[0005]

However, Bi is naturally a brittle element and the Sn-Bi solder alloy is also brittle. Even when Bi content of the Si-Bi solder alloy is decreased, it becomes brittle because Bi segregates in Sn. A solder joint soldered by using the Sn-Bi solder alloy may generate any cracks because of its brittleness when any considerable stress is added thereto so that its mechanical strength may deteriorate.

[0006]

Further, in order to cope with the miniaturization of the electronic parts, an area of the substrate which is used therefor must be narrower and a miniaturization of the electrode and/or a narrow pitch between the electrodes must be realized. Additionally, because an amount of the solder alloy used when performing the soldering is decreased, the mechanical strength of the solder joint deteriorates.

[0007]

So, Patent Document 1 discloses Sn-Bi-Cu-Ni lead-free solder alloy in which Cu and Ni are added to the Sn-Bi solder alloy in order to realize any solder joined portion that has a high joining strength. According to this document, this joined portion using this solder alloy improves its mechanical strength because any intermetallic compounds having hexagonal closest packing structure are formed in the solder joined portion and/or on a solder joining interface.

[DOCUMENT FOR PRIOR ART]

[PATENT DOCUMENT]

[0008]

Patent Document 1: Japanese Patent Application Publication No.2013-00744.

[SUMMARY]

[0008a]

In one aspect of the present disclosure, there is provided a lead-free solder alloy having an alloy composition which contains 31 to 59 mass % of Bi, 0.3 to 1.0 mass % of Cu, 0.01 to 0.06 mass %

of Ni and balance of Sn wherein the solder alloy has a melting point of 185 degrees C or less, a tensile strength of 70 MPa or more and elongation of 65 % or more.

In another aspect of the present disclosure, there is provided a solder joint formed on a Cu electrode having a Ni plating layer by using the lead-free solder alloy as described herein.

In a further aspect of the present disclosure, there is provided a substrate having a thickness of 5 mm or less and plural Cu electrodes each having Ni plating layer wherein each of the Cu electrodes includes a solder joint formed by using the lead-free solder alloy as described herein.

[PROBLEMS TO BE SOLVED]

[0009]

The electrode of the electronic parts is normally made of Cu and this Cu electrode is generally coated by electroless Ni plating, electroless Ni/Au plating or electroless Ni/Pd/Au plating. Thus, the electroless plating with noble metal such as Au and a combination of Au and Pd is performed on the Cu electrode. The Au plating suppresses oxidization of undercoated Ni plating and improves wettability to the molten solder. The electroless Ni plating forms Ni plating containing a considerable amount of P derived from a reducing agent (for example, sodium hypophosphite) which is used in the electroless plating. Such Ni plating contains at least some mass percent, for example, 2 through 15 mass% of P.

[0010]

However, although Patent Document 1 discloses that Cu and Ni are added to the Sn-Bi solder alloy to form the intermetallic compounds having hexagonal closest packing structure on the joining interface between the solder alloy and a Cu wiring part derived from the electrode, it does not disclose any alloy components specifically nor disclose any results for establishing an effect of high joining strength. Although the same document discloses a range of contents of Cu and Ni to be added to a component in which Sn is of 57 atm % and Bi is of 43 atm %, it is unknown to improve the joining strength within all this range.

[0011]

Further, although the same document discloses Cu wiring parts of the printing circuit board and wiring parts each containing no Cu as an object to be joined with the solder alloy, it is unknown what kind of configuration the object to be joined has except that the wiring parts are made of Cu. Since the same document does not disclose any alloy components of the solder alloy specifically as stated above, it does not disclose nor suggest any condition of the joining interface except that the intermetallic compounds are formed on the joining interface between the electrode and the solder alloy. Therefore, when all the solder alloys which meet contents of Bi, Cu and Ni disclosed in the same document are used for soldering the Cu electrode on which, for example, the electroless Ni plating has been performed, it is hard to think that the following problems can be solved thereby.

[0012]

[0018]

The present disclosure further provides the following:

(1) A lead-free solder alloy having an alloy composition which contains 31 to 59 mass % of Bi, 0.3 to 1.0 mass % of Cu, 0.01 to 0.06 mass % of Ni and balance of Sn wherein the solder alloy has a melting point of 185 degrees C or less, a tensile strength of 70 MPa or more and elongation of 65 % or more.

[0019]

(2) The lead-free solder alloy described in the above-mentioned item (1), further containing at least one element selected from a group consisting of P and Ge in a total of 0.003 to 0.05 mass %.

[0020]

(3) A solder joint formed on a Cu electrode having a Ni plating layer by using the lead-free solder alloy described in the above-mentioned item (1) or (2).

[0021]

(4) The solder joint described in the above-mentioned item (3) wherein the Ni plating layer includes an electroless plating layer containing P.

[0022]

(5) A substrate having a thickness of 5 mm or less and plural Cu electrodes each having Ni plating layer wherein each of the Cu electrodes includes a solder joint formed by the lead-free solder alloy described in the above-mentioned item (1) or (2) .

[0023]

(6) The substrate described in the above-mentioned item (5) wherein the Ni plating layer contains P.

The lead-free solder alloy according to the invention is applicable to a use of the soldering on the Cu electrode formed on a thin substrate having a thickness of 5 mm or less, on which electroless Ni plating is performed. The effect of the invention is best exhibited by using it for the soldering on an electrode having any electroless Ni plating layer. Therefore, curvature of the thin substrate when performing the soldering is limited to its minimum because of a low melting point of the solder alloy according to the invention. Thus, joining

or electroless Ni/Pd/Au plating is performed on the electrode, the shear strength of the solder joint is considerably improved by suppressing the diffusion of Ni to the solder alloy and suppressing growth of the brittle P-rich layer.

[0029]

Further, the lead-free solder alloy according to the invention has a low solubility of Cu because it contains predetermined amounts of Cu and Ni. For the Cu electrode having no electroless Ni plating layer, it is possible to suppress the diffusion of Cu to the solder alloy and to suppress excess formation of brittle Cu Sn compound formed in the joining interface and the solder alloy so that the shear strength of the solder joint is enhanced. As a result thereof, in this invention, it is possible to suppress any strain in the thin substrate when performing the soldering regardless of whether or not plating is performed on the Cu electrode, and to maintain the good joining reliability.

[0030]

As described before, the plating layer of noble metal such as Au and Au/Pd or its alloy is normally formed on the electroless Ni plating layer. The Au plating layer is formed on the Ni plating layer. The Au plating player, however, has a very thin thickness of about 0.05 μm and is diffused into the solder alloy to disappear when performing the soldering. Therefore, when assessing various kinds of characteristics in this invention, it is not necessary to particularly take into consideration the Au plating layer and other noble metal plating layer.

[0031]

In this invention, the reason why the components of the solder alloy are limited is as follows:

The content of Bi is of 31 % through 59 %. Bi reduces the melting point of the solder alloy. When the content of Bi is less than 31 %, the melting point thereof is high, so that the substrate is strained when performing the soldering. When the content of Bi is more than 59 %, tensile strength and ductility thereof deteriorates because of precipitation of Bi. The content of Bi is preferably of 32 % through 58 %, more preferably, 35 % through 58 %.

[0032]

The content of Cu is of 0.3 % through 1.0 %. Cu suppresses the diffusion of Ni in the electroless Ni plating layer to the solder alloy and suppresses the growth of P-rich layer generated on an interface between the Ni plating layer and the solder joined portion. Further, since it suppresses the diffusion of Cu, it suppresses excess formation of the brittle Cu Sn compound formed in the joining interface between the Cu electrode on which the electroless Ni plating is not performed and the solder joined portion and in the solder alloy so that the shear strength of the solder joint is enhanced. When the content of Cu is less than 0.3 %, it is impossible to suppress the P-rich layer or excess formation of the Cu Sn compound so that the shear strength thereof is reduced. When the content of Cu is more than 1.0 %, an intermetallic compound with Sn is excessively formed in the solder alloy so that ductility of the solder alloy is reduced. Further, the melting point of the solder alloy becomes very high so that wettability of the solder alloy is reduced. Additionally, any strain occurs in the substrate so that workability thereof deteriorates. The content of Cu is preferably of 0.3 % through 0.8 %, more preferably, 0. 3 % through 0.7 %.

[0033]

The content of Ni is of 0.01 % through 0.06 %. Addition of Ni helps any effect of Cu for suppressing the diffusion of Ni, and expresses an effect of suppressing the growth of P-rich layer to further improve the shear strength. When the content of Ni is less than 0.01 %, it is impossible to exhibit the effect of improving the shear strength. When content of Ni is more than 0.06 %, Sn and Ni compound is excessively formed in the solder alloy so that the ductility thereof is reduced. The content of Ni is preferably of 0.02 % through 0.05 %.

[0034]

The lead-free solder alloy according to the invention may contain at least one of elements selected from a group consisting of P and Ge, as optional elements, of a total of 0.003 % through 0.05 %. Addition of these elements suppresses the growth of P-rich layer to enhance the shear strength of the solder joint, similarly in a case where they are not added, and exhibits an effect to prevent the solder alloy from being discolored to yellow or the like (hereinafter, as referred to "yellow" appropriately) because of its oxidization. The lead-free solder alloy according to the invention can be used in a form of solder ball. The solder balls

[Embodiments]

[0041]

The solder alloys shown in Table 1 were manufactured. Using these solder alloys, the melting points of the solder alloys, tensile strength thereof, elongation (ductility) thereof were measured. Using the solder joint formed by using these solder alloys, thickness of P-rich layer, shear strength and exposure percentage of plate were obtained as follows. The result thereof is shown in the Table 1.

[0042] (Melting Points of Solder Alloys)

The melting points were measured at degrees C under a condition of temperature rising speed of 5 degrees C/min using Differential Scanning Calorimetry (DSC6200) by SEIKO Instrument Inc.

[0043] (Tensile Strength and Elongation (Ductility))

The solder alloys shown in Table 1 were formed so as to be a predetermined form. Their tensile strength (MPa) and elongation (%) were measured under a condition of stroke speed of 6.0 mm/min and strain speed of 0.33 %/sec using a tensile strength test machine (AUTO GRAPH AG-20kN by Shimazu Corporation). When it has the tensile strength of 70 MPa or more and the elongation of 65% or more, it can be used with having no problem in practical use.

[0044] (Thickness of P-rich Layer)

The soldering was performed so that the solder alloys shown in Table 1 were joined to Cu electrodes on PCB having a thickness of the substrate of 1.2 mm, on which the electroless Ni/Au plating had been performed (hereinafter, this Cu electrodes are referred to as "electroless Ni/Au electrodes"), each electrode having a diameter of 0.24 mm. The soldering was performed so that by using aqueous flux (WF-6400 made by SENJU METAL INDUSTRY CO., LTD), solder balls each having a diameter of 0.3 mm, which were manufactured by the solder alloys, were mounted on the substrate after the aqueous flux was applied thereto and they were soldered by reflow method under a reflow profile in which the peak temperature is set to be 210 degrees C. Thus, samples on which the solder joints were formed were obtained.

[0045]

The thickness of P-rich layer of each sample was determined on the basis of SEM photograph by inspecting a section of a neighborhood of an interface between the solder joined portion and the Ni plating layer. Specifically, photographs were analyzed using an electron microscope (JSM-7000F manufactured by Japan Electron Optics Laboratory), the P-rich layer and non P-rich layer were separated from each other by sorting them according to colors, and the thickness of the P-rich layer was measured at (μm). On 5 samples manufactured under the same condition, thicknesses of their P-rich layer were similarly measured and an average value thereof was determined to be the thickness of the P-rich layer.

[0046] (Shear Strength)

Regarding the electrodes on the above-mentioned PCB, two species of electrodes such as Cu electrodes on which any plating was not performed (hereinafter, merely referred to as "Cu electrodes") and the electroless Ni/Au electrodes were used and the soldering was performed so that they were joined to the solder alloys shown in Table 1 to form their solder joints. Shear strength of each of these samples was measured at (N) by a shear strength measurement apparatus (SERIES 4000HS manufactured by DAGE Corporation) under a condition of 1000 mm/sec. When the shear strength is 3.00N or more on the Cu electrodes and the shear strength is 2.60 N or more on the electroless Ni/Au electrodes, these solder joints can be used with having no problem in practical use.

[0047] (Plate Exposure Percentage)

The SEM photographs were photographed on a surface of each of the electroless Ni/Au electrodes of the shear strength tested samples after the solder joined portion was sheared and removed. A region from which Ni was exposed was identified by performing EDS analysis and by using image analysis software (Scandium) made by Seika Corporation, an area of the region was obtained. Finally, the plate exposure percentage (%) was calculated by dividing the area of the region from which Ni plating layer was exposed by whole area of electrode.

[0048]

[Table 1]

[0049]

As shown in Table 1, in the embodiments 1 through 33, all of the embodiments indicated such a result that the melting points thereof were 185 degrees C or less; the tensile strengths thereof were 70 MPa or more; the elongations thereof were 65 % or more; the thicknesses of P-rich layers thereof were 0.014 μm; the shear strengths of the solder joints formed by using the Cu electrodes were 3.00N or more; the shear strengths of the solder joints formed by using the electroless Ni/Au electrodes were 2.60 N or more; and the plate exposure percentages thereof were all 0 %.

[0050]

On the other hand, the comparison example 1 which was Sn-58Bi solder alloy and did not contain Cu and Ni indicated that the thickness of P-rich layer was thick; the shear strengths in the solder joints of the Cu electrodes and the electroless Ni/Au electrodes severely deteriorated; and the plate exposure percentage was also high.

[0051]

Both of the comparison example 2 which did not contain Ni and the comparison example 3 which did not contain Cu indicated that the thicknesses of P-rich layer were thick; and the shear strengths in the solder joints of the Cu electrodes and the electroless Ni/Au electrodes severely deteriorated. Particularly, the comparison example 3 which did not contain Cu indicated the high plate exposure percentage.

[0052]

Since the comparison example 4 which contained less amount of Bi indicated the high melting point and less elongation, it was certified that any strain occurred in the substrate. The comparison example 5 which contained much amount of Bi indicated that the alloy was inferior in the tensile strength and the elongation thereof. Further, it indicated that the shear strength in the solder joint of the electroless Ni/Au electrode was inferior.

[0053]

The comparison example 6 which contained less amount of Cu indicated that the shear strength in the solder joint of the electroless Ni/Au electrode was inferior, the thickness of P-rich layer was thick, and the plate exposure percentage was high. Both of the comparison example 7 which did not

contain Ni and contained much amount of Cu and the comparison example 8 which contained much amount of Cu indicated that these alloys had high melting points and were inferior in the elongation and the shear strengths in the electroless Ni/Au electrode were inferior.

[0054]

The comparison example 9 which contained less amount of Ni indicated that the shear strength in the solder joint of the Cu electrode was inferior. The comparison example 10 which contained much amount of Ni indicated that the alloy was severely inferior in the elongation thereof.

[0055]

FIG. 1 is a SEM photograph showing a sheared surface of electrode after the electroless Ni/Au electrode is soldered using Sn-58Bi solder alloy and the solder joined portion is sheared and removed. In all of the comparison examples 1, 3, 5 and 6, Ni plating layer was exposed as shown in FIG. 1. It is conceivable that this is because P-rich layer grows and peeling occurs at an interface between the P-rich layer and the electroless Ni/Au plating layer.

[0056]

FIGS. 2(a) and 2(b) are sectional SEM photographs each showing a neighborhood of an interface between the solder joined portion and the electrode within a solder joint when the solder joint is formed by soldering the electroless Ni/Au electrode. FIGS. 2(c) and 2(d) are sectional SEM photographs each showing a neighborhood of an interface between the solder joined portion and the electrode within a solder joint when the solder joint is formed by soldering the Cu electrode on which electroless Ni/Pd/Au plating has been performed. It was clear from FIGS. 2(a) and 2(c) that since Sn-58Bi solder alloy (of the comparison example 1: the shear strength in the solder joint of the electroless Ni/Au electrode was of 2.01 N) did not contain Cu, P-rich layer grew. On the other hand, it was clear from FIGS. 2(b) and 2(d) that since Sn-40Bi-0.5Cu-0.03Ni solder ally according to this invention (of Embodiment 7: the shear strength in the solder joint of the electroless Ni/Au electrode was of 2.85 N) contained predetermined amounts of Cu and Ni, this suppresses the growth of P-rich layer, so that any P-rich layer could not be confirmed from these photographs. Thus, from FIGS. 2, it is understood that the suppression of the growth in P-rich layer enables the shear strength to be considerably improved.

[0057]

Based on the results of Table 1, the relationships between contents of Cu and Ni in the solder alloy and shear strengths in the solder joints of the Cu electrodes and the electroless Ni/Au electrodes or elongation of the solder alloys are shown in FIGS. 3 through 8. In FIGS. 3 through 5, the results of the embodiments 6 through 9 and the comparison examples 3, 6 and 7 in which the solder alloys contain 40 % of Bi and 0.03 % of Ni have been used. In FIGS. 6 through 8, the results of the embodiments 7, 10 and 11 and the comparison examples 2, 8 and 9 in which the solder alloys contain 40 % of Bi and 0.5 % of Cu have been used. FIG. 3 is a graph showing a relationship between Cu content and shear strength (in the solder joint of the Cu electrode) in Sn-40Bi-(0-1.1)Cu-0.03Ni solder alloy. FIG.4 is a graph showing a relationship between Cu content and shear strength (in the solder joint of the electroless Ni/Au electrode) in Sn-40Bi-(0-1.1)Cu-0.03Ni solder alloy. FIG. 5 is a graph showing a relationship between Cu content and elongation of the alloy in Sn-40Bi-(0-1.1)Cu-0.03Ni solder alloy. From FIGS. 3 through 5, it becomes clear that the range of Cu indicating that the shear strength in the solder joint of the Cu electrode is 3.0 N or more, the shear strength in the solder joint of the electroless Ni/Au electrode is 2.6 N or more and the elongation is 65 % or more is of 0.3 through 1.0 %.

[0058]

FIG. 6 is a graph showing a relationship between Cu content and shear strength (in the solder joint of the Cu electrode) in Sn-40Bi-0.5Cu-(0-0.07)Ni solder alloy. FIG. 7 is a graph showing a relationship between Cu content and shear strength (in the solder joint of the electroless Ni/Au electrode) in Sn-40Bi-0.5Cu-(0-0.07)Ni solder alloy. FIG. 8 is a graph showing a relationship between Cu content and elongation of the alloy in Sn-40Bi-0.5Cu-(0-0.07)Ni solder alloy. From FIGS. 6 through 8, it becomes clear that the range of Ni indicating that the shear strength in the solder joint of the Cu electrode is 3.0 N or more, the shear strength in the solder joint of the electroless Ni/Au electrode is 2.6 N or more and the elongation is 65 % or more is of 0.01 through 0.06 %.