

DESCRIPTION

CYANIDE ROUGHENING SILVER ELECTROPLATING SOLUTION

Technical Field

[0001]

The present invention relates to a silver electroplating solution. Specifically, the present invention relates to a silver electroplating solution containing silver cyanide as a silver source and capable of obtaining a highly roughened plating film.

Background Art

[0002]

Silver has been often used for jewelry from the old days because of its white gloss. Silver production is relatively large among precious metals, and silver is inexpensive; therefore, silver plating is applied to decorative applications such as silver accessories and tableware even today. In addition, since silver has the highest electrical conductivity at room temperature among all metals, silver plating is also frequently used for lead frames and substrates for electronic devices such as ICs and transistors. In addition, since silver has the largest reflectance of visible light among all metals, silver plating is frequently used on lead frames and various substrates for light emitting devices represented by LEDs. In addition, silver plating is also used for bearing components and applications utilizing antibacterial

properties of silver.

[0003]

So far, various efforts have been made in the semiconductor industry to enhance reliability of an IC package. In particular, development of roughening plating has been advanced in order to prevent destruction of the IC package called a popcorn phenomenon. By roughening a plating surface of copper or nickel to be used as base plating, it is intended to improve adhesion between plating and resin by an anchor effect. For example, Patent Literature 1 describes a technique for improving the adhesion by making full use of two-layer roughening plating. However, only with these conventional techniques, there is a problem that the anchor effect is not sufficiently exhibited because precious metal plating applied to an outermost surface is covered. Thus, a method in which silver plating itself having excellent electrical characteristics is roughened and applied to the outermost surface is desired. On the other hand, silver plating has a characteristic that recrystallization by heat is likely to occur. Thus, in the case of silver plating, in needle-shaped plating as seen in conventional typical roughening copper plating and roughening nickel plating, the anchor effect may be deteriorated by heat treatment.

[0004]

A silver plating solution using a sulfur-based compound has been conventionally known. Patent Literature 2 discloses a silver plating solution containing thiols or a disulfide compound as a stabilizer for silver instead of

cyanide. Patent Literature 3 discloses a method for stabilizing a plating solution with thiosulfuric acid. As described above, a sulfur compound, particularly thiosulfuric acid, have been used particularly as a stabilizer and a reducing agent in a cyan-free silver plating solution and an electroless silver plating solution. However, thiosulfuric acid is famous as a detoxifying agent for a cyanide compound, and there is no example in which thiosulfuric acid or a salt thereof is used for a cyanide silver electroplating solution for the purpose of roughening plating.

Citation List

Patent Literature

[0005]

Patent Literature 1: WO 2017/077903 A

Patent Literature 2: JP 6608597 B1

Patent Literature 3: JP 3300519 B1

Summary of Invention

Technical Problem

[0006]

From the above circumstances, in the conventional technique, it is not easy to improve the adhesion between a resin and a precious metal, particularly silver having excellent electrical characteristics and solder wettability. In addition, needle-shaped silver has a concern of performance degradation due to recrystallization or whisker in which a metal single crystal naturally grows on a metal

surface. Thus, development of a silver plating solution capable of obtaining a silver film roughened in a non-needle shape is desired.

[0007]

An object of the present invention is to provide a silver electroplating solution capable of obtaining a highly roughened silver film.

Solution to Problem

[0008]

As a result of intensive studies, the present inventor has found that a highly roughened silver film that is not needle-like can be obtained by adding thiosulfuric acid and/or a salt thereof to a silver electroplating solution, and has completed the present invention. The present invention for solving the above problems will be described below.

[0009]

[1] A silver electroplating solution containing:

10 to 100 g/L of silver cyanide or silver cyanide salt in terms of silver;

1 to 200 g/L of electrically conductive salt; and

3 to 500 g/L of thiosulfuric acid and/or a salt thereof.

[0010]

[2] The silver electroplating solution according to [1], in which the electrically conductive salt is at least one selected from the group consisting of cyanate, phosphate, pyrophosphate, nitrate, citrate, tartrate, thiocyanate, sulfate, and boric acid or a salt thereof.

[0011]

[3] The silver electroplating solution according to [1], in which pH (25°C) is 7.0 to 13.0.

Advantageous Effects of Invention

[0012]

In a roughening silver electroplating solution of the present invention, a highly roughened silver film that is not needle-like is stably obtained. Specifically, as illustrated in Figs. 1 and 2, a film having such a shape that a massive crystal extends is obtained. As a result, the roughened shape is less likely to deteriorate due to recrystallization. In addition, large irregularities are generated in a direction in which plating grows, and a high anchor effect can be obtained when bonding is performed with a resin and the like. In addition, since stable performance is obtained, a manufacturing yield is improved.

Brief Description of Drawings

[0013]

Fig. 1 is a micrograph (370 ×) of a silver film obtained in Example 2.

Fig. 2 is a micrograph (5000 ×) of the silver film obtained in Example 2.

Fig. 3 is a micrograph (370 ×) of a silver film obtained in Comparative Example 6.

Fig. 4 is a micrograph (5000 ×) of the silver film obtained in Comparative Example 6.

Fig. 5 is a micrograph (370 ×) of a silver film obtained

in Comparative Example 7.

Fig. 6 is a micrograph (5000 ×) of the silver film obtained in Comparative Example 7.

Description of Embodiments

[0014]

The silver electroplating solution of the present invention contains 10 to 100 g/L of a silver cyanide complex in terms of silver as a silver salt, 1 to 200 g/L of electrically conductive salt, and 3 to 500 g/L of thiosulfuric acid or a salt thereof. Hereinafter, components constituting the silver electroplating solution of the present invention will be described.

[0015]

[Silver cyanide complex]

In the silver electroplating solution of the present invention, a silver cyanide complex known as a silver source can be used without limitation. Examples of the silver cyanide complex include silver cyanide, silver potassium cyanide, and silver sodium cyanide.

[0016]

The concentration of the silver cyanide complex in the silver electroplating solution of the present invention is preferably 10 to 100 g/L and more preferably 20 to 70 g/L in terms of silver ion concentration. When the silver ion concentration is less than 10 g/L, deposition efficiency decreases, and a desired silver film thickness may not be obtained. On the other hand, when the silver ion concentration exceeds 100 g/L, loss of a silver salt due to

loss of a plating solution by an object to be plated increases, which is not economical.

[0017]

[Electrically conductive salt]

The type of the electrically conductive salt to be blended in the silver electroplating solution of the present invention is not particularly limited as long as an aqueous solution thereof has electrical conductivity; however, it is preferable to contain at least one selected from cyanate, phosphate, nitrate, citrate, tartrate, thiocyanate, sulfate, and boric acid or a salt thereof in order to use the silver electroplating solution industrially stably and economically produce the silver electroplating solution. In addition, soluble organic acid salts and the like are also preferable. These may be used singly or in combination of two or more kinds thereof. Examples of the cyanate include potassium cyanide and sodium cyanide. Examples of the phosphate include potassium phosphate, sodium phosphate, and ammonium phosphate. Examples of the pyrophosphate include potassium pyrophosphate, sodium pyrophosphate, and ammonium pyrophosphate. Examples of the nitrate include potassium nitrate, sodium nitrate, and ammonium nitrate. Examples of the citrate include potassium citrate, sodium citrate, and ammonium citrate. Examples of the tartrate include potassium tartrate, sodium tartrate, and potassium sodium tartrate. Examples of the thiocyanate include potassium thiocyanate and sodium thiocyanate. Examples of the sulfate include potassium sulfate, sodium sulfate, and ammonium sulfate. Examples of the boric acid or the salt thereof

include boric acid, sodium borate, and potassium borate.

[0018]

The concentration of the electrically conductive salt in the silver electroplating solution of the present invention is preferably 1 to 200 g/L, more preferably 10 to 200 g/L, and particularly preferably 20 to 180 g/L. When the concentration of the electrically conductive salt is less than 1 g/L, electrical resistance of the plating solution becomes too high, and plating production with a suitable cathode current density cannot be performed.

[0019]

[Thiosulfuric acid (salt)]

Specific examples of thiosulfuric acid and/or a salt thereof (hereinafter, abbreviated as "thiosulfuric acid (salt)") to be blended in the silver electroplating solution of the present invention include thiosulfuric acid, potassium thiosulfate, and sodium thiosulfate. These may be used singly or in combination of two or more kinds thereof.

[0020]

The concentration of thiosulfuric acid (salt) in the silver electroplating solution of the present invention is preferably 3 to 500 g/L, more preferably 3 to 300 g/L, and still more preferably 3 to 150 g/L. When the concentration of thiosulfuric acid (salt) is less than 3 g/L, the shape and size of silver crystals to be precipitated are not uniform. When the concentration of thiosulfuric acid (salt) exceeds 500 g/L, precipitation may occur.

[0021]

[Other components]

In the silver electroplating solution of the present invention, in addition to the above components, a component such as a surfactant can be contained as long as the object of the present invention is not impaired in order to reduce the viscosity and suppress the occurrence of unevenness of the silver film. Examples of the surfactant include anionic surfactants such as sodium polyoxyethylene alkyl ether sulfate and nonionic surfactants such as polyoxyethylene alkyl ether condensate.

[0022]

The silver electroplating solution of the present invention can be produced by dissolving the above-described silver cyanide or silver cyanide salt, an electrically conductive salt, thiosulfuric acid and/or a salt thereof, and other components as necessary in water. It is also preferable that an electrically conductive salt, thiosulfuric acid and/or a salt thereof, and other components as necessary are dissolved in water in advance, and silver cyanide or a silver cyanide salt is added at the time of use.

[0023]

The silver electroplating solution of the present invention is preferably used at pH 7.0 to 13.0 (25°C, the same applies hereinafter), and more preferably used at pH 8.0 to 13.0. When the pH is less than 7.0, cathode current efficiency decreases, and the resulting film does not have a sufficient film thickness. When the pH exceeds 13.0, an appearance of the resulting film is deteriorated.

[0024]

A liquid temperature of the silver electroplating solution of the present invention is preferably 10 to 80°C, and more preferably 20 to 60°C. When the liquid temperature of a plating bath is out of the above range, the cathode current efficiency may be reduced, or stability of the plating bath may be impaired.

[0025]

The current density in the case of using the silver electroplating solution of the present invention is set in consideration of the composition and liquid temperature of the plating solution and other conditions. For example, when the plating solution is used at a liquid temperature of 60°C, the current density is preferably set to 30 to 100 A/dm². When the current density is not set to a suitable current density, an abnormality may occur in the plating appearance and the characteristics of the plating film. In addition, the plating bath becomes unstable, and a plating solution component may decompose.

Examples

[0026]

Hereinafter, the present invention will be specifically described with reference to Examples. The present invention is not limited to these Examples.

[0027]

(Examples 1 to 12, Comparative Examples 1 to 7)

A 0.1 dm² copper plate was used as an object to be plated. First, the copper plate was subjected to a degreasing treatment with an alkali-based degreasing liquid,

then neutralized with dilute sulfuric acid, and then subjected to non-glossy copper plating of about 1.7 μm with a cyan bath. Thereafter, silver plating was applied by about 0.1 μm with a cyan strike bath.

[0028]

Plating solutions of Examples 1 to 12 and Comparative Examples 1 to 7 were prepared with compositions described in Tables 1 and 2. 0.5 L of the prepared plating solution was blown up with a pump, the plating solution was applied to the object to be plated, which is masked while leaving a 1 cm square, a silver electroplating operation was performed until the silver film thickness reached 4 μm under the conditions described in Tables 1 and 2, and the object was washed with clean pure water, and then dried.

[0029]

For silver films of Examples 1 to 12 and Comparative Examples 1 to 7 obtained as described above, glossiness and arithmetic average roughness were measured. The glossiness referred to herein is a numerical value measured by a densitometer ND-11 manufactured by NIPPON DENSHOKU INDUSTRIES Co., Ltd. The arithmetic average roughness referred to herein is a value of arithmetic average roughness obtained by performing analysis at a magnification of 150 times using a profilometer laser microscope VK -9700 manufactured by KEYENCE CORPORATION. The measurement results are shown in Tables 1 and 2.

[0030]

The results of observing the silver films of Example 2 and Comparative Examples 6 and 7 with a scanning electron

microscope JSM-IT 300 HR manufactured by JEOL Ltd. are shown in Figs. 1 to 6.

[0031]

[Table 1]

(Table 1)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Silver potassium cyanide (as Ag) (g/L)	60	60	60	60	60	60	60	60	60	60	60	60
Potassium cyanide (g/L)	20	20	20									
Potassium phosphate (g/L)				20						10		
Potassium nitrate (g/L)					20					10		
Potassium citrate (g/L)						20				10		
Potassium tartrate (g/L)								40		10		
Potassium thiocyanate (g/L)				50	50	150	150				100	100
Potassium sulfate (g/L)									40	10		
Boric acid (g/L)					10					10		
Potassium thiosulfate (g/L)	100	100	100	20			3	20		30		
Sodium thiosulfate (g/L)					30	3			20		100	100
Liquid temperature (°C)	60	60	60	60	60	60	60	60	60	60	60	60
Current density (ASD)	50	70	90	50	70	50	70	50	70	70	50	70
Plating time (second(s))	8	5.7	4.4	8	5.7	8	5.7	8	5.7	5.7	8	5.7
Glossiness	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Arithmetic average roughness (µm)	0.81	0.85	0.63	0.65	0.54	0.38	0.30	0.64	0.56	0.65	0.88	1.04

[0032]

[Table 2]

(Table 2)

	Comp. Example 1	Comp. Example 2	Comp. Example 3	Comp. Example 4	Comp. Example 5	Comp. Example 6	Comp. Example 7
Silver potassium cyanide (as Ag) (g/L)	60	60	60	60	60	60	60
Potassium cyanide (g/L)	30						
Potassium phosphate (g/L)		30				20	
Potassium nitrate (g/L)			30				
Potassium citrate (g/L)				30			
Potassium tartrate (g/L)					30		
Potassium thiocyanate (g/L)						10.0	50.0
Potassium sulfate (g/L)						10.0	
Boric acid (g/L)				10.0	10.0	10.0	
Potassium thiosulfate (g/L)							1.0
Sodium thiosulfate (g/L)					10.0	100.0	
Liquid temperature (°C)	60	60	60	60	60	60	60
Current density (ASD)	50	70	70	70	50	50	70
Plating time (second(s))	8	5.7	5.7	5.7	8	8	5.7
Glossiness	0.34	0.32	0.23	0.18	0.00	0.00	0.00
Arithmetic average roughness (μm)	0.23	0.28	0.26	0.20	0.23	0.25	0.24

[0033]

All of the silver films obtained in Examples 1 to 12 had a glossiness of 0.0 and an arithmetic average roughness of 0.30 μm or more. The color tone was white, and a good appearance without unevenness was obtained. As illustrated in Figs. 1 and 2, massive crystals were uniformly precipitated. Bath stability was also good.

[0034]

All of the silver films obtained in Comparative Examples 1 to 4 had a glossiness of 0.1 or more and an arithmetic average roughness of less than 0.30 μm . The color tone was white, and a good appearance without unevenness was obtained. Bath stability was also good.

[0035]

The silver films obtained in Comparative Examples 5 and 6 both had a glossiness of 0.0 and an arithmetic average roughness of less than 0.30 μm . The color tone was white, and a good appearance without unevenness was obtained. Bath stability was also good.

Although the present inventor has found that the silver plating is roughened even when an iodide salt is used instead of thiosulfuric acid (salt), as illustrated in Figs. 3 and 4, needle-shaped and plate-shaped silver crystals are precipitated, and the appearance is hardly enough for a uniform appearance as long as it is confirmed with an electron microscope.

[0036]

The silver film obtained in Comparative Example 7 had a glossiness of 0.0 and an arithmetic average roughness of

less than 0.30 μm . The color tone was white, and a good appearance without unevenness was obtained. In addition, as illustrated in Figs. 5 and 6, the crystal sizes were sparse. The bath stability was good.

CLAIMS

1. A silver electroplating solution comprising:
10 to 100 g/L of silver cyanide or silver cyanide salt
in terms of silver;
1 to 200 g/L of electrically conductive salt; and
3 to 500 g/L of thiosulfuric acid or a salt thereof.
2. The silver electroplating solution according to claim 1,
wherein the electrically conductive salt is at least one
selected from the group consisting of cyanate, phosphate,
pyrophosphate, nitrate, citrate, tartrate, thiocyanate,
sulfate, and boric acid or a salt thereof.
3. The silver electroplating solution according to claim 1,
wherein pH (25°C) is 7.0 to 13.0.