand at ambient temperature for 30 days from production.

[Description of Embodiments]

[0027]

(Measurement of thickness of internal oxidation film)

A copper dilute-nickel alloy in which copper (Cu) having a purity of 99.9999% by mass and a nominal oxygen content of 5 mass ppm contained 1.2% by mass of nickel (Ni) having a purity of 99.995% by mass was continuously cast into a copper dilute-nickel alloy ingot of 300 mm in diameter. This ingot was formed into bonding wire having a diameter of 20  $\mu\text{m}$  by continuous cold wire drawing. This wire was left to stand at ambient temperature for 30 days, and the oxygen (O) concentration was then measured in the

depth direction from the surface layer (apparatus: secondary ion mass spectrometer, model ims5f, manufactured by CAMECA). The results are shown in Fig. 1.

The oxygen in the bonding wire was measured by a combustion method (apparatus: oxygen analyzer, RO-600, manufactured by LECO Corporation). The amount was 44 mass ppm (as the total amount of solid solution oxygen and oxygen in the surface oxide film).

In the measurement results shown in Fig. 1, a thickness when the counted number of oxygen atoms is one-tenth of that in the surface layer is defined as the thickness of the internal oxide layer. In the measurement of this time, the thickness was 172 nm.

The oxygen concentration continuously decreases from the surface layer toward the inside, which shows that internal oxidation is still progressing. That is, this means that no unstable hemispheric pattern is formed on the surface of the bonding wire even if the wire is left as it stands at ambient temperature.

Similar measurement was also performed for conventional high-purity copper alloy wire having a purity of 99.997% and a nominal oxygen content of 5 mass ppm. The results are shown in Fig. 1. The thickness of the internal oxide layer was 19 nm.

[0028]

(Measurement of thickness of oxide film of surface layer)

The copper dilute-nickel alloy wire described above was left to stand at ambient temperature for 30 days, and

the bright-field image thereof was observed with a transmission electron microscope (TEM) (HF-2000, manufactured by Hitachi High-Technologies Corporation) at 2200000 $\times$  magnification. The image is shown in Fig. 2. As obvious from Fig. 2, a uniform  $\text{Cu}_2\text{O}$  film of 1.8 nm was observed in the middle and a  $\text{Cu}_{2-x}\text{O}$  internal oxide layer was observed as a black patchy pattern below the  $\text{Cu}_2\text{O}$  film, but a hemispheric copper oxide pattern, which was observed in conventional high-purity copper alloy (Fig. 3), was not observed.

Furthermore, minute NiO particles were not observed with an FE-SEM (apparatus: field emission type scanning electron microscope, JSM-7800F, manufactured by JEOL Ltd.) at 100000 $\times$  magnification.

In addition, it was observed in the copper dilute-nickel alloy thin wire of the present invention that the internal oxidation rate penetrating into a copper dilute-nickel alloy matrix was extraordinarily faster than the solid-phase diffusion rate of forming a copper oxide in the surface layer (Fig. 2). (This penetration of oxygen of the internal oxide layer is ten times deeper than that in other copper dilute-noble metal alloy fine wire.)

Similarly, the conventional high-purity copper alloy wire having a purity of 99.997% and a nominal oxygen content of 5 mass ppm was observed with a TEM. The results are shown in Fig. 3. Unlike the copper dilute-nickel alloy of the present invention shown in Fig. 2, growth of a hemispheric copper oxide was observed.

[0029]

(Bondability test of second bond)

Each wire was left to stand at room temperature for 30 days and was then used for bonding to a silver-plated copper plate (plating thickness: 2.5  $\mu\text{m}$ ) with a bonding machine (apparatus: model IConn manufactured by Kulicke and Soffa Industries, Inc.) under various bonding conditions, and bonding process window was evaluated (herein, the "window area" refers to a range allowing appropriate bonding and defined mainly by ultrasonic power and load ). Wire having a wider bonding process window is hardly affected by various noises during real operation and can be stably used.

This time, the bond power was set from 0 to 200 at intervals of 20, and the bond force was changed from 20 to 200 at intervals of 20 for every bond power. The evaluation was performed under 110 different bonding conditions in total. Continuous bonding of 100 points was performed under each bonding condition. When the bonding was completed without stopping the continuous bonding, the condition was evaluated as OK, and when the bonding was stopped even once due to, for example, non-adhesion, the condition was evaluated as NG. As an index of the bondability of second bond of wire, the number of the bonding conditions evaluated as OK in the 110 bonding conditions was recorded to determine the window area.

[0030]

Subsequently, bonding was performed 10000 times at a bond power of "100" and a bond force of "120", and the number of bonding defects was determined. The results are shown in the column "Bonding reliability of second bond" of Table 1.

[0031]

[Table 1]

|                      | Ni<br>Concen-<br>tratio<br>n | Cu<br>Raw<br>material<br>purity | P<br>Concen-<br>tratio<br>n | O<br>Concen-<br>tratio<br>n | Surface<br>oxide layer<br>thickness<br>a (nm) | Internal<br>oxide layer<br>thickness<br>b (nm) | b/a  | Al splash<br>in first<br>bond | Window<br>area of<br>second<br>bond | Bonding<br>reliability<br>of second<br>bond |
|----------------------|------------------------------|---------------------------------|-----------------------------|-----------------------------|-----------------------------------------------|------------------------------------------------|------|-------------------------------|-------------------------------------|---------------------------------------------|
| Conventional example |                              |                                 |                             |                             |                                               |                                                |      |                               |                                     |                                             |
|                      | 0                            | 99.999                          | 0                           | 50                          | 11.5                                          | 19                                             | 1.7  | ×                             | 27                                  | 127                                         |
| Example              |                              |                                 |                             |                             |                                               |                                                |      |                               |                                     |                                             |
| 1                    | 0.2                          | 99.999                          | 0                           | 48                          | 2.3                                           | 150                                            | 65.2 | ○                             | 58                                  | 0                                           |
| 2                    | 0.8                          | 99.999                          | 0                           | 45                          | 1.9                                           | 169                                            | 88.9 | ○                             | 69                                  | 0                                           |
| 3                    | 1.2                          | 99.999                          | 0                           | 44                          | 1.8                                           | 172                                            | 95.6 | ○                             | 70                                  | 0                                           |
| 4                    | 1.4                          | 99.999                          | 0                           | 43                          | 1.9                                           | 165                                            | 86.8 | ○                             | 68                                  | 0                                           |
| 5                    | 1.2                          | 99.997                          | 0                           | 46                          | 2.2                                           | 152                                            | 69.1 | ○                             | 61                                  | 0                                           |
| 6                    | 1.2                          | 99.999                          | 1                           | 44                          | 1.8                                           | 168                                            | 93.3 | ○                             | 75                                  | 0                                           |
| 7                    | 1.2                          | 99.999                          | 5                           | 44                          | 1.8                                           | 174                                            | 96.7 | ○                             | 78                                  | 0                                           |
| 8                    | 1.2                          | 99.999                          | 10                          | 44                          | 1.8                                           | 171                                            | 95.0 | ○                             | 77                                  | 0                                           |
| Comparative Example  |                              |                                 |                             |                             |                                               |                                                |      |                               |                                     |                                             |
| 1                    | 0.08                         | 99.999                          | 0                           | 50                          | 5.1                                           | 130                                            | 25.5 | ○                             | 40                                  | 27                                          |
| 2                    | 1.6                          | 99.999                          | 0                           | 42                          | 2                                             | 154                                            | 77.0 | ×                             | 62                                  | 0                                           |
| 3                    | 1.2                          | 99.99                           | 0                           | 52                          | 4.2                                           | 60                                             | 14.3 | ○                             | 32                                  | 78                                          |

[0032]

In the bonding wire of a conventional example, since the value of internal oxide layer thickness/surface oxide layer thickness was small, 1.7, the window area of second bond was also narrow, 27. Thus, it can be understood that the bonding conditions of second bond are unstable.

In also the bonding wire in Comparative Examples 1 and 3, since the values of internal oxide layer thickness/surface oxide layer thickness were small, 25.5 and 14.3, respectively, the window areas of second bond were also low, 40 and 32, both are lower than 50. Thus, it can be understood that the bonding conditions of second bond are unstable.

[0033]

(Bondability test of first bond)

Each wire was left to stand at room temperature for 30 days, and ball bonding of the cooper alloy wire to an Al-0.5% Cu pad having a thickness of 0.8  $\mu\text{m}$  on a chip (thickness: 0.35 mm) was performed with a bonding machine (apparatus: model IConn manufactured by Kulicke and Soffa Industries, Inc.). The conditions for producing a free air ball (FAB) were set such that the FAB diameter was twice the diameter of the wire. The conditions of the ultrasonic wave and load of first bond were set such that the ball deformed diameter was 1.5 times the diameter of the FAB. The loop length and height were controlled to 5 mm and 300  $\mu\text{m}$ , respectively. The bonding was performed to 100 points, and turn-up of the pad (Al splash) was observed with an SEM (apparatus: scanning electron microscope, VE-9800, manufactured by Keyence Corporation). Wire caused turn-up with a width of 5  $\mu\text{m}$  or more in the pad was evaluated as  $\times$  (bad), and wire caused turn-up with a width of less than 5  $\mu\text{m}$  was evaluated as  $\circ$  (good).

Large turn-up of a pad, such as a width of 5  $\mu\text{m}$  or more, has a risk of a short circuit with adjacent pads. Accordingly, wire causing a large amount of turn-up having a width of 5  $\mu\text{m}$  or more is unsuitable as bonding wire.

[0034]

In addition to the evaluation described above, in the bonding wire of a conventional example, since the surface oxide layer had a thickness of 11.5 nm, Al splash occurred in the first bond, and the bonding reliability of second bond was low. In the bonding wire of Comparative Example 2, since the concentration of nickel (Ni) was 1.6% by mass, which is higher than the upper limit of the present invention, the molten ball was hard to cause Al splash in the first bond.

Similarly, in the bonding wire of Comparative Example 1, since the concentration of nickel (Ni) was only 0.08% by mass, which is lower than the lower limit of the present invention, the window area of second bond was narrow, and the bonding reliability of second bond was low. In the bonding wire of Comparative Example 3, the purity of copper (Cu) was only 99.99% by mass, and the bonding wire contained impurities such as 40 mass ppm of silver (Ag), 20 mass ppm of sulfur (S), 10 mass ppm of arsenic (As), and 10 mass ppm of antimony (Sb). In the bonding wire of Comparative Example 3, the window area of second bond was narrow as in the bonding wire of Comparative Example 1, and the bonding reliability of second bond was low.

[Industrial Applicability]

[0035]

In the bonding wire of the present invention, an oxide film hardly grows even if the wire is left to stand for a long time, and the bondability of second bond during bonding is satisfactory. Accordingly, the bonding wire is useful as bonding wire for electronic components used in personal computers and cellular phones.

## CLAIMS

### [Claim 1]

A structure of copper dilute-nickel alloy wire for bonding a semiconductor device, wherein the copper dilute-nickel alloy wire for bonding a semiconductor device has a reduction in area of 99% or more by continuous wire drawing and comprises a surface layer composed of a copper oxide growth layer, an internal oxide layer composed of a metal deficient-type copper oxide matrix and nickel oxide particles finely dispersed in the matrix, and an alloy layer of a copper (Cu) matrix having a purity of 99.995% by mass or more in which 0.1% to 1.5% by mass of nickel (Ni) is uniformly solid-soluted; and

the internal oxide layer has a thickness at least 60 times larger than the thickness of the surface layer, where the region in which the concentration of oxygen is reduced to one-tenth of that of the surface layer is defined as the thickness of the internal oxide layer.

### [Claim 2]

A structure of copper dilute-nickel alloy wire for bonding a semiconductor device, wherein the copper dilute-nickel alloy wire for bonding a semiconductor device has a reduction in area of 99% or more by continuous wire drawing and comprises a surface layer composed of a copper oxide growth layer, an internal oxide layer composed of a metal deficient-type copper oxide matrix and nickel oxide particles finely dispersed in the matrix, and an alloy layer of a copper (Cu) matrix having a purity of 99.995% by mass or more in which 0.1% to 1.5% by mass of nickel (Ni) and 1 to 5 mass ppm of phosphorus (P) are uniformly solid-soluted; and

the internal oxide layer has a thickness at least 60 times larger than the thickness of the surface layer, where the region in which the concentration of oxygen is reduced to one-tenth of that of the surface layer is defined as the thickness of the internal oxide layer.

[Claim 3]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the internal oxide layer has a thickness at least 80 times larger than the thickness of the surface layer.

[Claim 4]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the copper dilute-nickel alloy layer includes remainder copper (Cu) having a purity of 99.998% by mass or more.

[Claim 5]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the copper dilute-nickel alloy layer includes remainder nickel (Ni) in an amount of 0.8% to 1.2% by mass.

[Claim 6]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the copper dilute-nickel alloy wire has an oxygen (O) content of 10 to 150 mass ppm.

[Claim 7]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the continuous wire drawing is performed by cold continuous wire drawing.

[Claim 8]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the bonding of a semiconductor device is performed by wedge bonding.

[Claim 9]

The structure of copper dilute-nickel alloy wire for bonding a semiconductor device according to Claim 1 or 2, wherein the bonding of a semiconductor device is performed by ball bonding and stitch bonding.