

SPECIFICATION

[TITLE OF THE INVENTION]

Electrolytic Hard Gold Plating Solution and
5 Plating Method Using the Same

[TECHNICAL FIELD]

[0001]

The present invention relates to an electrolytic hard
10 gold plating solution low in throwing power and suitable for
partial plating, as well as to a plating method using the
plating solution. The plating solution and the plating
method using the plating solution are suitable, for example,
for the production of a gold-plated connector wherein a Ni
15 barrier layer is formed, in a connector material, between the
contact portion of connector material (hereinafter referred
to simply as contact portion, in some cases) and the
substrate-bonding portion of connector material (hereinafter
referred to simply as substrate-bonding portion, in some
20 cases).

[BACKGROUND ART]

[0002]

In recent years, electric appliances such as mobile
25 phone, notebook computer and the like have become lighter and
smaller and have come to possess higher performance. In
these electric appliances, connectors as electrical
connecting membrane are used. For the surface treatment of
the material for connector, gold plating, soldering plating,
30 etc. are used.

[0003]

The plating of connector material is conducted as follows. First, nickel plating is applied on a copper material which is to become the electrical contact portion of connector, whereby a nickel film is formed on the copper material. Then, hard gold plating is applied to the nickel film-formed contact portion. Meanwhile, to the substrate-bonding portion of the copper material is applied lead-tin solder plating (hereinafter, the plating by this method is referred to as di-chromatic plating, in some cases).

[0004]

Gold is highly superior in physical property (low hardness), chemical property (very stable) and electrical property (low resistance). Hence, gold plating is widely used in production of not only connector but also other electronic parts (e.g. printed circuit board).

[0005]

Meanwhile, the main stream of solder plating has become lead-free solder plating because the use of lead was regulated by the RoHS directive. The plating solution used in lead-free solder plating, however, cause various problems such as low stability of plating solution, low stability of plating film appearance, poor solder wetting, necessity of complicated bath control, and the like.

[0006]

Hence, in connectors of high precision and high durability, there is on rise whole-surface-gold-plated connector in which hard gold plating is applied not only to the contact portion but also to the substrate-bonding portion. However, the whole-surface-gold-plated connector material, as

compared with conventional di-chromatic-plated connector material, causes a problem in solder bonding.

[0007]

In the conventional di-chromatic-plated connector material, a nickel base of several mm is exposed between the
5 hard gold-plated contact portion and the solder-plated, substrate-bonding portion. The nickel oxide film at the surface of the nickel base is low in solder wetting. Therefore, the solder used for bonding remains at the
10 substrate-bonding portion of connector material and a sufficient solder bonding strength can be obtained.

[0008]

Meanwhile, in the whole-surface-gold-plated connector, gold plating is first applied, in its production, on the
15 whole surface of connector material. Consequently, the nickel base is not exposed and hard gold plating is present at the contact portion the substrate-bonding portion. The gold plating film is high in solder wetting. Therefore, the solder used for bonding does not remain at the substrate-
20 bonding portion of connector material and spreads as far as the contact portion. This causes a problem of reduction in solder bonding strength at the substrate-bonding portion. This problem has become more serious in recent years because the smaller size of connector has made narrower the pitch
25 between the contact portion and the substrate-bonding portion.

[0009]

Fig. 2 shows the bonding between connector material and substrate, in conventional whole-surface-gold-plated connector. 21 is a connector base material made of a copper
30 material. On the connector base material 21 is formed a Ni

base 23 by nickel plating. Then, on the Ni base is formed a gold plating film 25 by gold plating. In Fig. 2, the arrow a side becomes a contact portion of connector material and the arrow b side becomes a substrate-bonding portion. The connector material 20 gold-plated on the whole surface is bonded to a substrate 27 by bonding solder 29. In this case, since the nickel base 23 is not exposed, the bonding solder 29 does not remain at the substrate-bonding portion and spreads as far as the contact portion.

10 [0010]

In the whole-surface-gold-plated connector, an exposing the nickel base between the contact portion and the substrate-bonding portion is being made in order to allow the bonding solder to remain at the substrate-bonding portion and prevent its spreading to the contact portion (hereinafter, the exposed nickel base is referred to as Ni barrier layer, in some cases).

[0011]

For formation of the Ni barrier layer, a laser method and a gold plating film-stripping method are known.

[0012]

In the laser method, a laser is applied to a hard gold plating film to form a gold-nickel alloy layer covered with nickel oxide of low solder wetting.

25 [0013]

In the gold plating film-stripping method, first, partial plating is applied to the contact portion and the substrate-bonding portion (that is, a plating solution is sprayed to desired portions and plating is made only on the sprayed portions). In this case, the partial plating need be

made so that no gold plating is made on the portion of connector material which becomes a Ni barrier layer (the portion is hereinafter referred to as Ni barrier portion).

[0014]

5 After the partial plating, the gold plating film formed on the whole surface of connector material is subjected to gold stripping using a gold-stripping agent. By this gold stripping, all the gold plating film on the Ni barrier portion (the gold plating film formed by plating leakage) is
10 stripped, whereby a Ni barrier layer is formed.

[0015]

 There is a difference in the thickness of gold film between the gold-plated portions (contact portion and substrate-bonding portion) formed by partial bonding and the
15 Ni barrier portion. Therefore, even if the thin gold plating film of the Ni barrier portion has been stripped completely, gold plating film remains at the gold-plated portions (contact portion and substrate-bonding portion) of thick gold
20 plating film, whereby desired film thicknesses can be obtained at these portions. The gold plating film-stripping method has become a main stream because the laser method is high in treating cost.

[0016]

 In connection with the recent shift to smaller
25 connector, the Ni barrier portion is becoming finer as well. As a result, when partial plating is applied using a current plating solution, the plating solution spreads even to the Ni barrier portion, making difficult the selective plating for contact portion and substrate-bonding portion.

30 [0017]

For example, when partial plating is applied using a hard gold plating solution containing first and second brightener agents, disclosed in Patent Literature 1, there is obtained highly uniform deposition on the to-be-plated surface. As a result, when partial plating is applied to the to-be-plated portions (contact portion and substrate-bonding portion) using the above plating solution, the solution spreads widely and a thick gold plating film is formed even on the Ni barrier portion (hereinafter, this phenomenon is referred to as plating leakage, in some cases). Therefore, a long time is needed to completely strip the film formed on the Ni barrier portion, by the gold plating film-stripping method. As a result, the gold films on the contact portion and the substrate-bonding portion are stripped excessively, making it impossible to obtain films of desired thicknesses.

[Prior Art Literature]

[0018]

Patent Literature 1: Patent No. JP3933930B

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[SUMMARY OF THE INVENTION]

[Tasks to Be Achieved by the Invention]

[0019]

The present invention was made in view of the current situation that selective partial plating is difficult in the partial plating using conventional plating solution. Hence, the present invention has a task of providing a gold plating solution used in partial plating (e.g. partial plating for forming a Ni barrier layer in a connector material for recent smaller connector), which can highly suppress the formation

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of plating film in an unintended portion. The present invention has another task of providing a method for applying gold plating to a connector material using the above gold plating solution.

5 **[Means for Achieving the Tasks]**

[0020]

 In order to achieve the above tasks, the present inventors made a study particularly on the Ni barrier layer. As a result, it was found that, since the feeding amount of
10 plating solution is small and plating is made at a low current density, at the Ni barrier portion, suppression of gold deposition at low current density portion can suppress the formation of plating film at the Ni barrier portion. It was further found that the suppression of gold deposition at
15 low current density portion can be attained by the inclusion of a nitrogen group-containing compound (as an organic oxidant) in gold plating solution. The findings have led to the completion of the present disclosure.

[0021]

20 The nitro group-containing compound uniquely increases the oxidation-reduction potential of gold at the low current density portion (Ni barrier portion) and suppresses the deposition of gold. Further, in the medium to high current density portions (to-be-plated portions), normal gold films
25 are formed without receiving the influence of gold deposition suppression at low current density.

[0022]

 In order to achieve the above tasks, the present disclosure provides the following.

30 [0023]

[1] According to a first aspect, there is provided an electrolytic hard gold plating solution containing

a gold cyanide and/ or a salt thereof,

a cobalt salt,

5 a conductive organic acid salt,

a nitro group-containing compound, and

at least one kind of compound selected from the group consisting of a carboxylic acid, an oxycarboxylic acid, and salts thereof.

10 [0024]

[2] The electrolytic hard gold plating solution according to [1], wherein the concentration of the nitro group-containing compound is 0.1 to 20 g/L.

[0025]

15 [3] According to a second aspect, there is provided a method for plating a connector material, which comprises applying partial plating to the contact portion and substrate-bonding portion of a connector material using an electrolytic hard gold plating solution set forth in [1].

20 **[Effect of the Invention]**

[0026]

When a connector is produced using the electrolytic hard gold plating solution of the present invention, as compared with when using conventional gold plating solution, 25 the formation of plating film at the Ni barrier portion is suppressed strikingly. Consequently, a Ni barrier layer can be formed even in recent smaller connector. The Ni barrier layer can allow the solder for bonding to remain at the substrate-bonding portion. As a result, the connector 30 material having a Ni barrier layer can have a sufficient solder bonding strength.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0027]

Fig. 1 shows bonding of a connector material having a Ni barrier layer formed using the electrolytic hard gold plating solution of the present invention, with a substrate.

Fig. 2 shows bonding of a conventional connector material gold-plated on the whole surface, with a substrate.

[MODE FOR CARRYING OUT THE INVENTION]

10 [0028]

The electrolytic hard gold plating solution of the present invention is described in detail below.

[0029]

The electrolytic hard gold plating solution of the present invention contains a gold cyanide compound as a gold salt. As the gold cyanide compound, there can be mentioned gold potassium cyanide, gold sodium cyanide, gold ammonium cyanide, etc. In the electrolytic hard gold plating solution of the present invention, the concentration of the gold is 0.1 to 20 g/L, preferably 2 to 15 g/L in terms of gold concentration. When the concentration is less than 0.1 g/L, the cathode current efficiency is low, making it difficult to obtain an intended gold film thickness. When the concentration is more than 15 g/L, the cathode current efficiency does not increase in proportion to the gold concentration and the loss of gold due to drag out of plating solution is large, which is not economical.

[0030]

The electrolytic hard gold plating solution of the present invention contains a nitro group-containing compound

as an organic oxidant. The nitro group-containing compound uniquely increases the oxidation-reduction potential of gold at a low current density range (a current density of 10 A/dm² or lower), suppressing gold deposition. Further, with the electrolytic hard gold plating solution of the present invention, there is no suppression of gold deposition seen at a low current density, at a medium to high current density range (a current density of 20 to 200 A/dm²); therefore, a normal gold film is obtained.

10 [0031]

As the nitro group-containing compound, there can be mentioned 2-nitrobenzenesulfonic acid and salt thereof, 3-nitrobenzenesulfonic acid and salt thereof, 4-nitrobenzenesulfonic acid and salt thereof, 2,4-dinitrobenzenesulfonic acid and salt thereof, 3-amino-2-hydroxy-5-nitrobenzenesulfonic acid and salt thereof, 3-amino-4-hydroxy-5-nitrobenzenesulfonic acid and salt thereof, 4-aminonitrobenzenesulfonic acid and salt thereof, 2-nitrobenzoic acid and salt thereof, 3-nitrobenzoic acid and salt thereof, 4-nitrobenzoic acid and salt thereof, 3,5-dinitrobenzoic acid and salt thereof, 4-amino-2-nitrobenzoic acid and salt thereof, 4-amino-3-nitrobenzoic acid and salt thereof, 5-amino-2-nitrobenzoic acid, 2-amino-5-nitropyridine, 2-hydroxy-3-nitropyridine, 2-hydroxy-3-nitropyridine, 5-nitroquinoline, 6-nitroquinoline, 8-nitroquinoline, nitroisatin, 3-nitrophthalimide, 4-nitrophthalimide, 5-nitrouracil, 1-methyl-6-nitrouracil, 5-nitrobarbituric acid, 2-nitro-1,3-indandione, etc. These nitro group-containing compounds may be used singly or in combination of two or more kinds. In the electrolytic hard gold plating solution of the

present invention, the concentration of the nitro group-containing compound is 0.1 to 20 g/L, preferably 0.5 to 5 g/L. When the concentration is less than 0.1 g/L, the gold plating leakage into Ni barrier portion is large, resulting in reduced plating selectivity. Even if the concentration is more than 20 g/L, there is no effect corresponding thereto, which is not economical.

[0032]

The electrolytic hard gold plating solution of the present invention can be used at a pH range of 3.0 to 7.0 and is preferably used at a pH range of 4.0 to 5.0. When the pH is lower than 4.0, the cathode current efficiency is low, making it impossible to obtain an intended gold plating thickness. When the pH is higher than 5.0, the gold film has a reddish appearance, making it impossible to obtain a normal gold film. Incidentally, it is possible to use, as a pH-adjusting agent, sodium hydroxide, potassium hydroxide, ammonium hydroxide, water-diluted sulfuric acid, etc.

[0033]

The electrolytic hard gold plating solution of the present invention contains a cobalt salt. As the cobalt salt, there can be mentioned cobalt sulfate, cobalt nitrate, cobalt chloride, cobalt basic carbonic acid, etc. These cobalt salts may be used singly or in combination of two or more kinds. In the electrolytic hard gold plating solution of the present invention, the concentration of the cobalt salt is 0.01 to 10 g/L, preferably 0.1 to 1.0 g/L. When the concentration is less than 0.1 g/L, it is impossible to obtain the film properties of hard gold, such as film hardness and the like. Even if the concentration is higher

than 1.0 g/L; there is no effect corresponding thereto, which is not economical. By using the cobalt salt, the hardness of the plating film obtained becomes 150 to 200 HV.

[0034]

5 The electrolytic hard gold plating solution of the present invention contains a conductive organic acid salt. As the conductive organic acid salt, there can be mentioned potassium citrate, potassium phosphate, potassium nitrate, potassium succinate, etc. These conductive organic acid
10 salts may be used singly or in combination of two or more kinds. In the electrolytic hard gold plating solution of the present invention, the concentration of the conductive organic acid salt is 10 to 200 g/L, preferably 50 to 100 g/L. When the concentration is less than 10 g/L, there is, for
15 example, deterioration in plating film appearance, making it impossible to obtain a gold film of normal appearance. Even if the concentration is higher than 200 g/L, there is no effect corresponding thereto, which is not economical.

[0035]

20 The electrolytic hard gold plating solution of the present invention contains a chelating agent. As the chelating agent, there are used a carboxylic acid and a salt thereof, and an oxycarboxylic acid and a salt thereof. There can be mentioned, for example, formic acid, glycolic acid,
25 lactic acid, oxybenzoic acid, oxalic acid, malonic acid, succinic acid, malic acid, tartaric acid, phthalic acid, diglycolic acid, citric acid, and salts thereof. These may be used singly or in combination of two or more kinds. In the electrolytic hard gold plating solution of the present
30 invention, the concentration of the chelating agent is 1 to

50 g/L, preferably 5 to 20 g/L. When the concentration is less than 5 g/L, inorganic impurities are taken into the gold film formed, which tends to invite deterioration in gold film appearance and gold film properties. Even if the
5 concentration is higher than 20 g/L, there is no effect corresponding thereto, which is not economical.

[0036]

The electrolytic gold plating solution of the present invention can be used at a solution temperature of 20 to 90°C
10 and is used preferably at 40 to 70°C. When used at a temperature of lower than 40°C, the cathode current efficiency is low and an intended gold film thickness tends to be unobtainable. Also, when used at a temperature of higher than 70°C, an intended effect tends to be unobtainable.

15 [0037]

The current density in plating is preferably 20 to 200 A/dm², more preferably 50 to 150 A/dm².

[0038]

The plating of a connector having a Ni barrier layer,
20 using the electrolytic hard gold plating solution of the present invention is conducted, for example, as follows. First, a nickel plating film is formed on a copper connector material by electrolytic plating. This nickel plating film can be formed by a known method. Then, onto the nickel
25 plating film is applied partial plating, at the contact portion of connector and the substrate-bonding portion of connector, using the electrolytic hard gold plating solution of the present invention. Thereafter, the gold plating film formed is stripped by a known method, to obtain a gold-plated
30 connector having a Ni barrier layer.

[0039]

Fig. 1 shows bonding of a connector material having a Ni barrier layer formed using the electrolytic hard gold plating solution of the present invention, with a substrate. 11 is a connector base material consisting of a copper material. On the connector base material 11 is formed a Ni base 13 by nickel plating. Then, on the Ni base is formed a gold plating film 15, using the electrolytic hard gold plating solution of the present invention. In Fig. 1, the arrow a side becomes the contact portion of connector material, and the b side becomes the substrate-bonding portion. The plated connector material 10 is bonded to a substrate 17, using a bonding solder 19. Since there is present a Ni barrier layer 14 in which the nickel base 13 is exposed, the bonding solder 29 remains at the substrate-bonding portion and a high bonding strength can be obtained.

[0040]

The electrolytic hard gold plating solution of the present invention may contain other substances as long as the effect of the present invention is not impaired thereby.

[EXAMPLES]

[0041]

The present invention is described in more detail below by way of Examples. The present invention is not restricted to these Examples.

[0042]

There was used, as a sample, a copper plate on which a nickel film had been formed in a thickness of 2 μ m. Nickel film was formed by plating using nickel sulfamate solution.

[0043]

The constitution of the equipment and the method of evaluation, both used in the test are as follows.

[0044]

5 A silicone sheet was attached onto an acrylic mask plate that has opening of 10 mm x 10 mm. Thereon was placed a sample. The sample was pressed from above with a pressing block under which a silicone sheet had been attached, to fix the sample. A gold plating solution was sprayed through a
10 platinum-made nozzle of 5 mm in diameter (functioning as an anode) by circulating the solution by a pump, whereby partial plating was conducted. A notch of 5 mm x 10 mm was made in a side of 10 mm x 10 mm opening in the silicone sheet attached onto the mask plate; the silicone sheet of the notch portion
15 was removed and leakage portion was formed; thereby, there were made possible the remaining of the plating solution between the mask and the pressing block when the plating solution had been sprayed, and subsequent leakage plating. The evaluation of the plating was made by measuring the gold
20 film thickness formed on the sample of the leakage portion. The measurement of the gold film thickness was made at a point 5 mm apart from the interface between the opening of 10 mm x 10 mm and the leakage portion, using a fluorescent X-ray film thickness tester (SEA 5120, a product of SII).

25 [0045]

(Example 1)

Formulation of plating solution

Potassium gold cyanide: 5 g/L (as gold)

Potassium citrate: 120 g/L

30 Potassium formate: 20 g/L

Cobalt sulfate: 0.96 g/L

Sodium m-nitrobenzenesulfonate: 2 g/L

Water

[0046]

5 The above solution was adjusted to pH 4.2. Using the
solution and the above equipment, partial plating was
conducted at a solution temperature of 55°C by adjusting the
plating time so that the gold film thickness obtained became
0.2 μm at each current density shown in Table 1. The gold
10 film formed by deposition had a lemon yellow color and a
uniform satisfactory appearance. The gold film thickness at
the Ni barrier portion (leakage portion) was below 0.01 μm at
each current density and there was striking suppression for
plating leakage.

15 [0047]

(Example 2)

Formulation of plating solution

Potassium gold cyanide: 5 g/L (as gold)

Potassium citrate: 120 g/L

20 Potassium formate: 20 g/L

Cobalt sulfate: 0.96 g/L

Sodium m-nitrobenzoate: 2 g/L

Water

[0048]

25 The above solution was adjusted to pH 4.2. Using the
solution and the above equipment, partial plating was
conducted at a solution temperature of 55°C by adjusting the
plating time so that the gold film thickness obtained became
0.2 μm at each current density shown in Table 1. The gold
30 film formed by deposition had a lemon yellow color and a

uniform satisfactory appearance. The gold film thickness at the Ni barrier portion (leakage portion) was below 0.01 μm at each current density and there was striking suppression for plating leakage.

5 [0049]

(Example 3)

Formulation of plating solution

Potassium gold cyanide: 5 g/L (as gold)

Potassium citrate: 120 g/L

10 Potassium formate: 20 g/L

Cobalt sulfate: 0.96 g/L

5-Nitrouracil: 2 g/L

Water

[0050]

15 The above solution was adjusted to pH 4.2. Using the solution and the above equipment, partial plating was conducted at a solution temperature of 55°C by adjusting the plating time so that the gold film thickness obtained became 0.2 μm at each current density shown in Table 1. The gold
20 film formed by deposition had a lemon yellow color and a uniform satisfactory appearance. The gold film thickness at the Ni barrier portion (leakage portion) was below 0.01 μm at each current density and there was striking suppression for plating leakage.

25 [0051]

(Comparative Example 1)

Formulation of plating solution

Potassium gold cyanide: 5 g/L (as gold)

Potassium citrate: 120 g/L

30 Potassium formate: 20 g/L

Cobalt sulfate: 0.96 g/L

Water

[0052]

The above solution was adjusted to pH 4.2. Using the
5 solution and the above equipment, partial plating was
conducted at a solution temperature of 55°C by adjusting the
plating time so that the gold film thickness obtained became
0.2 μm at each current density shown in Table 1. The gold
film formed by deposition had a lemon yellow color and a
10 uniform satisfactory appearance. The gold film thickness at
the Ni barrier portion (leakage portion) was 0.030 to 0.042
 μm at each current density.

[0053]

Table 1

	Current density (A/dm ²)	Gold film thickness (μm)
Example 1	20	0.003
	40	0.005
	60	0.004
Example 2	20	0.002
	40	0.004
	60	0.003
Example 3	20	0.005
	40	0.007
	60	0.008
Comparative Example 1	20	0.030
	40	0.039
	60	0.042

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[0054]

The plating solution of the present invention can be
used also in the following formulations, for example.

Formulation example 1 of plating solution

20

Potassium gold cyanide: 2 g/L (as gold)

Potassium citrate: 120 g/L
Potassium formate: 20 g/L
Cobalt sulfate: 0.96 g/L
Sodium m-nitrobenzenesulfonate: 2 g/L
5 Water

[0055]

Formulation example 2 of plating solution

Potassium gold cyanide: 15 g/L (as gold)
Potassium citrate: 120 g/L
10 Potassium formate: 20 g/L
Cobalt sulfate: 0.96 g/L
Sodium m-nitrobenzenesulfonate: 2 g/L
Water

15 **[EXPLANATION OF NUMERICAL SYMBOLS]**

[0056]

10: a connector material having a Ni barrier layer
11: a connector base material made of copper
13: a Ni base
20 14: a Ni barrier layer
15: a gold plating film
17: a substrate
19: a bonding solder
20: a connector material gold-plated on the whole
25 surface
21: a connector base material made of copper
23: a Ni base
25: a gold plating film
27: a substrate
30 29: a bonding solder

CLAIMS

1. An electrolytic hard gold plating solution containing
a gold cyanide and/ or a salt thereof,
5 a cobalt salt,
a conductive organic acid salt,
a nitro group-containing compound, and
at least one kind of compound selected from the group
consisting of a carboxylic acid, an oxycarboxylic acid, and
10 salts thereof.
2. The electrolytic hard gold plating solution according
to Claim 1, wherein the concentration of the nitro group-
containing compound is 0.1 to 20 g/L.
- 15 3. A method for plating a connector material, which
comprises applying partial plating to the contact portion and
substrate-bonding portion of a connector material using an
electrolytic hard gold plating solution set forth in Claim 1.

20

**Electrolytic Hard Gold Plating Solution and Plating Method
Using the Same**

ABSTRACT

5

[Task]

To provide a gold plating solution which, in the
partial plating for forming a Ni barrier layer in a
connector material, can suppress the formation of gold
10 plating film in the Ni barrier portion (an unintended
portion) of the connector material.

[Means for Achieving the Task]

The formation of gold plating film in Ni barrier
portion can be suppressed by conducting partial plating a
15 connector material using an electrolytic hard gold plating
solution containing

a gold cyanide and/ or a salt thereof,
a cobalt salt,
a conductive organic acid salt,
20 a nitro group-containing compound, and

at least one kind of compound selected from the group
consisting of a carboxylic acid, an oxycarboxylic acid, and
salts thereof.

[Selected Drawing]

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Fig. 1