A silver plating solution is provided. The silver plating solution, including: a silver salt; a complexing agent, comprising ethylenediamine and potassium ferrocyanide; a surfactant, comprising peregual; and an addition agent, comprising benzotriazole; wherein the value of pH of the silver plating solution is 7.8 to 9.6. A method of silver plating by chemical replacement is provided, including: placing the workpiece to be plated into the silver plating solution, wherein the silver plating solution is the silver plating solution of the present disclosure.
Silver plating solution and method of silver plating by chemical replacement

Cross-reference to related application

This application claims priority to, and benefits of Chinese Patent Application Serial No. 201310375535.2, filed with the State Intellectual Property Office of P. R. C. on August 26, 2013, the entire content of which is incorporated herein by reference.

Field

Exemplary embodiments of the present disclosure relate generally to a chemical plating field, and more particularly to a chemical silver plating solution and a method of silver plating by chemical replacement.

Background

The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

Silver has a lot of good characteristics, such as good weldability, weather fastness and electrical conductivity, therefore the technology of using chemical silver plating to protect the copper substrate has been applied in the field of printed circuit board. At present, there are two kinds of common methods of chemical silver plating on the copper substrate: 1. redox chemical silver plating method; 2. chemical replacement silver plating method. A reductant is required in the redox chemical silver plating method, so that the silver plating solution is unstable. A sensitization on the metal substrate is required, and the cost of production is high, therefore the chemical replacement silver plating method is superior to the redox chemical silver plating method. Edipotassium cyanide is used as a complexing agent in the silver plating solution to improve the stability of the silver plating solution, but the edipotassium cyanide is highly toxic, which may pollute the environment. In the chemical replacement silver plating method, the copper reacts with the silver ions in the silver plating solution to make silver plating on the surface of the copper, just because the metallic activity of the copper is higher than that of the silver. At present, the congeneric potion mainly has strong acid, which may etch the substrate, make the plating layer
rough and cannot meet the requirement of the precision improvement of the related products in the electron field.

CN101182637A has disclosure an alkalescent chemical silver electroless plating solution, which comprises: 0.01-20 g/L silver ion or silver complex ion, 0.1-150 g/L amine complexing agent, 0.1-150 g/L amino acids complexing agent, and 0.1-150 g/L polyhydroxy acids complexing agent. The alkalescent chemical silver plating solution provided of CN101 182637 has a poor stability, low utilization, and the plating layer is easy to be oxidized to yellowing.

SUMMARY

Embodiments of the present disclosure seek to solve at least one of the problems. A silver plating solution may be provided, which may be fine and smooth and have burnish of plating.

According to a first aspect of the present disclosure, a silver plating solution is provided. The silver plating solution includes: a silver salt; a complexing agent, comprising ethylenediamine and potassium ferrocyanide; a surfactant, comprising peregal; and an addition agent, comprising benzotriazole; wherein the pH value of the silver plating solution is about 7.8 to about 9.6.

According to a second aspect of the present disclosure, a method of silver plating by chemical replacement is provided. The method of silver plating by chemical replacement includes: contacting a workpiece to be plated with a silver plating solution according to the present disclosure to form a silver layer on the workpiece.

Thus, with the silver plating solution according to the present disclosure, by adding the ethylenediamine and potassium ferrocyanide as a complexing agent, and adding the nonionic surfactant peregal and the addition agent benzotriazole, which may act as a chemical reaction bridge to cut down the surface tension and the surface free energy of the workpiece, the silver ion of the silver plating solution may fully contact with the metal on the surface of the workpiece to form a fine and smooth silver layer which has a metallic lustre, and a plurality of layers of protective films may be formed on the surface of the silver layer, thus an oxidation reduction may not happen on the surface of the silver layer and the anti-corrosion and stability of the surface of the silver layer may be improved. In the meantime, the stability of the silver plating solution may be improved.

Additional aspects and advantages of embodiments of present disclosure will be given in part
in the following descriptions, become apparent in part from the following descriptions, or be learned from the practice of the embodiments of the present disclosure.

DETAILED DESCRIPTION

Reference will be made in detail to embodiments of the present disclosure. The embodiments described herein with reference to drawings are explanatory, illustrative, and used to generally understand the present disclosure. The embodiments shall not be construed to limit the present disclosure. The same or similar elements and the elements having same or similar functions are denoted by like reference numerals throughout the descriptions.

According to a first aspect of the present disclosure, a silver plating solution is provided. The silver plating solution includes: a silver salt; a complexing agent, comprising ethylenediamine and potassium ferrocyanide; a surfactant, comprising peregal; and an addition agent, comprising benzotriazole; wherein the pH value of the silver plating solution is about 7.8 to about 9.6.

With the silver plating solution according to the present disclosure, by adding the ethylenediamine and potassium ferrocyanide as a complexing agent, and adding the nonionic surfactant peregal and the addition agent benzotriazole, which may act as a chemical reaction bridge to cut down the surface tension and the surface free energy of the workpiece, the silver ion of the silver plating solution may fully contact with the metal on the surface of the workpiece to form a fine and smooth silver layer which has a metallic lustre, and a plurality of layers of protective films may be formed on the surface of the silver layer, thus an oxidation reduction may not happen on the surface of the silver layer and the anti-corrosion and stability of the surface of the silver layer may be improved. In the meantime, the stability of the silver plating solution may be improved.

Specially, silver salt is taken as the main salt of the silver plating solution of the present disclosure, and used for providing silver ions. In the present disclosure, there is no special limit on the silver salt, it may be any common silver salt used in the prior redox chemical silver plating solution or chemical replacement silver plating solution, for example, the silver salt is at least one selected from a group consisting of silver nitrate, methanesulfonic acid silver, arachidonic acid silver and silver iodide. In order to ensure that the chemical replacement goes on smoothly, the silver salt is preferably selected of methanesulfonic acid silver, but not limited to. The content of
the silver salt may be a common content of the silver salt of the prior chemical replacement silver plating solution, preferably, in the present disclosure, the silver plating solution includes the silver salt having a concentration of about 0.1 g/L to about 12 g/L.

The inventors of the present disclosure have unexpectedly found that, in the chemical replacement silver plating solution of the present disclosure, in order to get a better plating layer, ethylenediamine and potassium ferrocyanide are used together as a complexing agent. In which, the ethylenediamine reacts with the silver ion, so as to make the silver ion exist in the form of complex, avoid hydroxide and oxide, thus making the solution more stable. The potassium ferrocyanide reacts with the silver ion to make the bath solution of the silver plating solution more stable and have a good dispersing ability, and the plating layer may be more smooth and bright after a codeposition of the bath solution and the silver plating layer. Advantageously, the silver plating solution includes the ethylenediamine having a concentration of about 0.1 g/L to about 2.5 g/L, the potassium ferrocyanide having a concentration of about 0.1 ppm to about 10 ppm.

In the silver plating solution of the present disclosure, the complexing agent may further include other common complexing agents, such as water-soluble citrate having a concentration of about 0.2 g/L to about 12 g/L.

In the present disclosure, the peregal takes a role of surfactant. Peregal, such a good non-ionic surfactant, has a relative good emulsification, foaming, wettability, strong resistance to hard water, a good stability, and a good dispersibility. The inventors of the present disclosure have unexpectedly found that, the peregal and the potassium ferrocyanide are both used in the silver plating solution of the present disclosure, so as to make the plating layer more smooth and bright after chemical silver plating. The inventors of the present disclosure found that, the peregal reacts with the potassium ferrocyanide in the process of chemical silver plating, so as to get a more smooth, brighter silver layer, which has a good metallic lustre, besides that, the adhesion between the plating layer and the workpiece to be plated may be improved. Advantageously, in the silver plating solution of the present disclosure, the peregal has a concentration of about 1 ppm to about 20 ppm.

According to the present disclosure, the surfactant may further include other common surfactants, such as an anionic surfactant, which has a good wettability to cut down the surface tension of the workpiece, thus accelerates the silver plating. In which, the anionic surfactant
includes, but not limited to, at least one of lauryl sodium sulfate and sodium dodecyl benzene sulfonate.

As discussed above, the silver plating solution includes an addition agent, including benzotriazole, which may prevent the silver from changing colour in the reaction. Advantageously, the silver plating solution includes the benzotriazole having a concentration of about 0.2 ppm to about 10 ppm.

According to the present disclosure, the addition agent further includes a eerie sulfate. The codeposition of the eerie sulfate with the plating layer may make the plating layer smoother and brighter. Advantageously, the silver plating solution includes the eerie sulfate having a concentration of about 0.1 ppm to about 10 ppm.

In the present disclosure, the silver plating solution is alkalescent, and the pH value of the silver plating solution is about 7.8 to about 9.6. When preparing the silver plating solution of the present disclosure, firstly other constituents are mixed together uniformity, and then the pH-modifier is added to adjust the pH value during about 7.8 to about 9.6. Therefore, the silver plating solution of the present disclosure further includes a pH-modifier to adjust the pH value of the silver plating solution of the present disclosure, and the pH-modifier is at least one selected from a group consisting of sodium hydroxide and potassium hydroxide. Then content of the pH-modifier may be selected according to the pH value of the reaction system.

According to a second aspect of the present disclosure, a method of silver plating by chemical replacement is provided. The method of silver plating by chemical replacement includes: contacting a workpiece to be plated with a silver plating solution according to the present disclosure to form a silver layer on the workpiece.

In order to get a better effect, preferably, the plating temperature of the silver plating solution ranges from about 46 °C to about 55 °C, and the workpiece is plated in the silver plating solution for about 5 minutes to about 12 minutes.

In order to protect the silver plating layer, preferably, the method of silver plating by chemical replacement further includes protecting the silver layer after the contacting. The protecting includes forming an organic protective membrane by combining the coordination compound (such as benzotriazole, benzoazotetrazolium, or 1-dodecanethiol) together with the silver via a chemical bond, thus preventing the silver layer from being corroded by sulfide.
In order to make the silver plating layer have a better adhesion, the step of the pretreatment of the method of silver plating by chemical replacement further includes subjecting the workpiece to a pretreatment before the contacting. Washing several times after at least one of degreasing and acid etching.

Although explanatory embodiments have been shown and described, it would be appreciated by those skilled in the art that the above embodiments cannot be construed to limit the present disclosure, and changes, alternatives, and modifications can be made in the embodiments without departing from spirit, principles and scope of the present disclosure.

Example 1

A silver plating solution according to a first embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 0.1 g/L, sodium citrate at a concentration of 0.2 g/L, ethylenediamine at a concentration of 0.1 g/L, eerie sulfate at a concentration of 0.1 ppm, potassium ferrocyanide at a concentration of 0.1 ppm, benzotriazole at a concentration of 0.2 ppm, lauryl sodium sulfate at a concentration of 5 ppm and peregal at a concentration of 1 ppm. In the chemical plating process, the pH value of the silver plating solution was adjusted to 9.6 by 40 wt% sodium hydroxide solution to obtain a silver plating solution Al.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution Al was heated to a temperature of 53 °C, and then the workpiece after step 2 was plated at a temperature of 53 °C by using this silver plating solution Al for 10 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzoctetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample SI.

A process of water washing several times was processed between the above steps.
Example 2

A silver plating solution according to a second embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution is adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A2.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A2 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution A2 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S2.

A process of water washing several times was processed between the above steps.

Example 3

A silver plating solution according to a third embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 12 g/L, sodium citrate at a concentration of 12 g/L, ethylenediamine at a concentration of 2.5 g/L, eerie sulfate at a concentration of 10 ppm, potassium ferrocyanide at a concentration of 10 ppm, benzotriazole at a concentration of 10 ppm, lauryl sodium sulfate at a concentration of 25 ppm and peregal at a concentration of 20 ppm. In the chemical plating process, the pH value of the silver plating
solution was adjusted to 7.8 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A3.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A3 was heated to a temperature of 48 °C, and then the workpiece after step 2 was plated at a temperature of 48 °C by using this silver plating solution A3 for 6 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S3.

A process of water washing several times was processed between the above steps.

**Example 4**

A silver plating solution according to a fourth embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution is adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A4.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A4 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution A4 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S5.

A process of water washing several times was processed between the above steps.

Example 5

A silver plating solution according to a fifth embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution was adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A5.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A5 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution A5 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S5.

A process of water washing several times was processed between the above steps.
Example 6

A silver plating solution according to a sixed embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution was adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A6.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A6 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution A6 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S6.

A process of water washing several times was processed between the above steps.

Example 7

A silver plating solution according to a seventh embodiment was described with the components and amounts as follows: arachidonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution is adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A7.
1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A7 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution A7 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S7.

A process of water washing several times was processed between the above steps.

Example 8

A silver plating solution according to a eighth embodiment was described with the components and amounts as follows: silver nitrate at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution was adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution A8.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution A8 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution A8 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty
alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample S8.

A process of water washing several times was processed between the above steps.

**Comparative Example 1**

The silver plating solution of this comparative example 1 was the silver plating solution according to the example 1 of CN101182637A, then a silver plating sample CSI was formed after chemical silver plating.

**Comparative Example 2**

A silver plating solution according to a second comparative embodiment is described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm and peregal at a concentration of 8 ppm. In the chemical plating process, the pH value of the silver plating solution was adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution CA2.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution CA2 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution CA2 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample CS2.

A process of water washing several times was processed between the above steps.
Comparative Example 3

A silver plating solution according to a third comparative embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, potassium ferrocyanide at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm. In the chemical plating process, the pH value of the silver plating solution was adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution CA3.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution CA3 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution CA3 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample CS3.

A process of water washing several times was processed between the above steps.

Comparative Example 4

A silver plating solution according to a fourth comparative embodiment was described with the components and amounts as follows: methanesulfonic acid silver at a concentration of 2 g/L, sodium citrate at a concentration of 4 g/L, ethylenediamine at a concentration of 1 g/L, eerie sulfate at a concentration of 3 ppm, benzotriazole at a concentration of 5 ppm, lauryl sodium sulfate at a concentration of 12 ppm. In the chemical plating process, the pH value of the silver
plating solution was adjusted to 8.9 by 40 wt% sodium hydroxide solution to obtain a silver plating solution CA4.

1. Degreasing: the copper workpiece to be plated was degreased under ultrasonic;
2. Acid etching: the workpiece after step 1 was soaked into diluent acid to remove out the surface oxide layer of the workpiece to be plated;
3. Chemical silver plating: the silver plating solution CA4 was heated to a temperature of 50 °C, and then the workpiece after step 2 was plated at a temperature of 50 °C by using this silver plating solution CA4 for 9 minutes;
4. Protective treatment: the workpiece after step 3 was put in a silver protective agent with a temperature of 44 °C for 3 minutes, wherein the silver protective agent included fatty alcohol-polyoxyethylene ether at a concentration of 14 wt%, benzotetrazolium at a concentration of 4 wt%, benzotriazole at a concentration of 4 wt%, 1-dodecanethiol at a concentration of 6 wt%, and remainder of water; then dried to form a silver plating sample CS4.

A process of water washing several times was processed between the above steps.

Performance Test

1. Appearance

The surface of each of the samples S1-S8, CS1-CS4 was observed with an optical magnifying glass under a magnification value of 400. The results on the appearance were recorded in Table 1.

2. Adhesion

The adhesion of the plating layers of the samples S1-S8, CS1-CS4 was tested with a Cross-Cut Tester according to the method of ASTM D3359, under the conditions: separation distance of 1 mm, pull-up angle of 60°, an adhesive tape of 3M600. The results on the adhesion were recorded in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Appearance</th>
<th>Adhesion/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>smooth, bright</td>
<td>5</td>
</tr>
<tr>
<td>S2</td>
<td>smooth, bright</td>
<td>5</td>
</tr>
</tbody>
</table>
Referring to Table 1, it can be seen that the surface of the samples prepared according to the embodiments of the present disclosure was smooth and bright, and the surface of the samples prepared according to the comparative examples was darkly.

Referring to Examples 1-3 and Examples 4-6, it can be seen that when using any one of sodium citrate, eerie sulfate or lauryl sodium sulfate, the quality of the plating layer may be better. Referring to Examples 1-3 and Examples 7-8, it can be seen that when using the methanesulfonic acid silver as the silver salt, the quality of the plating layer may be better. Compared to the above comparative examples, using a chemical silver plating solution provided by an example of the present disclosure resulted in overcoming problems existing in the chemical silver plating processes commonly used at present.

Reference throughout this specification to "an embodiment," "some embodiments," "one embodiment", "another example," "an example," "a specific example," or "some examples," means that a particular feature, structure, material, or characteristic described in connection with the embodiment or example is included in at least one embodiment or example of the present disclosure. Thus, the appearances of the phrases such as "in some embodiments," "in one embodiment", "in an embodiment", "in another example," "in an example," "in a specific example," or "in some examples," in various places throughout this specification are not necessarily referring to the same embodiment or example of the present disclosure. Furthermore,
the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments or examples.

Although explanatory embodiments have been shown and described, it would be appreciated by those skilled in the art that the above embodiments cannot be construed to limit the present disclosure, and changes, alternatives, and modifications can be made in the embodiments without departing from spirit, principles and scope of the present disclosure.
WHAT IS CLAIMED IS:

1. A silver plating solution, comprising:
   a silver salt;
   a complexing agent, comprising ethylenediamine and potassium ferrocyanide;
   a surfactant, comprising peregal; and
   an addition agent, comprising benzotriazole; wherein
   the value of pH of the silver plating solution is about 7.8 to about 9.6.

2. The silver plating solution of claim 1, wherein the silver plating solution comprises the silver salt at a concentration of about 0.1 g/L to about 12 g/L, the ethylenediamine at a concentration of about 0.1 g/L to about 2.5 g/L, the potassium ferrocyanide at a concentration of about 0.1 ppm to about 10 ppm, the peregal at a concentration of about 1 ppm to about 20 ppm, and the benzotriazole at a concentration of about 0.2 ppm to about 10 ppm.

3. The silver plating solution according to claim 1 or 2, wherein the silver salt is at least one selected from a group consisting of silver nitrate, methanesulfonyl acid silver, arachidonic acid silver and silver iodide.

4. The silver plating solution according to claim 1 or 2, wherein the complexing agent further comprises a water-soluble citrate having a concentration of about 0.2 g/L to about 12 g/L.

5. The silver plating solution according to claim 1 or 2, wherein the surfactant further comprises an anionic surfactant having a concentration of about 5 ppm to about 25 ppm.

6. The silver plating solution according to claim 5, wherein the anionic surfactant comprises at least one of lauryl sodium sulfate and sodium dodecyl benzene sulfonate.
7. The silver plating solution according to claim 1 or 2, wherein the addition agent further comprises a eerie sulfate having a concentration of about 0.1 ppm to about 10 ppm.

8. The silver plating solution according to claim 1 or 2, wherein the silver plating solution further comprises a pH-modifier, and the pH-modifier is at least one selected from a group consisting of sodium hydroxide and potassium hydroxide.

9. A method of silver plating by chemical replacement, comprising:

contacting a workpiece to be plated with a silver plating solution according to any one of claims 1-8 to form a silver layer on the workpiece.

10. The method according to claim 9, wherein the temperature of the silver plating solution ranges from about 46 °C to about 55 °C, and the workpiece is plated in the silver plating solution for about 5 minutes to about 12 minutes.

11. The method according to claim 9, further comprising protecting the silver layer after the contacting.

12. The method according to claim 11, wherein the protecting comprises forming an organic protective membrane by combining the coordination compound with the silver via a chemical bond.

13. The method according to claim 9, further comprising subjecting the workpiece to a pretreatment before the contacting.

14. The method according to claim 13, wherein the pretreatment comprises at least one of degreasing and acid etching.
### A. CLASSIFICATION OF SUBJECT MATTER
C23C 18/42(2006.01)j

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)

CPRS, WIPO, EPDOC, CNTXT, TWTXT, CNKI: sliver, plat+, displac+, electroless w plat+, chemical w plat+, ferrocyanide

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search: 29 October 2014
Date of mailing of the international search report: 21 November 2014

Name and mailing address of the ISA/CN

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Authorized officer: WANG, Aohan

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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