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(54) **ELECTROLYTIC COPPER-STRIPPING LIQUID AND ELECTROLYTIC STRIPPING METHOD**

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(57) **ABSTRACT**

The present invention provides an electrolytic copper-stripping liquid free from a cyan compound, which comprises a copper compound or an aromatic nitro compound as a copper-oxidizing agent, and which has a pH of from 9 to 12. Also disclosed is an electrolytic stripping method using the electrolytic stripping liquid.

FIG. 1

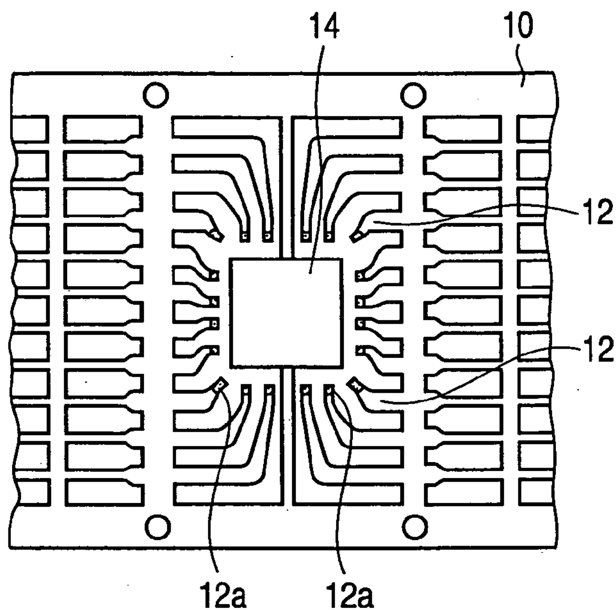


FIG. 2A

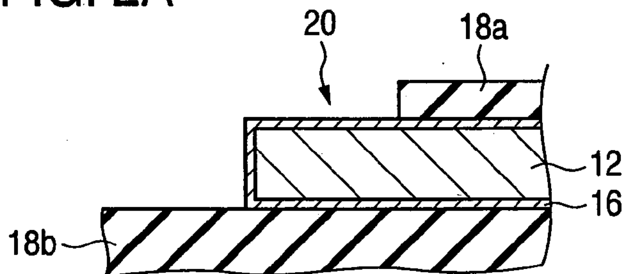


FIG. 2B

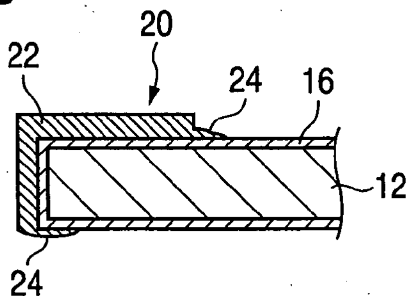


FIG. 2C

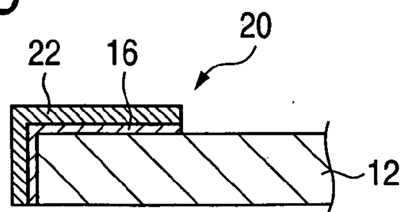


FIG. 3

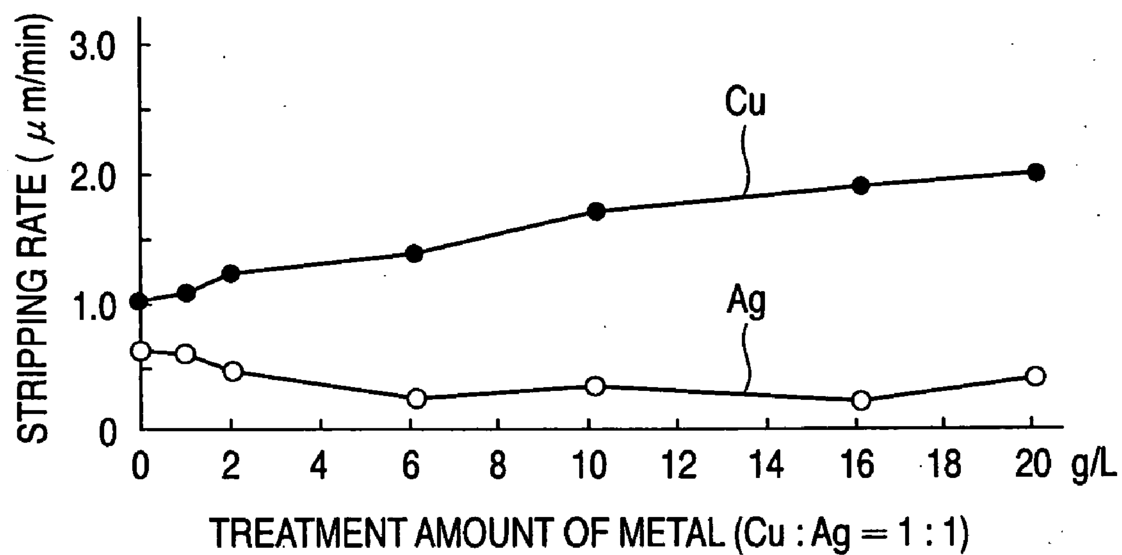
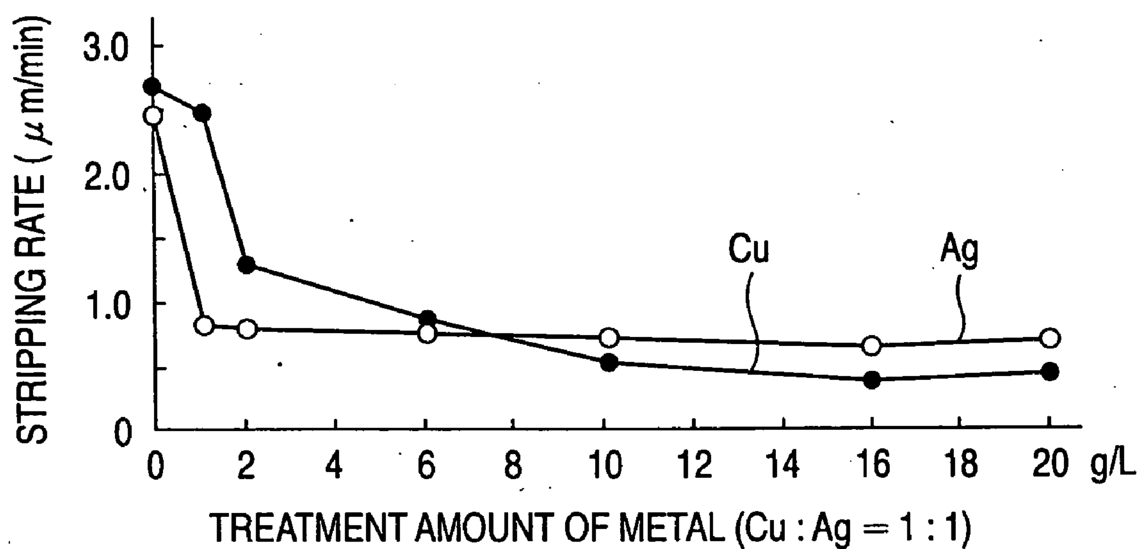


FIG. 4



ELECTROLYTIC COPPER-STRIPPING LIQUID AND ELECTROLYTIC STRIPPING METHOD

FIELD OF THE INVENTION

[**0001**] The present invention relates to an electrolytic copper-stripping liquid and an electrolytic stripping method. In more detail, the invention relates to an electrolytic copper-stripping liquid for stripping a copper plating film exposed from a silver plating film that partially covers a copper plating film formed on the entire surface of a member by electrolytic stripping, and to an electrolytic stripping method to carry out such electrolytic stripping.

BACKGROUND OF THE INVENTION

[**0002**] In a lead frame to be used in semiconductor devices, as illustrated in **FIG. 1**, at a tip portion of each of inner leads **12** constructing a lead frame **10** made of an iron based alloy material such as an iron-nickel alloy (42 alloy) in the side of a die pad **14** (this tip portion will be hereinafter referred simply as "tip portion"), a bonding portion **12***a* to be connected with one end portion of a gold wire, the other end portion of which is connected to a semiconductor element mounted on the die pad **14**, is formed.

[**0003**] On such a bonding portion **12***a,* a silver plating film is formed, and the foregoing one end portion of the gold wire is connected to the bonding portion **12***a*.

[**0004**] As illustrated in **FIG. 1**, in forming the die bonding portion **12***a* having a silver plating film formed thereon, at the tip portion of each of the inner leads **12** of the lead frame **10** made of an iron based alloy, a copper plating film is formed on the entire surrounding of the lead frame **10** by electrolytic copper plating.

[**0005**] As illustrated in **FIG. 2A**, the lead frame **10** having such a copper plating film formed thereon is put between rubber-made mask plates **18***a* and **18***b* in such a manner that only a copper plating film **16** of a portion for forming the bonding portion **12***a* is exposed at a tip portion **20** of the inner lead **12**, and electrolytic silver plating for forming a silver plating film on the exposed copper plating film **16** is carried out.

[**0006**] Next, as illustrated in **FIG. 2B**, after completion of the electrolytic silver plating, when the mask plates **18***a* and **18***b* are removed, a partial silver plating film **22** is formed only at the portion for forming the bonding portion **12***a* of the tip portion **20** of the inner lead **12**.

[**0007**] Thereafter, the lead frame **10** is dipped in an electrolytic stripping liquid, and the copper plating film **16** which is exposed without being covered by the partial silver plating film **22** is removed by electrolytic stripping using the lead frame **10** as an anode. Thus, as illustrated in **FIG. 2C**, the bonding portion **12***a* comprising the copper plating film **16** and the partial silver plating film **22** is formed only at the portion for forming the bonding portion **12***a* of the tip portion **20** of the inner lead **12**.

[**0008**] Now, in putting the lead frame **10** between the mask plates **18***a* and **18***b* and forming a silver plating film on the exposed copper plating film **16**, a thin silver plating film **24** due to leakage of an electrolytic silver plating liquid (hereinafter sometimes referred to as "leaking silver **24**") is also formed at a portion having covered by the mask plates **18***a* and **18***b* as illustrated in **FIG. 2B** because of strains of the mask plates **18***a* and **18***b,* etc. This leaking silver **24** is also removed by electrolytic stripping of the copper plating film **16**, and as illustrated in **FIG. 2C**, the partial silver plating film **22** is formed only at the portion for forming the bonding portion **12***a* of the tip portion **20** of the inner lead **12**.

[**0009**] For electrically stripping the leaking silver **24** and the copper plating film **16** without substantially stripping the partial silver plating film **22**, an electrolytic stripping liquid containing a cyan compound has been used as described in the following Patent Document 1.

[**0010**] Patent Document 1: JP 59-031900 A (pages 2 to 3)

[**0011**] As described in Patent Document 1, by dipping the lead frame **10**, on which the partial silver plating film **22** is formed only at the tip portion **20** of the inner lead **12**, in an electrolytic stripping liquid containing a cyan compound and carrying out electrolytic stripping of copper using this lead frame **10** as an anode and a stainless steel plate as a cathode, it is possible to electrolytically strip the leaking silver **24** and the copper plating film **16** without substantially stripping the partial silver plating film **22**.

[**0012**] However, if the electrolytic stripping liquid containing a cyan compound is continuously used, in electrolytically stripping the leaking silver **24** and the copper plating film **16**, a stripping rate of the copper plating film **16** and the leaking silver **24** is reduced within a relatively short period of time. For this reason, it is required to frequently exchange such an electrolytic stripping liquid.

[**0013**] Also, the electrolytic stripping liquid containing a cyan compound is required to pay special attentions in exchange and so on in view of safety.

SUMMARY OF THE INVENTION

[**0014**] Accordingly, an object of the invention is to provide an electrolytic copper-stripping liquid, which is a cyan compound-free electrolytic stripping liquid and the life of which can be greatly extended as compared with that of cyan compound-containing electrolytic stripping liquids.

[**0015**] Another object of the invention is to provide an electrolytic stripping method using the electrolytic copper-stripping liquid.

[**0016**] Other objects and effects of the invention will become apparent from the following description.

[**0017**] To achieve the foregoing objects, the present inventors made extensive investigations. As a result, it has been found that by using a cyan compound-free electrolytic stripping liquid which is an electrolytic copper-stripping liquid containing a copper compound or an aromatic nitro compound as an oxidizing agent and carrying out electrolytic stripping with respect to the lead frame **10** on which the partial silver plating film **22** is formed only at the tip portion **20** of the inner lead **12** as illustrated in **FIG. 2B**, it is possible to electrolytically strip the leaking silver **24** and the copper plating film **16** without substantially stripping the partial silver plating film **22**.

[**0018**] Further, it has been found that the life of this electrolytic stripping liquid is longer than that of cyan

compound-containing electrolytic stripping liquids, leading to accomplishment of the invention.

[0019] Specifically, the invention relates to an electrolytic copper-stripping liquid, which is free from a cyan compound, which comprises a copper compound or an aromatic nitro compound as a copper-oxidizing agent, and which has a pH of from 9 to 12.

[0020] Also, the invention relates to an electrolytic copper-stripping method comprising electrolytically stripping a copper plating film exposed from a silver plating film that partially covers a copper plating film formed on the entire surface of a member, using the foregoing electrolytic copper-stripping liquid, wherein the member is dipped in the electrolytic copper-stripping liquid and is used as an anode.

[0021] In the invention, the copper-oxidizing agent contained in the electrolytic stripping liquid is preferably a copper ammonium complex. The copper ammonium complex can be formed by adding, to the electrolytic stripping liquid, ammonia water or an ammonium salt as an ammonium source, and copper sulfate, copper carbonate, copper oxalate or copper hydroxide as a copper source.

[0022] It is possible to adjust the electric conductivity of the electrolytic stripping liquid by further adding thereto at least one compound selected from the group consisting of phosphoric acid and salts thereof, organic acids including citric acid and tartaric acid and salts thereof, carbonates, hydrogencarbonates, and amino carboxylic acids including glutamic acid and aspartic acid and salts thereof.

[0023] Also, it is possible to rapidly strip leaking silver and the like by adding a compound that reacts with silver to form a complex, as a silver-stripping agent, to the electrolytic stripping liquid. Examples of the compound that reacts with silver to form a complex include pyridinecarboxylic acid, a thiocyanic acid salt, dimethylhydantoin, and succinic acid imide.

[0024] Further, it is possible to enhance wettability of a member to be subjected to electrolytic stripping by adding a surfactant to the electrolytic stripping liquid. Examples of the surfactant that can be suitably used include polyoxyethylene chain-containing surfactants and fluorine-containing surfactants.

[0025] As the member for which the electrolytic copper-stripping liquid according to the invention is used, a lead frame made of an iron based alloy material can be suitably used. In carrying out the electrolytic stripping, it is preferred to use an electrode made of a metal which does not elute in the electrolytic stripping liquid as a cathode.

[0026] The reasons why the life of cyan compound-containing electrolytic stripping liquids which have been used so far is short may be considered as follows.

[0027] A cyan compound in an electrolytic stripping liquid gradually raises a silver concentration in the electrolytic stripping liquid with an increase of the treatment amount of electrolytic stripping. When the silver concentration in the electrolytic stripping liquid rises, a silver ion in the electrolytic stripping liquid gives rise to displacement reaction with copper of a copper plating film to be stripped, thereby reducing the stripping rate of copper.

[0028] Further, since the cyan compound easily forms a complex with also silver, not only stripping of a copper plating film but also stripping of a partial silver plating film take place. For this reason, when stripping of the copper plating film has been completed, the surface of the partial silver plating film tends to have been roughed, thereby deteriorating the appearance.

[0029] On the other hand, the electrolytic stripping liquid according to the invention is a cyan compound-free electrolytic stripping liquid and contains a copper compound or an aromatic nitro compound as a copper-oxidizing agent.

[0030] In this way, since a cyan compound which likely forms a complex with silver is not added to the electrolytic stripping liquid according to the invention, it is possible to strip the copper plating film selectively relative to the partial silver plating film during the electrolytic stripping.

[0031] However, even the electrolytic stripping liquid according to the invention can strip leaking silver formed on the copper plating film though its stripping rate is slow as compared with that against the copper plating film.

[0032] Though a silver ion eluted from such a partial silver plating film and leaking silver, etc. may be present in a certain amount in the electrolytic stripping liquid according to the present invention, the eluted silver is mostly deposited on a cathode, etc., whereby it becomes possible to suppress an increase of the silver concentration in the electrolytic stripping liquid.

[0033] As a result, according to the electrolytic stripping liquid according to the invention, it is possible to prevent a reduction in the stripping rate of the copper plating film due to accumulation of silver in the electrolytic stripping liquid and roughing of the appearance of the partial silver plating film. Thus, it is possible to greatly extend its life as compared with that of conventional electrolytic stripping liquids containing a cyan compound.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] **FIG. 1** is a partial plan view to explain a lead frame as a member to be subjected to electrolytic stripping.

[0035] **FIG. 2A** to **2C** are partial cross-sectional views to explain partial silver plating to be formed on a lead frame as shown in **FIG. 1** and leaking silver.

[0036] **FIG. 3** is a graph showing measurement results of stripping rates of copper and silver exhibited by an electrolytic stripping liquid of the invention after treating prescribed amounts of copper and silver.

[0037] **FIG. 4** is a graph showing measurement results of stripping rates of copper and silver exhibited by a cyan compound-containing electrolytic stripping liquid after treating prescribed amounts of copper and silver.

[0038] The reference numerals used in the drawings denote the followings, respectively.

[0039] **10**: Lead frame

[0040] **12**: Inner lead

[0041] **12***a:* Bonding portion

[0042] **14**: Die pad

[0043] **16**: Copper plating film

[0044] **20**: Tip portion of inner lead

[0045] **22**: Partial silver plating film

[0046] **24**: Leaking silver

DETAILED DESCRIPTION OF THE INVENTION

[0047] It is important that the electrolytic stripping liquid according to the invention is a cyan compound-free electrolytic stripping liquid and contains a copper compound or an aromatic nitro compound as a copper-oxidizing agent.

[0048] As the copper compound as the copper-oxidizing agent, a copper ammonium complex is suitable. Such a copper ammonium complex can be formed by adding, to the electrolytic stripping liquid, ammonia water or an ammonium salt as an ammonium source and copper sulfate, copper carbonate, copper oxalate or copper hydroxide as a copper source.

[0049] The copper ammonium complex that is formed in the electrolytic stripping liquid having an ammonium source and a copper source added thereto comprises at least one of $[Cu(NH_{3)2}]^{2+}$, $[Cu\ (NH_3)_4]^{2+}$, and $[Cu(NH_3)_6]^{2+}$.

[0050] As the aromatic nitro compound, chloronitrobenzoic acid, 2-chloro-4-nitrobenzoic acid, o-nitrobenzoic acid, m-nitrobenzoic acid, p-nitrobenzoic acid, ethyl p-nitro-benzoate, and sodium p-nitrobenzoate can be suitably used.

[0051] Here, an electrolytic stripping liquid which contains a copper compound or an aromatic nitro compound as a copper-oxidizing agent but to which a cyan compound is added cannot be expected to have a prolonged life, though it may provide a good appearance of the partial silver plating.

[0052] The amount of the copper-oxidizing agent used in the electrolytic stripping liquid of the present invention is generally from 1 to 100 g/liter, preferably from 5 to 40 g/liter.

[0053] Further, it is required that the electrolytic stripping liquid according to the invention is adjusted so as to have a pH of from 9 to 12. The pH adjustment may be achieved by using ammonia water as the ammonium source to be added as a compound capable of forming a copper ammonium complex, or using a pH adjustor such as sodium hydroxide.

[0054] Here, in the case where the pH of the electrolytic stripping liquid is less than 9, or in the case where the pH of the electrolytic stripping liquid exceeds 12, the stripping rate of the copper plating film is reduced.

[0055] In the electrolytic stripping liquid according to the invention, it is possible to adjust an electric conductivity of the electrolytic stripping liquid by adding at least one compound selected from the group consisting of phosphoric acid and salts thereof, organic acids including citric acid and tartaric acid and salts thereof, carbonates, hydrogencarbonates, and amino carboxylic acids including glutamic acid and aspartic acid and salts thereof to the electrolytic stripping liquid.

[0056] Examples of the phosphoric acid and salts thereof to be used herein, which are effective for adjusting the electric conductivity of the electrolytic stripping liquid, include phosphoric acid, metaphosphoric acid, orthophosphoric acid, and ammonium salts, potassium salts and sodium salts of these acids (specific examples thereof include ammonium dihydrogenphosphate, diammonium hydrogenphosphate, triammonium phosphate, dipotassium hydrogenphosphate, monopotassium dihydrogenphosphate, disodium hydrogenphosphate, sodium dihydrogenphosphate, and potassium pyrophosphate). Of these compounds, phosphoric acid, ammonium dihydrogenphosphate, diammonium hydrogenphosphate, triammonium phosphate, dipotassium hydrogenphosphate, monopotassium dihydrogenphosphate, disodium hydrogenphosphate, and sodium dihydrogenphosphate can be suitably used.

[0057] Also, examples of the organic acids and salts thereof, which are effective for adjusting the electric conductivity of the electrolytic stripping liquid, include formic acid, acetic acid, oxalic acid, propionic acid, butyric acid, valeric acid, citric acid, lactic acid, tartaric acid, succinic acid, benzoic acid, benzenesulfonic acid, nicotinic acid, isonicotinic acid and ammonium salts, potassium salts and sodium salts of these acids (specific examples thereof include ammonium formate, potassium formate, ammonium acetate, potassium acetate, ammonium hydrogenoxalate, ammonium dihydrogencitrate, diammonium hydrogencitrate, triammonium citrate, potassium dihydrogencitrate, tripotassium citrate, ammonium tartarate, potassium tartarate, ammonium succinate, and potassium succinate). Of these organic acids and salts thereof, formic acid, citric acid, tartaric acid, succinic acid, ammonium formate, ammonium dihydrogencitrate, diammonium hydrogencitrate, triammonium citrate, potassium dihydrogencitrate, tripotassium citrate, ammonium tartarate, potassium tartarate, ammonium citrate, and potassium citrate can be suitably used.

[0058] Further, examples of the carbonates and hydrogencarbonates, which are effective for adjusting the electric conductivity of the electrolytic stripping liquid, include ammonium carbonate, ammonium hydrogencarbonate, potassium carbonate, potassium hydrogencarbonate, sodium carbonate, and sodium hydrogencarbonate. Of these compounds, ammonium carbonate, ammonium hydrogencarbonate, potassium carbonate, and potassium hydrogencarbonate can be suitably used.

[0059] Also, glycine and the amino carboxylic acids including glutamic acid and aspartic acid and salts thereof are effective for adjusting the electric conductivity of the electrolytic stripping liquid, and examples thereof include glycine, glutamic acid, aspartic acid, cysteine, methionine, threonine, serine, alginine, and ammonium salts, potassium salts and sodium salts of these acids. Of these compounds, glycine, glutamic acid, and aspartic acid can be suitably used.

[0060] The amount of the above-cited salts to be used as the above-mentioned at least one compound in the electrolytic stripping liquid of the present invention is generally from 10 to 300 g/liter, preferably from 50 to 200 g/liter. The amount of the above-cited acids is adjusted so as to give a pH of the resulting electrolytic stripping liquid of 9 to 12.

[0061] Incidentally, for enhancing the wettability of each surface of the copper plating film and the leaking silver, which are to be subjected to the stripping, against the electrolytic stripping liquid, for example, a polyoxyethylene chain-containing surfactant or a fluorine based surfactant may be added as a surfactant.

[0062] In this way, in carrying out electrolytic stripping with respect to the lead frame **10** in which the leaking silver

24 as illustrated in **FIG. 2B** is formed on the copper plating film **16** using the electrolytic stripping liquid according to the invention, it is possible to strip the copper plating film **16** while stripping the leaking silver **24** as illustrated in **FIG. 2B**.

[**0063**] At this time, in the case where it is intended to further enhance the stripping rate of the leaking silver **24**, a compound that reacts with silver to form a complex, such as pyridinecarboxylic acid, thiocyanic acid salts, dimethylhydantoin, and succinic acid imide, may be added as a silver-stripping agent. The amount of the compound that reacts with silver to form a complex, to be added in the electrolytic stripping liquid of the present invention is generally from 0.1 mg to 100 g/liter.

[**0064**] The method for preparing the electrolytic stripping liquid of the present invention is not particularly limited, and the electrolytic stripping liquid can be obtained by simply mixing the above-described components in an ordinary manner.

[**0065**] In electrolytically stripping the leaking silver **24** and the copper plating film **16** of the lead frame **10** as illustrated in **FIG. 2B** using the electrolytic stripping liquid according to the invention which has been described, by passing a direct current between the lead frame **10** as an anode and a cathode, both of which are dipped within a stripping vessel storing the electrolytic stripping liquid, it is possible to electrolytically strip the leaking silver **24** and the copper plating film **16**.

[**0066**] In the electrolytic stripping, an electrode made of a metal which does not elute in the electrolytic stripping liquid, such as an electrode made of platinum or stainless steel, can be suitably used as a cathode. In this way, by using an electrode made of a metal which does not elute in the electrolytic stripping liquid as a cathode, it is possible to deposit a silver ion on the cathode in the electrolytic stripping liquid; it is possible to control the silver concentration in the electrolytic stripping liquid at a low concentration; and it is possible to easily recover silver.

[**0067**] Incidentally, in this electrolytic stripping, the current density is generally from about 0.01 to 20 A/dm^2, and preferably from about 0.1 to 10 A/dm^2; and the treatment time is preferably from about 2 to 30 seconds.

EXAMPLES

[**0068**] The present invention will be illustrated in greater detail with reference to the following Examples, but the invention should not be construed as being limited thereto.

Example 1

[**0069**] A copper plating film **16** having a thickness of from 0.1 to 0.2 μm was formed on the entire surface of a lead frame **10** made of an iron-nickel alloy (42 alloy) by electrolytic copper plating. Thereafter, the lead frame **10** was put between rubber-made mask plates **18***a* and **18***b* in such a manner that only the copper plating film **16** of a portion for forming a bonding portion **12***a* was exposed at a tip portion **20** of the inner lead **12** as illustrated in **FIG. 2A**, followed by forming a partial silver plating film **22** having a thickness of from 3 to 6 μm on the exposed copper plating film **16** by electrolytic silver plating.

[**0070**] Next, when the mask plates **18***a* and **18***b* were removed, the partial silver plating film **22** was formed on the portion for forming the bonding portion **12***a* of the tip portion **20** of the inner lead **12** as illustrated in **FIG. 2B**.

[**0071**] However, leaking silver **24** was formed in places at a portion covered by the mask plates **18***a* and **18***b* as illustrated in **FIG. 2B**.

[**0072**] The lead frame **10** was dipped within a stripping vessel storing an electrolytic stripping liquid shown in the following Table 1, and a direct current was passed between the lead frame **10** as an anode and a cathode made of a platinum electrode, thereby carrying out electrolytic stripping with respect to the leaking silver **24** and the copper plating film **16**.

TABLE 1

Electrolytic stripping liquid 1	Triammonium phosphate:	50 g/L
	p-Nitrobenzoic acid:	20 g/L
	25% ammonia water	(for pH adjustment)
	pH:	9.5
Electrolytic stripping liquid 2	Triammonium phosphate:	50 g/L
	Copper(II) hydroxide:	5 g/L
	25% ammonia water	(for pH adjustment)
	pH:	11.0
Electrolytic stripping liquid 3	L-Glutamic acid:	100 g/L
	p-Nitrobenzoic acid:	10 g/L
	Potassium hydroxide	(for pH adjustment)
	pH:	10.0
Electrolytic stripping liquid 4	Ammonium tartarate:	50 g/L
	Copper(II) hydroxide:	5 g/L
	Isonicotinic acid:	20 g/L
	25% ammonia water	(for pH adjustment)
	pH:	9.5
Electrolytic stripping liquid 5	Triammonium phosphate:	100 g/L
	Copper(II) hydroxide:	10 g/L
	Polyethylene glycol:	1 g/L
	25% ammonia water	(for pH adjustment)
	pH:	10.0
Electrolytic stripping liquid 6	Ammonium carbonate:	200 g/L
	Copper carbonate:	20 g/L
	25% ammonia water	(for pH adjustment)
	pH:	10.0
Electrolytic stripping liquid 7	Triammonium phosphate:	100 g/l
	Copper(II) hydroxide:	2 g/L
	Ammonium thiocyanate:	1 g/L
	25% ammonia water	(for pH adjustment)
	pH:	10.0
Electrolytic stripping liquid 8	Triammonium phosphate:	100 g/L
	p-Nitrobenzoic acid:	10 g/L
	Nicotinic acid:	20 g/L
	25% ammonia water	(for pH adjustment)
	pH:	9.0
Electrolytic stripping liquid 9	Potassium cyanate:	80 g/L
	p-Nitrobenzoic acid:	10 g/L
	pH:	11.0

[**0073**] The electrolytic stripping liquid, the current density, and the treatment time employed for the electrolytic stripping are shown in the following Table 2. Also, the results of the electrolytic stripping are shown in the following Table 2. At respective levels shown in Table 2, remaining exposed copper plating film **16** and remaining leaking silver **24**, discoloration of the partial silver plating film **22**, and corrosion of the **42** alloy constituting the lead frame **10** were not observed.

TABLE 2

No.	Electrolytic stripping liquid	Current density (A/dm^2)	Treatment time (sec)	Partial silver plating film	
				Presence of spots	Presence of glossiness change
1	Electrolytic stripping liquid 1	1	10	No	No
2	"	0.5	10	No	No
3	Electrolytic stripping liquid 2	0.5	4	No	No
4	"	0.5	10	No	No
5	Electrolytic stripping liquid 3	1	30	No	No
6	Electrolytic stripping liquid 4	0.5	3	No	No
7	Electrolytic stripping liquid 5	1	2	No	No
8	"	2	5	No	No
9	Electrolytic stripping liquid 6	1	3	No	No
10	Electrolytic stripping liquid 7	0.3	10	No	No
11	Electrolytic stripping liquid 8	0.5	20	No	No
12*	Electrolytic stripping liquid 9	1	2	No	No
13*	"	2	5	Yes	Yes (burnt)

Note)
Nos. 1 to 11 are Examples; and No. 12* and No. 13* are Comparative Examples.
The term "burnt" represents the phenomenon or state where the silver surface is roughened and made uneven as the result of a local etching with uneven surface stripping.

[**0074**] As is clear from Table 2, according to the levels of Nos. 1 to 12, the results were so good that neither spots nor glossiness change of the partial silver plating film **22** was observed. In contrast, according to the level of No. 13, spots and glossiness change of the partial silver plating film **22** were observed.

Example 2

[**0075**] Prescribed amounts of copper and silver were treated using the electrolytic stripping liquid **5** shown in Table 1, and then, the subsequent stripping rates of copper and silver were measured. The stripping rates were obtained by previously treating equivalent amounts of copper and silver in the electrolytic stripping liquid **5**, and then carrying out electrolytic stripping under the electrolytic stripping conditions of No. 7 of Table 2 against a copper plate or a silver plate dipped as an anode in the electrolytic stripping liquid **5** to measure a reduction of the weight of the copper plate or the silver plate after the electrolytic stripping.

[**0076**] **FIG. 3** shows the results obtained with respect to the stripping rates of copper and silver as measured by changing the treatment amounts of copper and silver to be previously treated with the electrolytic stripping liquid **5**.

[**0077**] As is clear from **FIG. 3**, even when the previous treatment amounts of copper and silver increase, though the stripping rate of copper tends to become slightly fast, and the stripping rate of silver tends to become slightly low, the both are approximately the same rate, respectively in comparison with the stripping rates of copper and silver at the time when the previous treatment amounts of copper and silver are each zero (immediately after initial make-up of an electrolytic bath).

[**0078**] In this way, according to the electrolytic stripping liquid **5**, even though the treatment amounts of copper and silver increase, it is possible to keep the stripping rates of copper and silver the same as those in the electrolytic stripping liquid immediately after initial make-up of an electrolytic bath, whereby an exchange interval of the electrolytic stripping liquid **5** can be prolonged.

Comparative Example

[**0079**] **FIG. 4** shows the results obtained with respect to the stripping rates of copper and silver in the electrolytic stripping under the electrolytic stripping conditions of No. 12* of Table 2, measured in the same manner as in Example 2.

[**0080**] As is clear from **FIG. 4**, though when the previous treatment amounts of copper and silver are each zero (immediately after initial make-up of an electrolytic bath), the stripping rates of copper and silvers are good, the stripping rate of copper is abruptly reduced with the increase of the previous treatment amounts of copper and silver, and thereafter, it becomes an approximately constant value.

[**0081**] It can be considered that such a phenomenon is caused by the fact that the cyan compound easily forms a complex with each of copper and silver. Namely, it can be considered that though the electrolytic stripping liquid containing a cyan compound has a very high stripping ability against not only copper but also silver at the beginning, when the silver concentration in the electrolytic stripping liquid rises, the silver ion in the electrolytic stripping liquid gives rise to displacement reaction with copper of the copper plating film to be stripped, resulting in a reduction in the stripping rate of copper.

[**0082**] As is clear from such **FIG. 4**, for the sake of keeping the stripping rates of copper and silver exhibited by the electrolytic stripping liquid **9** immediately after initial make-up of an electrolytic bath, it is required to frequently exchange the electrolytic stripping liquid **9**.

[**0083**] While the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[**0084**] This application is based on Japanese patent application No. 2003-413387 filed on Dec. 11, 2003, the contents thereof being herein incorporated by reference.

What is claimed is:

1. An electrolytic copper-stripping liquid free from a cyan compound, which comprises a copper compound or an aromatic nitro compound as a copper-oxidizing agent, and which has a pH of from 9 to 12.

2. The electrolytic copper-stripping liquid according to claim 1, wherein the copper compound is a copper ammonium complex derived from:

an ammonium source selected from the group consisting of ammonia water and an ammonium salt; and

a copper source selected from the group consisting of copper sulfate, copper carbonate, copper oxalate and copper hydroxide.

3. The electrolytic copper-stripping liquid according to claim 1, further comprising at least one compound selected from the group consisting of phosphoric acid and salts thereof, organic acids and salts thereof, carbonates, hydrogencarbonates, and amino carboxylic acids and salts thereof.

4. The electrolytic copper-stripping liquid according to claim 1, further comprising, as a stripping agent for silver, a compound that reacts with silver to form a complex.

5. The electrolytic copper-stripping liquid according to claim 4, wherein the compound that reacts with silver to form a complex is pyridinecarboxylic acid, a thiocyanic acid salt, dimethylhydantoin, or succinic acid imide.

6. The electrolytic copper-stripping liquid according to claim 1, further comprising a surfactant.

7. The electrolytic copper-stripping liquid according to claim 6, wherein the surfactant is a polyoxyethylene chain-containing surfactant or a fluorine-containing surfactant.

8. An electrolytic copper-stripping method comprising electrolytically stripping a copper plating film exposed from a silver plating film that partially covers a copper plating film formed on the entire surface of a member, using the electrolytic copper-stripping liquid according to claim 1,

wherein the member is dipped in the electrolytic copper-stripping liquid and is used as an anode.

9. The electrolytic copper-stripping method according to claim 8, wherein an electrode made of a metal which does not elute in the electrolytic stripping liquid is used as a cathode.

10. The electrolytic copper-stripping method according to claim 8, wherein the member is a lead frame made of an iron based alloy material.

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