

[Document Name] Specification

[Title of the Invention] High Purity Copper Wire for Connecting Semiconductor Apparatuses

[Technology Field]

[0001]

The present invention relates to a high purity copper wire used to connect an electrode on a semiconductor device to an external electrode, and more particularly, a high purity copper wire which has a strengthened texture and a diameter on submicron order, and is made of a copper-based alloy formed by doping infinitesimal amount of silver (Ag) to copper (Cu) of 99.9999 mass % purity.

[Background Technology]

[0002]

A bonding pad is installed on semiconductor devices, which are made of materials such as silicon (Si), silicon carbide (SiC) and gallium nitride (GaN), and consists of a base plate that may be made of aluminum (Al), aluminum-based alloy such as aluminum-plus-1-mass % silicon alloy, copper, nickel (Ni), silver, and platinum (Pt). Such base plates may be coated with a noble metal such as gold (Au) and silver by wet plating or dry plating like magnetron sputtering and vapor deposition, or may be plated with nickel. In this specification, "aluminum pad" means any of these base plates unless otherwise explained. Now, the high purity copper wire is used to connect an aluminum pad of a semiconductor device to a lead frame or the like by methods such as ball bonding, ultrasonic bonding and a hybrid of these two methods.

[0003]

Of the high purity copper wires, a round-section fine wire having a wire diameter of 0.1 mm - 0.9 mm is generally used; there are occasions on which an extra fine wire having a wire diameter of 0.01 mm - 0.025 mm is adopted, and also a flat type wire (tape),

which is made by flattening a round-section wire, may be used for semiconductor apparatus. In some cases, these extra fine wires and not-that fine wires may be clad with a thin silver coating before use.

A high purity copper wire made of a copper-based alloy made from a copper of 99.9995 mass % to 99.99994 mass % purity and an infinitesimal amount of silver (0.0006 mass % or lower) is also used in the above-described application (hereinafter this copper-based alloy is referred to as "silver-doped copper alloy" for simplicity); in this case, it is a general practice that the wire is subjected to a final thermal treatment of 500 degrees C for the purpose of releasing the strain caused by the wire drawing (ref. IP Publication 1 and IP Publication 2, which are described herein-below). This is to make use of the fact that the high purity copper wire which is drawn continuously has a densely packed sectional texture, and that such high purity copper wire is scarcely affected by the heat of 500 degrees C or lower (ref. Fig. 1).

[0004]

Fig. 1 shows a situation wherein the crystal grains in the texture of a heavily drawn wire are affected by heat such that the neighboring crystal grains unite with each other to transform to a recrystallized structure after microstructure recovery, and some of the crystal grains begin to recrystallize. Incidentally, each of Figs. 1 through 5 depicts almost entire cross section of respective wire.

On the other hand, when a continuously drawn high purity copper wire is heated to a temperature of 500 degrees C or higher in a reducing atmosphere, it generally happens that the drawn structure transforms to recrystallized structure after microstructure recovery, and then grains start growing.

However, in the case of a high purity copper wire made of a copper alloy made from 99.9995 mass % to 99.99994 mass %-pure copper and infinitesimal amount of silver, this kind of transformation

in the internal texture proceeds at higher speeds, and some of the crystal grains enlarge coarsely (ref. Fig. 2), and this transformation propagates throughout the entire wire and an annealed situation is established (ref. Fig. 3). In Fig. 2, the diameter of the central crystal grain is seen to be about 40 % of the wire diameter. In Fig. 3, the diameters of the large crystal grains are seen to exceed 50 % of the wire diameter.

[0005]

The ultrasonic bonding method can be applied to the high purity copper wire which has been subjected to a final thermal treatment of lower than 500 degrees C by pressing a carbide tool on the high purity copper wire and effecting a bonding between the high purity copper wire and the aluminum pad by virtue of its load and the energy of ultrasonic wave vibration emanating from the carbide tool. The effects of the application of the ultrasonic wave vibration include enlargement of the contact area for promotion of the transformation of the high purity copper wire, destruction and removal of the surface oxide film having a thickness of 5 - 10 nanometers (nm), which forms all over the high purity copper wire, to thereby expose the metal atoms such as aluminum where the wire and the bonding pad made of aluminum, nickel or the like meet each other, and creating a plastic flow in the interface between the bonding pad and the copper wire, to thereby invite atom-to-atom bonding between these two while expanding the newly created face where the two are closely adjacent to each other.

[0006]

On the other hand, in the case of an application of the ball bonding method to the high purity copper wire which has been subjected to a final thermal treatment of 500 degrees or higher, a high voltage is impressed on the high purity copper wire to thereby make a molten ball at its end while blowing to the high purity copper wire an inert gas such as nitrogen gas or a reducing gas such as nitrogen gas mixed with hydrogen by 5%, and the molten ball is pressed onto the aluminum pad by means of a carbide tool to thereby effect a bonding between the high purity copper wire and the aluminum pad.

[0007]

However, even the copper wire made of a copper alloy made from 99.9995 mass % to 99.99994 mass %-pure copper and infinitesimal amount of silver (Ag) may contain oxygen on an order of several mass ppm to several tens mass ppm, which originates from the raw material high purity copper powder. Also, a layer of Cu oxides measuring 5 - 10 nm in thickness (consisting of a cuprous oxide layer and a copper oxide layer, the latter being on top of the former) is inevitably formed on the surface of the high purity copper wire at stages such as: manufacturing a wire preform of high purity copper by continuous casting; conducting an intermediate thermal treatment on this wire preform in the atmosphere; manufacturing a high purity copper wire by continuously drawing from this wire preform; and letting the high purity copper wire sit in the atmosphere.

[0008]

For this reason, even when a ball bonding is conducted while a reducing gas is kept blowing to the high purity copper wire, the oxygen existing inside the high purity copper wire and in the grain boundaries moves endlessly into the oxide layer on the surface, so that it is difficult to eradicate the Cu oxide layer from the surface; therefore, even when a free air ball (FAB) was made from a high-purity copper extra fine wire having a wire diameter of 0.01 - 0.08 mm for ball bonding, the molten ball tended to be hard and it often caused a crack in a silicon chip. Also, even if a good first bonding connection was made between a 0.06 mm - 1.0 mm-diameter high purity copper wire for stitch bonding and an aluminum pad, if it is let to sit at a high temperature, an aluminum oxide grows from the bonding interface between the copper of the high purity copper wire and the aluminum of the aluminum pad, and forms an oxide layer before long, which leads to detachment of the high purity copper wire from the bonding interface.

This phenomenon was more difficult to prevent in the case of thinner wires having diameters of 0.06 mm to 0.1 mm, for which controlling of the load is difficult.

[0009]

On the other hand, in the case of a high purity copper wire having a sub-millimeter diameter such as 0.1 mm - 1.0 mm, it is difficult to prevent the cracking of chips, because the crystal texture immediately after the wire drawing or the texture after a thermal treatment of about 500 degrees C conducted immediately after the wire drawing remains densely packed recrystallized structure (ref. Fig. 1) so that even if it is welded to a copper pad by ultrasonic wave, the impressed load required becomes larger as the wire diameter becomes larger. Furthermore, although it is possible to conduct a bonding upon a copper base plate or a nickel base plate, the greater the wire dimension is the poorer the bondability becomes, so that it has not been industrially practiced.

On the other hand, when a ultrasonic bonding is conducted with a high purity copper wire which has been subject to a thermal treatment of about 800 degrees C for several hundred milliseconds or shorter immediately after the wire drawing and thereby has a texture as shown in Fig. 3, while a reducing gas is kept blown to the high purity copper wire (such as a high purity copper extra fine wire of a diameter 0.01 mm - 0.08 mm for ball bonding, a high purity copper wire of a diameter 0.06 mm - 1.0 mm for stitch bonding, and a high purity copper wire of a sub-millimeter diameter), although the silicon chip will not be cracked during the first bonding because these copper wires do not make a molten ball, but as they are so soft that the bonding strength at the first bonding is insufficient and a phenomenon occurs in which as the thermal cycle test is repeated the bonding strength decreases. This phenomenon is similarly experienced by copper wires for audio equipment wherein the grain size is relatively large and approximately uniform (ref. JP Publication 3 hereinafter described).

[0010]

On account of this, it has been a general practice to prevent a formation of the oxide layer on the surface of the high purity copper wire by thinly providing a layer of a noble metal such

as palladium (Pd) on the surface of the high purity copper wire. However, a thin noble metal layer is not free of crack, pinhole and the like in it, and during the final thermal treatment at high temperatures it has been thought that it is impossible to stop passing of the oxygen from the atmosphere through the noble metal layer, and thus such wires with an overlayer experienced similar problems as the wires without overlayer did.

[0011]

On the other hand, the high purity copper wire is thought to be useful for semiconductor devices, which require durability against high temperatures such as 100 - 200 degrees C, especially for power semiconductor devices used in an air conditioner, a photo-voltaic power generation system, a hybrid car, an electrically-powered car and the like, which experience frequent repetition of on-off switching at high temperatures, and its field of application is expanding. The working conditions for these power semiconductor devices are more demanding than those for normal semiconductor devices on account of high temperature specification. For example, in the case of a power semiconductor used in a vehicle, it is necessary for the high purity copper wire to withstand the repetition of temperature changes through, normally, maximum 100 - 150 degrees C at the bonding positions. As there is a problem of oxidation under such high temperature circumstances, the high purity copper wire without overlayer has not been industrially used. This is on account of the fact that if a high purity copper wire has been held at a high temperature, it undergoes a change - even if it is a high purity copper wire having a crystal texture as shown in Fig. 1 immediately after the wire drawing - a change whereby the wire drawing texture in the high purity copper wire transforms from recovered microstructure to recrystallized structure, and the grains begin to grow, and part of the wire starts turning saggy and in the end the entire wire becomes soft (ref. Fig. 3).

[Prior Art Publications]

[IP Publications]

[0012]

[IP Publication 1]

Japanese Patent Application Publication 2004-064033

[IP Publication 2]

Japanese Patent Application Publication 2010-153539

[IP Publication 3]

Japanese Patent 4815878

[Summary of the Invention]

[Problems the Invention Seeks to Solve]

[0013]

It is an object of the present invention to do away with a situation that after a first bonding of a high purity copper wire on an aluminum pad the bonding strength between the copper of the high purity copper wire and the aluminum of the aluminum pad becomes unstable, and also a situation that when a semiconductor device is let to sit at a high temperature after the first bonding, oxides of aluminum grow from the interface between the copper and the aluminum of the aluminum pad and eventually the high purity copper wire is detached from the aluminum pad.

[Means to solve the Problems]

[0014]

In order to solve the above-described problems, the inventors of the present inventions first paid an attention to the fact that there is a time lag between, on one hand, the solid-vapor phase stage wherein when the high purity copper wire is heated to a high temperature in an inert atmosphere the oxygen in the surface of and inside the high purity copper wire is expelled into the vapor phase and, on the other hand, the solid phase stage wherein after the solid-vapor phase stage has taken place the wire drawing texture in the high purity copper wire transforms from the recovery structure to the recrystallization structure and grain growth takes place. In other words, when the temperature of high purity copper wire is raised while the wire is kept tensed by a constant tension the speed of the expulsion of the oxygen from the high purity copper wire is increased. Then, during the short time prior to the occurrence of the grain

growth, that is, during the short moment of less than several hundred milliseconds in which the heated high purity copper wire is quickly cooled by water or the like, the growth of the grains of the high purity copper wire is stopped and at the same time intensify the hardness of the high purity copper wire by causing numerous number of crystal defects such as pit and void to occur, by effecting thermal contraction while maintaining the constant tension, in the vicinity of the recrystallized structure in the outer layer which is defined as having a thickness of  $1/20$  or smaller of the diameter of the high purity copper wire.

[0015]

In addition, gasses such as inert gas are taken into the crystal defects in the surface of the high purity copper wire during the quick cooling with a result that the crystal grain boundaries in the surface of the high purity copper wire are sealed with the inert gas and other gasses the entrance of oxygen through the crystal grain boundaries is prevented. By consolidating the internal texture before the grains start growing from the recrystallized structure in the high purity copper wire, it becomes possible to prevent the cracks in the high purity copper wire from growing and to prevent the high purity copper wire itself from sagging during the wire's service life while the frequent repetition of on-off switching operation at high temperatures merely promotes lattice relaxation of the numerous crystal defects in the surface layer gradually.

[0016]

The high purity copper wire of the present invention for connecting the semiconductor apparatus is characteristic in that, in the continuously drawn high purity copper wire which is clad with an oxide film, has a purity of 99.999 mass % - 99.99994 mass %, and has a wire diameter of not smaller than 0.01 mm but smaller than 1 mm, the copper wire has a sectional structure in which largest 10 grains have a total crystal grain area accounting for 5-25% of the total area of the sectional structure, and 80 % or more of this crystal grain area is interior to a surface layer, which is defined to have a thickness of  $1/20$  or smaller of the wire diameter.

[0018]

The purity of the high purity copper wire need be such that the copper accounts for 99.999 mass % - 99.99994 mass %. The mechanical strength of the high purity copper wire is determined predominantly by the internal texture of the wire, and secondly by the Cu oxide layer ( $\text{CuO}/\text{Cu}_2\text{O}$ ) having a thickness of several nanometers.

When a material worked is heated, the densely packed texture after the wire drawing transforms from the recovery texture to recrystallized structure and then the grains start growing, and in response to this series of changes in the crystal grain texture caused by heating, the oxygen in the copper matrix moves through the grain boundaries from the Cu oxide ( $\text{CuO}/\text{Cu}_2\text{O}$ ) layer to the exterior, and as the result the Cu oxide ( $\text{CuO}/\text{Cu}_2\text{O}$ ) layer in the surface becomes thinner. The amount of the impurities excluding silver is 30 mass ppm or smaller. The main impurities in a high purity copper are iron (Fe), nickel, tin (Sn), silicon, phosphor (P) and sulfur (S). If the total amount of these impurities exceeds 30 mass ppm, the pinning effect of the impurities alters the crystal texture and renders it impossible to control the crystal texture through heating and cooling.

[0019]

These impurity elements are difficult to separate in the copper matrix, as they have affinity to the copper matrix, and even if they form oxides in the copper matrix, they scarcely thwart the series of changes in the crystal grain texture formed of the copper oxide caused by thermal changes. For this reason, it becomes possible to alter the crystal grain texture of the high purity copper wire in response to thermal energy amount created by heating. It is necessary that the high purity copper wire has a purity of 99.997 mass %. If a power semiconductor apparatus is switched on and off repetitively at high speeds, as in the case of an inverter controller, cracking occurs in the wire caused by thermal fatigue, but with a purity of 99.997 mass % or higher, this is prevented because the recrystallization temperature is low and thus the recrystallization promptly

removes the residual strain of machining and renders it difficult for sub-grains to form in the wire. Consequently, the purity of the high purity copper wire need be 99.997 mass % or higher, and preferably it is 99.999 mass % or higher, and more preferably 99.9999 mass % or higher.

However, when the purity exceeds 99.99994 mass %, the over high purity causes the recrystallization to take place at room temperature, and this leads to a wider disparity in the diameter of the deformed ball at the time of bonding; furthermore, in the case of an extra fine wire for ball bonding, which has a wire diameter of 0.01 mm - 0.08 mm, the rigidity of the wire itself is lost.

Consequently, the purity of the high purity copper wire need be in a range of 99.999 mass % - 99.99994.

Also, since the high purity copper wire has high thermal conductivity, it is preferable that the wire diameter is on sub-millimeter level from the viewpoint of controllability of the crystal texture of the high purity copper wire. If the diameter is smaller than 0.1 mm, the wire itself is so weak that it becomes necessary to do such things as molding the entire wire with a resin after the bonding or designing a shorter loop distance.

[0020]

When the total amount of the impurities (excluding silver, referred to later) is 30 mass ppm or greater, these impurities form oxides in the copper matrix after coupling with the oxygen existing in the copper matrix. The grains of these oxides are liable to separate in the grain boundaries of strongly machined densely packed crystal grains, and are more resistive against the temperature changes than the crystal grain texture of the high purity copper so that it predominates the crystal texture of the high purity copper wire. For this reason, as a heating is conducted so as to change the densely packed inner texture (ref. Fig. 1) to an annealed inner texture (ref. Fig. 3), the

transformation takes place at once at a certain temperature or higher and it is not possible to change the crystal grain texture of the high purity copper wire gradually.

[0021]

Silver element exists in the copper matrix as a complete solid solute with the copper, and silver does not separate in the grain boundaries of the copper crystal grains. On the other hand, although silver is close to copper in ionization tendency and chemical properties, it is more electropositive than copper and less reactive with oxygen than copper is. Silver bulk takes oxygen into silver matrix without being oxidized by it, and allows oxygen to pass through it. For this reason, even if silver as much as 1 - 25 mass ppm is contained in an oxide film-clad copper of a purity of 99.997 mass % - 99.9994 mass %, this does not ill-affect the mutual interaction between the copper matrix and the oxygen. However, if the silver content exceeds 25 mass ppm, the relative decrease in the purity of copper is such that it becomes difficult to change the crystal grain texture of the high purity copper wire in response to the heat energy amount created by heating. Hence the content of the silver is specified as 1 - 25 mass ppm.

[0022]

The largest of the crystal grains in the sectional structure of the high purity copper wire can expand suddenly by thermal energy as shown in Fig. 2. However, in the case of an oxide film-clad copper having a purity of 99.997 mass % - 99.9994 mass %, the thermal energy is equally distributed throughout the matrix, and thus large crystal grains grow nearly uniformly (ref. Fig. 4). As a result, not a small number of substantially large crystal grains are formed, and as the sizes of individual large crystal grains are in a relative sense reduced, and thus the average grain diameter of a large crystal grain is specified as 5 - 25 % of the wire diameter. As a result, it becomes possible to control the small change in the thermal energy which takes place between the solid-vapor phase stage wherein the interior oxygen is expelled into the vapor phase and the solid phase stage which happens immediately before the grain growth takes place.

[0023]

In the present invention, it is preferable that the average grain diameter of the largest crystal grains is as small as possible, for the reason that the mechanical strength of the high purity copper wire is covered by the crystal grain texture, and thus the magnitude of the average grain diameter of the largest crystal grains as of the time immediately following the expulsion of the oxygen into the vapor phase from inside the copper matrix is specified as 5 - 25 % of the wire diameter. Preferably, the average grain diameter of the largest crystal grains is 5 - 20 % of the wire diameter (Fig. 4).

[0024]

In the present invention it is also necessary that the sum of the crystal grain areas of the largest 10 grains in the sectional structure of the high purity copper wire is 5 - 25 % of the total area of the sectional structure of the high purity copper wire and that 80 % or more of the sum of the crystal grain areas of the largest 10 grains is interior to the surface layer, which is defined as having a thickness of  $1/20$  of the wire diameter. Preferably, the sum of the crystal grain areas of the largest 10 grains is 10 - 20 % of the total area of the sectional structure and also that 90 % or more of the sum of the crystal grain areas of the largest 10 grains is interior to the surface layer, which is defined as having a thickness of  $1/20$  of the wire diameter (ref. Fig. 4). The reason for this specifying is that in the present invention the largest crystal grains grow nearly equally and if small crystal grains in which the dislocation of strong strain is accumulated toward the walls of the grain boundaries exist in the surface layer, the mechanical strength of the high purity copper wire is intensified owing to the double structure effect.

[0025]

It is also preferable in the present invention that the thickness of the oxide film is 1 - 6 nm. This is because of the fact that when the oxygen inside the copper matrix is expelled into the vapor phase as a result of thermal treatment the thickness of the oxide film becomes thinner, and when the thickness of the

oxide film is as small as less than 1 nm, the amount of oxygen inside the copper matrix becomes too small for a clear-cut crystal boundary to exist, and as a result the mechanical strength inside the high purity copper wire becomes weak. On the other hand, if the thickness of the oxide film is 6 nm or larger, even if a good first bonding is achieved, the oxygen in the copper matrix, which exists plentifully in this case, permeates, during the use, into the bonding interface and diffuses through oxide layer, and the bonding strength is weakened.

[0026]

Now, the continuously drawn high purity copper wire is kept under a constant tension while it is heat treated. This constant tension is basically imposed on the wire from the exit of the final diamond die to the entrance of the winding spool in the continuous drawing system, and it is so designed that the vibration occurring in other stages does not propagate to the copper wire through a dancer roller or the like, and the tension is kept constant between the thermal treatment stage and the cooling stage, and it is made possible to impart to the high purity copper wire a predetermined thermal energy, whose magnitude is determined depending on the temperature of the thermal treatment and thermal treatment location.

[0027]

It is preferable that the copper wire after being continuously drawn is heated rapidly at a temperature of 600 degrees C to 800 degrees C for a brief moment of several hundred milliseconds or shorter while successively kept under the constant tension. In order to securely control the crystal texture of the high purity copper wire it is more preferable to adopt a temperature between 650 degrees C and 750 degrees C. If the high purity copper wire is heated in a non-oxidizing atmosphere, the first thing that happens is expelling of oxygen into the vapor phase from the surface and interior of the high purity copper wire. The higher the thermal treatment temperature is, the longer the constantly tensed high purity copper wire is expanded whereby the crystal grain boundaries are pulled in forward and backward directions as well as right and left directions, and as a result

the expulsion of oxygen into the vapor phase proceeds more effectively, but the time span until the grain growth starts becomes shorter, and it becomes difficult to control the number of the crystal grains in the high purity copper wire by means of quick cooling by water or the like.

Incidentally, when the heating temperature is 500 degrees C or so and the heating time is several hundreds of milliseconds or shorter, a use of a reducing atmosphere would not much reduce the Cu oxide layer of several nanometers thick in the surface of the high purity copper wire.

Also, if the amount of impurity elements is too great, the Cu oxide layer of a thickness of several nanometers existing in the surface of the high purity copper wire becomes difficult to lessen because these impurity elements easily react with the oxygen in the copper matrix to form oxides, so that the chip breakage becomes more liable to occur during the bonding.

[0028]

It is thought that the solid-vapor stage wherein the Cu oxide layer lessens has the following mechanism.

The outermost cupric oxide ( $\text{CuO}$ ) layer of the high purity copper wire comes off one atomic layer after another when heated to a high temperature and is released in the inert atmosphere. Then the cuprous oxide ( $\text{Cu}_2\text{O}$ ) layer, which was immediately beneath the outermost layer of the high purity copper wire, separates copper and becomes a cupric oxide ( $\text{CuO}$ ) layer. This reduced copper couples with oxygen which arrives from the copper matrix after first passing through the crystal grain boundaries, and forms again a cuprous oxide ( $\text{Cu}_2\text{O}$ ) layer. However, since the amount of the oxygen in the copper matrix is so small that the oxygen to be passed through the crystal boundaries run out before long, and thus the reduced copper which existed in the original cuprous oxide ( $\text{Cu}_2\text{O}$ ) layer is absorbed into the copper matrix. As a result, the thickness of the outermost cupric oxide ( $\text{CuO}$ ) layer gradually decreases, while the immediately underneath

cuprous oxide ( $\text{Cu}_2\text{O}$ ) layer thins more promptly.

When a high temperature thermal treatment at about 800 degrees C is applied in a reducing atmosphere, the thickness of the Cu oxide layer (which is the sum of that of the cupric oxide ( $\text{CuO}$ ) layer and that of the cuprous oxide ( $\text{Cu}_2\text{O}$ ) layer) which used to be 6 nm or greater decreases to about 1 nm.

[0029]

When the copper wire which has been continuously drawn is next subjected to a rapid heating at a temperature of 600 degrees C or higher for a span of several hundreds milliseconds or shorter and maintained at a certain temperature in a non-oxidizing atmosphere, the copper wire begins to undergo a change such that the crystal texture after the wire drawing as shown in Fig. 1 transforms to the crystal texture after recrystallization as shown in Fig. 4. The atmosphere for the thermal treatment of the present invention shall be non-oxidizing atmosphere, namely, either inert atmosphere or reducing atmosphere. Since the recrystallized structure in the high purity copper wire is formed in a non-oxidizing atmosphere, no extra oxygen exists in the crystal boundaries of the copper matrix. Incidentally, as the temperature becomes higher the heat lost in the environment increases, so that it becomes difficult to measure the temperature of the wire directly; however, the high purity copper wire was seen to have a dark-red heat color to cherry red color by visual observation and is assumed to be in a range of 600 - 800 degrees C.

Now, when the temperature of the thermal treatment becomes too high, the wire being drawn starts expanding very loosely at a certain temperature of higher, and the high purity copper wire breaks, and hence the above-mentioned upper temperature limit. Possible method for the heating may include heating by electric furnace, electrical heating, heating by light irradiation and steam heating.

[0030]

A rapid cooling of a high purity copper wire from a high temperature

down to the room temperature while maintaining the wire under a certain tension would not cause a change in the crystal texture of recrystallized high purity copper wire, but the thermal contraction caused by the rapid cooling gives rise to numerous crystal defects such as pit, void and crack in the vicinity of the recrystallized structure in the copper matrix, as the wire solidifies. For this reason, the texture of the grain boundaries in the high purity copper wire (ref. Fig. 4) becomes harder than the texture of the crystal grains which have been coarsely expanded by the complete annealing (ref. Fig. 3), and by virtue of these crystal defects in the harder crystal boundaries, the high purity copper wire is provided with a certain expansiveness and a certain breaking strength, that is, the high purity copper wire is provided with mechanical strength. Also, numerous crystal defects such as pit and void occur in the surface of the high purity copper wire as a result of a water contact and a contact in the vapor phase involving steam which had been a part of the water, and this causes the surface of the solidified high purity copper wire to have a heightened mechanical strength.

[0031]

This kind of phenomenon of defects occurrence and solidification similarly takes place in the case where a thin noble metal coat is laid on the high purity copper wire of the present invention, and palladium (Pd) is especially effective because it occludes hydrogen at a high temperature. Furthermore, by making use of electric heating, it becomes possible to submerge the high purity copper wire in water while the wire is kept heated from inside, so that a large number of strain points such as dislocation occurs in the crystal grain boundaries, and thereby the crystal boundaries become clear-cut and the internal mechanical strength of the high purity copper wire is intensified. Also, by virtue of the differences in the thermal expansiveness and contractiveness between the oxide film in the surface of the high purity copper wire and the interior copper matrix metal, the oxide film on the wire surface having a thickness of smaller than 6 nm, preferably 4 nm or smaller, becomes easy to destroy at the time of bonding, so that the chip breakage becomes less

frequent, and the bonding strength is improved and the disparity in the bonding strength is mitigated.

As the recrystallized structure in the high purity copper wire is formed in non-oxidizing atmosphere, no unwelcome external oxygen enters the crystal grain boundaries in the copper matrix so that no oxidation of the surface of the high purity copper wire proceeds from inside the copper matrix before the first bonding. Also, no oxygen would be added from inside the copper matrix during the service of the semiconductor apparatus.

[Effects of the Invention]

[0032]

With the high purity copper wire for connecting semiconductor apparatuses according to the present invention, for the reason of the dual structure of the high purity copper wire wherein the crystal texture in the copper matrix contains a mixture of several largest crystal grains and small crystal grains (ref. Fig. 4) and for the reason of the controlling, by a grain wall of the small crystal grains, of the strain that occurs with respect to the crystal defects and the like in the surface layer of the copper during the rapid cooling, it is possible to secure the mechanical strength of the high purity copper wire. Also, according to the present invention, no surplus oxygen exists in the copper matrix and thus oxygen tends to be too lean, so that when high purity copper wire after the first bonding is subjected to repetition of on-off switching, which assimilates a situation of leaving it in a high temperature circumstance, the high purity copper wire would hardly detach from the bonding interface with an aluminum pad of a semiconductor apparatus to which it bonded. Furthermore, as the copper wire itself is of high purity, it is possible even for a high purity copper wire of a thickness on submicron order to be bonded on an aluminum pad, which has been difficult in the past, if a hard barrier metal is laid underneath the aluminum pad, and due to the low recrystallization temperature, a heat cycle fatigue does not occur.

[0033]

On the other hand, in the case of ultrasonic wave bonding on a copper base plate or nickel base plate, which constitutes the second bonding, the result would be naturally favorable because of the existence of the extra thin Cu oxide layer having a thickness of no greater than 1 - 6 nm. Furthermore, if an electrical heating is adopted as the thermal treatment means, it is possible to increase the number of the crystal defects in the copper's surface layer such as voids, whereby it becomes easier to manage the temperature and the time of treatment on the high purity copper wire with a result that controlling of the dual structure system becomes unmistakable. Furthermore, it becomes possible to bond the wire on a semiconductor chip made of silicon carbide or gallium nitride (GaN) (the pad being usually made of aluminum, copper, nickel or gold).

[0034]

It is most favorable if the high purity copper wire for connecting semiconductor apparatuses of the present invention is one having a wire diameter of 0.1 mm - 0.6 mm. Conditions for the thermal treatment are preferably such that the temperature is raised to 700 degrees C - 850 degrees C suddenly and at the same time the time that lapses from the start of the thermal treatment stage to the start of the cooling stage is as short as 0.05 - 1.3 second, and more preferably, it is 0.1 - 1.0 second. If the thermal treatment temperature is lower than the above the required thermal treatment time becomes longer and although this makes controlling easier, the required length of the heat treat furnace becomes greater. The length of the furnace is generally 0.5 - 2.0 meters. The higher the purity of the copper is, the shorter will the required thermal treatment time be. As the purity of the copper increases, the recrystallization temperature becomes lower, but since there is no proportionality relation between the velocity at which the wire temperature rises by heat and the velocity at which the wire texture transforms from the recrystallization structure to the grain growth texture, timely controlling becomes very important. The thermal treatment time may be controlled by elongating a vertical heat

treatment furnace or by reducing the speed at which the high purity copper wire passes through the heat treatment furnace.

[0035]

Also, the above-mentioned non-oxidizing atmosphere is preferably a reducing atmosphere not without hydrogen gas. From the viewpoint of removal of the oxide layer of the high purity copper wire and removal of the oxygen in the copper matrix, hydrogen atmosphere is the most preferable; however, in consideration of the economy and safety, a nitrogen atmosphere mixed with 3 - 5 % of hydrogen is preferred. Now, in a case where the high purity copper wire is coated with a noble metal of palladium (Pd), hydrogen atmosphere is recommended since palladium occludes hydrogen atom. If a coating is applied with a film of a noble metal of silver having a purity of 99.99 mass % or higher, or preferably 99.999 mass % or higher, the silver is caused to diffuse into the copper matrix by thermal treatment.

[0036]

In the present invention the reason that water cooling is adopted in the cooling stage is to infallibly achieve the cooling of the high speed, high temperature copper wire to the room temperature. Here, the "room temperature" means a temperature at which there occurs little transformation of the grain boundary texture of recrystallization to the grain growth texture in the copper matrix; however, as the recrystallization temperature of the high purity copper wire is so low, it is preferably as low as possible. As the thermal conductivity of the high purity copper wire is rather high, when it is put in water, it cools immediately. It is possible to use hydrogen ion-containing water such as electrolytic reduction ion water, ammonia water, alcohol water and the like. Incidentally, when an organic solvent such as benzotriazole is added, the amount should be as small as possible since it leaves residual carbon during bonding.

[Examples]

[0037]

We will describe examples of the present invention.

{Example 1}

An oxide film of a copper wire preform having a diameter of 2 mm and made of copper of a purity of 99.99992 mass % consisted of a 0.5-nm-thick copper dioxide outermost layer and a 3-nm-thick copper monoxide sub-layer. The preformed copper wire was continuously drawn to obtain a copper wire of 0.2 mm diameter (ref. Fig. 1). As is clearly seen in the sectional photo of Fig. 1, there was still minute texture caused by the wire drawing in the copper matrix even after a low temperature thermal treatment of 500 degrees C.

[0038]

This copper wire was run through a vertical heat treatment furnace (700 degrees C indication; 50 cm in length) having a forming gas atmosphere of 5 % hydrogen and 95 % nitrogen at a speed of 100 m/minute, and it was cooled in pure water of 20 degrees C. After the water cooling, it was wound on a spool; the oxide film of the high purity copper wire had thinned, and it consisted of outermost 0.1-nm-thick copper dioxide layer and 3-nm-thick copper monoxide layer. The elongation percentage of this high purity copper wire was 28 %, and the breaking strength was about 22.6 kPa (23 kgf/mm<sup>2</sup>). The sectional structure of the recrystallized structure of this copper wire is shown in Fig. 4. As is seen in the sectional photo of Fig. 4, the minute texture attributable to wire drawing had disappeared and been totally replaced by recrystallized structure in the copper matrix. Also, the sectional photo of Fig. 4 shows that the copper wire's surface part, which is about 1/10 as wide as the wire diameter is dominated by uniform minute crystal grains. The sectional photo of Fig. 4 discloses that there are three equally-sized large crystal grains about the middle of the copper matrix, that there are ten or nine somewhat lesser-sized crystal grains in the copper matrix and that minute crystal grains fill in the gaps amongst these crystal grains. The average diameter of the large crystal grains in the high purity copper wire of Fig. 4 is 6.7 % of the wire diameter.

[0039]

With the high purity copper wire of Fig. 4, an ultrasonic bonding

was conducting. We call this Example 1.

The conditions of the ultrasonic bonding were as follows.

The wire diameter of the high purity copper wire was 0.48 mm, loop length was 10 mm, and loop height was 3 mm. The inventors conducting an ultrasonic bonding of this high purity copper wire, using a totally automatic wire bonder Type BJ935, which is a wire bonder for thick wires, manufactured by H & K Corporation, on a base plate assimilating a chip (an aluminum base plate measuring 50 mm x 50 mm x 0.6 mm (thickness), to which 10-micrometer-thick copper layer had been coated by magnetron sputtering) while blowing nitrogen gas over the base plate. Other bonding conditions were such that the frequency was 120 kHz, the load and the ultrasonic pattern was adjusted arbitrarily, and the first and the second ultrasonic bonding operations were applied equally to a total of 100 samples ( $n = 40$ ). The ultra hard tools and bonding guides used were ones manufactured by H & K Corporation, which were commensurate with the wire size. The disparity in diameter of the deformed ball after the first bonding (aimed at wire diameter x 1.3) was rated as the initial bondability, and the result obtained is shown in Table 1 below.

[0040]

Next, the inventors conducted a reliability test on the thus bonded high purity copper wire of Example 1. This reliability test consisted of letting the wire sit for 96 hours at 250 degrees C, and then the wire was made to go through 10,000 temperature cycles, each cycle consisting of a 3-minute-long heating at 200 degrees C followed by a 3-minute-long cooling at -60 degrees C. Thereafter the shear strength of the first bond was measured, and the result obtained is shown in Table 1.

Now, the reliability (specific strength) in the shear test refers to a value obtained by dividing the shear strength measured after the reliability test by the (initial) shear strength measured immediately after the bonding. In other words, the greater the specific strength is, the higher the reliability is rated.

As is clear from this result, the dual structured high purity copper wire shown in Fig. 4 would have a deformed ball diameter similar to that in the case of the copper wire after wire drawing, and has a rigidity of its own, and has a stabilized shear strength. Also, observation of the peeled surface after the shear test showed no evidence of oxide peeling, which is caused by an aggregation of oxides in the bonding interface.

[0041]

{Example 2}

An oxide film of a copper wire preform having a diameter of 5 mm and made of a five-nine-pure copper comprising 20 mass ppm of silver, 2 mass ppm of iron and balance 99.9997 mass % of copper had a 0.5-nm-thick copper dioxide outermost layer and a 4-nm-thick copper monoxide sub-layer, like the wire preform of Example 1. This copper wire preform was continuously drawn to obtain a copper wire of 0.5 mm diameter. The sectional structure of this copper wire was roughly similar to the one shown in Fig. 4.

[0042]

This copper wire was run through a red-hot (about 800 degrees C) vertical heat treatment furnace (100 cm in length), containing a nitrogen gas atmosphere, at a speed of 50 m/minute, and it was cooled in pure water of 30 degrees C. After the water cooling, it was wound on a spool; like in the case of Example 1, the oxide film of the high purity copper wire consisting of the copper dioxide layer and the copper monoxide layer had thinned to 3 nm. The elongation percentage of this high purity copper wire was 30 %, and the breaking strength was about 21.6 kPa (22 kgf/mm<sup>2</sup>). The sectional structure of this copper wire was similar to the one shown in Fig. 4, consisting mostly of recrystallized structure, and beginning of grain growth was observable at locations. The average diameter of the large crystal grains in the high purity copper wire of Example 2 is 6.3 % of the wire diameter.

With this high purity copper wire an ultrasonic bonding was

conducted in the similar manner as in Example 1, and an estimation similar to the one done in Example 1 was conducted. The result is included in Table 1 below.

[0043]

{Example 3}

An oxide film of a copper wire preform having a diameter of 5 mm and made of a copper comprising 5 mass ppm of silver, 5 mass ppm of iron, 2 mass ppm of nickel, 5 mass ppm of silicon, 10 mass ppm of phosphorus and balance 99.9997 mass % of copper had a 0.5-nm-thick copper dioxide outermost layer and 5-nm-thick copper monoxide sub-layer. This copper wire preform was continuously drawn to obtain a copper wire of 0.5 mm diameter. The sectional structure of this copper wire was roughly similar to the one shown in Fig. 4.

[0044]

This copper wire was run through a red-hot (about 800 degrees C) vertical heat treatment furnace (100 cm in length), containing a nitrogen gas atmosphere, at a speed of 50 m/minute, and it was cooled in pure water of 30 degrees C. After the water cooling, it was wound on a spool; the oxide film of the high purity copper wire consisting of the copper dioxide layer and the copper monoxide layer had thinned to 4 nm. The average diameter of the large crystal grains in the high purity copper wire of Example 3 is 7.1 % of the wire diameter.

With this high purity copper wire an ultrasonic bonding was conducted in the similar manner as in Example 1, and an estimation similar to the one done in Example 1 was conducted. The result is included in Table 1 below.

[0045]

As is clear from these results, the high purity copper wire of the kind similar to the one shown in Fig. 4 would have a deformed ball diameter similar to that in the case of the copper wire after wire drawing, and has a rigidity of its own, and has a stabilized shear strength. Also, observation of the bonding interface after dissolving away the high purity copper wire with acid, revealed that the peeled surface after the shear test showed

no evidence of oxide peeling, which is caused by an aggregation of oxides in the bonding interface.

[Comparative Example 1]

[0046]

We will now explain about the comparative examples to the present invention.

{Comparative Example 1}

The same procedure was followed as Example 1 except that the copper wire similar to the one used in Example 1 was rapidly cooled from a dark-red hot state (500 degrees Celsius a little higher). After the water cooling, the high purity copper wire was wound on a spool; the oxide film of the high purity copper wire consisting of a 0.5-nm-thick outermost copper dioxide layer and a 4-nm-thick copper monoxide sub-layer did not undergo a change during the thermal treatment. The elongation percentage of this high purity copper wire was 6 %, and the breaking strength was about 31.4 kPa (32 kgf/mm<sup>2</sup>). The sectional texture of this copper wire did not change before and after the thermal treatment and did not have a recrystallized structure of Fig. 1. The average grain diameter of the large crystal grains in this high purity copper wire is 0.2 % of the wire diameter.

[0047]

With this high purity copper wire an ultrasonic bonding was conducted in the similar manner as in Example 1, and an estimation similar to the one done in Example 1 was conducted. The result is included in Table 1 below. It is clear from these results that the high purity copper wire of Comparative Example 1 produces an appropriately-sized deformed ball, but the reliability (specific strength) as the result of the shear test was too weak and high temperature bonding strength is not assuring. Also, an observation of the bonding interface of this high purity copper wire having a low bonding strength revealed that the peeled face showed an evidence of oxide peeling, which is caused by an aggregation of oxides.

[0048]

{Comparative Example 2}

The same procedure was followed as Example 2 except that a copper wire preform having a diameter of 5 mm and made of a copper comprising 25 mass ppm of silver, 10 mass ppm of iron, 6 mass ppm of nickel, 8 mass ppm of silicon, 15 mass ppm of phosphorus and balance 99.9997 mass % of copper was drawn and rapidly cooled from a cherry-red hot state (850 degrees C or littler higher). After the water cooling, the drawn wire was wound on a spool; the oxide film of the high purity copper wire consisting of the copper dioxide layer and the copper monoxide layer had a thickness of 2 nm from the surface. The elongation percentage of this high purity copper wire was 15 %, and the breaking strength was about 17.7 kPa (18 kgf/mm<sup>2</sup>). The sectional texture of this copper wire is shown in Fig. 3. As is clear from the sectional photo of Fig. 3, all the crystal grains in the copper matrix had grown. The average grain diameter of the crystal grains in this high purity copper wire is 25 % of the wire diameter.

The result of estimation of this high purity copper wire is included among others in the table below. As is clear from these results, the high purity copper wire of Comparative Example 2 had a substantial disparity in the size of the deformed ball and thus unstable. The shear test showed low reliability of the high purity copper wire and its high temperature bonding strength was not stable either.

[0049]

[Table 1]

|                       | crystal texture      |                     | test result                     |                                 |
|-----------------------|----------------------|---------------------|---------------------------------|---------------------------------|
|                       | average diameter (%) | corresponding Fig.  | disparity in deformed ball size | reliability (specific strength) |
| Example 1             | 6.7                  | Fig. 4              | 0.046                           | 0.86                            |
| Example 2             | 6.3                  | Fig. 5              | 0.044                           | 0.81                            |
| Example 3             | 7.1                  | (similar to Fig. 4) | 0.040                           | 0.75                            |
| Example 4             | 6.5                  | (similar to Fig. 4) | 0.0058                          | 0.82                            |
| Example 5             | 6.9                  | (similar to Fig. 4) | 0.0024                          | 0.85                            |
| Comparative Example 1 | 25.0                 | (similar to Fig. 1) | 0.035                           | 0.68                            |

|                          |  |        |       |      |
|--------------------------|--|--------|-------|------|
| Comparative<br>Example 2 |  | Fig. 3 | 0.073 | 0.49 |
|--------------------------|--|--------|-------|------|

[0050]

As is seen clear from the above table, the disparity in the deformed ball size (R) was good except in the case of Comparative Example 2. With regard to the reliability (specific strength), Comparative Examples 1 and 2 were poor while others were good, and it is seen that the higher the copper purity is, the better the effect of the dual structure of the present invention worked.

Incidentally, in the examples and the comparative examples, the inventors used a 0.48-mm-diameter wire, and if this is drawn thinner the distinction of the dual structure becomes difficult to perceive, but it was confirmed that the tendency of the result of the above tests did not alter when a wire of a diameter of 0.06 mm (60 micrometers) was used for stitch bonding and when a wire of a diameter of 0.025 mm (25 micrometers) was used for ball bonding (FAB bonding).

[Brief Description of the Drawings]

[0051]

[Fig. 1]

Fig. 1 is a photo of the sectional structure taken of the high purity copper wire after it was continuously drawn and thermally treated for several hundreds of milliseconds at 500 degrees C.

[Fig. 2]

Fig. 2 is a photo of the sectional structure in a case in which the thermal treatment was overdone.

[Fig. 3]

Fig. 3 is a photo of the sectional structure in a case in which the thermal treatment was extremely overdone.

[Fig. 4]

Fig. 4 is a photo of the sectional structure in the case of Example 1 after the appropriate amount of thermal treatment.

[Fig. 5]

Fig. 5 is a photo of the sectional structure in the case of Example 2 having received the most appropriate amount of thermal

treatment.

[Document Name] Scope of the Claims

[Claim 1]

A continuously drawn high purity copper wire which is clad with an oxide film, has a purity of 99.999 mass % - 99.99994 mass %, has a wire diameter of not smaller than 0.01 mm but smaller than 1 mm, and is useful for connecting semiconductor apparatuses, wherein said wire has a sectional structure in which largest 10 grains have a total crystal grain area accounting for 5 - 25 % of the total area of the sectional structure, and 80 % or more of said crystal grain area is interior to a surface layer, which is defined as having a thickness of 1/20 or smaller of the wire diameter.

[Claim 2]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein said oxide film has a thickness of 1 - 6 nm.

[Claim 3]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein a total content of silver, iron, nickel, tin, silicon, phosphorus and sulfur is less than 10 mass ppm.

[Claim 4]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein the total amount of iron, nickel, tin, silicon, phosphorus and sulfur is less than 1 mass ppm.

[Claim 5]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein said largest 10 grains have the total crystal grain area accounting for 10 - 20 % of the total area of the sectional structure.

[Claim 6]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein 90 % or more of said total crystal grain area of the largest 10 grains is interior

to said surface layer, which is defined to have a thickness of 1/20 or smaller of the wire diameter.

[Claim 7]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein said high purity copper wire has a diameter of 0.1 mm - 1.0 mm.

[Claim 8]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein said high purity copper wire has a diameter of 0.06 mm - 0.1 mm.

[Claim 9]

A high purity copper wire for connecting semiconductor apparatuses as claimed in Claim 1, wherein said high purity copper wire has a diameter of 0.01 mm - 0.08 mm.