United States Patent [15] **3,644,184**

Smith et al. [45] **Feb. 22, 1972**

[54] ELECTROLYTIC GOLD PLATING SOLUTIONS AND METHODS FOR USING SAME

[72] Inventors: **Paul T. Smith**, Pascoag; **Augustus Fletcher**, Coventry, both of R.I.

[73] Assignee: **Sel-Rex Corporation**, Nutley, N.J.

[22] Filed: **June 29, 1970**

[21] Appl. No.: **50,969**

[52] **U.S. Cl.** **204/46**

[51] **Int. Cl.** **C23b 5/28**

[58] **Field of Search** ....204/46, 43, 110, 123; 106/1; 117/130 E

[56] **References Cited**

UNITED STATES PATENTS

3,562,120	2/1971	Duva et al.	204/46

Primary Examiner—G. L. Kaplan
Attorney—Stanley H. Lieberstein

[57] ABSTRACT

Electrolytic solutions containing gold and small amounts of thallium wherein the solution is neutral or alkaline yield uniformly deposited gold platings possessing good aesthetic qualities and having good attachability to surfaces. Thallium inclusion in the range of from about 1 to 140 milligrams per liter of solution are especially suitable.

10 Claims, No Drawings

ELECTROLYTIC GOLD PLATING SOLUTIONS AND METHODS FOR USING SAME

This invention relates to electrodeposition processes and eo electrolytic baths used therein. More particularly, it relates to novel compositions used in, and novel methods for, electrodepositing gold.

BACKGROUND OF THE INVENTION

In many fields, and especially in the semiconductor field, it is frequently desired to gold plate small parts as a precursor to further fabrication. The art has encountered significant difficulty in plating such small parts since frequently the gold is not uniformly distributed on the part. This problem is particularly aggravated where the parts are irregularly shaped or have small protrusions or sharp angles. In order to compensate for this deficiency of the art process, it has become necessary to "overplate" the part such that those areas which otherwise would receive little or no plating are plated to some extent. Attending this, of course, is the concurrent deposition of too much gold in those areas that would ordinarily receive good deposition.

As will be appreciated, the uneven distribution which results from the attempts described above constitutes economic waste. Indeed, the approach is not itself a suitable solution to the problem, since, very often bare spots and minimum plated spots are encountered resulting in materials which are unpredictable and inconsistent in respect of their properties of heat resistance and attachability.

It is apparent that the art is in need of means for obtaining uniformly distributed gold plate which at the same time possesses desirable properties of color, finish and grain size and is attachable to other surfaces.

In U.S. Pat. application, Ser. No. 577,618, now U.S. Pat. No. 3,562,120, filed Sept. 7, 1966 and assigned to the same assignee as that of the instant specification, there is described an electrolytic process and bath which overcomes many of the disadvantages referred to above. In that application, the gold plating process is described as being carried out in a bath which contains from 0.001 to 25 grams of thallium (calculated as the metal) in addition to the gold, and has a pH in the range of from 3 to 6. The combination of the specified amount of thallium with the pH characteristics results in an electrolytic solution from which uniform, smooth electrodepositions are formed. The thallium is present in solution in the form of its ion and is provided in the bath via soluble thallium salts.

Several advantages are described in said pending application resulting from the inclusion of the stated amount of thallium and operating the bath within the pH range recited. For example, pure gold deposits which are uniformly distributed over small irregularly shaped pieces were obtained without the codeposition of thallium into the plate (except for possible trace amounts of the metal).

In accordance with the present invention it has now been discovered that the presence of very small amounts of thallium in a neutral or alkaline gold containing electrolyte solution, facilitates the uniform deposition of gold plate, especially onto small, irregularly shaped pieces. Moreover, a smooth, lemon yellow colored plate is obtained without the codeposition of thallium. This is all the more surprising in view of the fact that the art indicates that a thallium-containing bath would result in the formation of a gold-thallium alloy. For example, in U.S. Pat. No. 2,393,905 the patentee describes the formation of a thallium-gold alloy to serve as a new bearing composition. The alloy is said to be producible by electrodeposition. This is consistent with other art which further shows electrodeposition of thallium from a bath. Such codeposited thallium alloys are extremely undesirable in some areas of application. This is especially true in semiconductor areas where the plated surface will subsequently be attached to other pieces. The alloy is not readily attachable and is therefore not of significant use.

To the contrary however, the present invention is based on the discovery that small amounts of thallium in the electrolytic solution employed within a defined pH range have a beneficial effect on the gold deposit, providing a plate of acceptable aesthetic qualities as well as one which is uniformly distributed and readily attachable to other surfaces. By small amounts is meant not more than 140 mg./l. and preferably between 3 to 50 milligrams of thallium per liter of plating solution. In order to obtain the benefits of the invention, these limits should be observed since operation outside of this range and especially on the high side, yields gold deposits which are unsuitable in one or more of several respects, especially in attachability to other surfaces. The gold present in the electrolytic solution of the present invention is added in the form of the gold-cyanide double salt of an alkali metal. Typically, potassium or sodium gold-cyanide are employed. The bath may contain sufficient gold to perform under the conditions desired by the plater but ordinarily the amount present in the bath is suitably in the range of from 1 to 75 grams per liter and preferably 8 to 12 grams per liter.

The electrolytic bath also contains sufficient conducting and buffering materials to give a pH in the range of at least 6.5 and preferably from about 7 to about 13. The advantages of the invention are best obtained from baths having a pH on the alkaline side, that is in the range of from about 10 to 12 and this constitutes the most preferred mode of the invention. The desired pH may be obtained in a variety of ways known to those skilled in the art. For example, if the inherent pH of the bath is within the desired range, then additional buffer materials need not be supplied. If, however, the pH is either too high or too low, appropriate acidic or basic materials can be added to reach the desired pH. As acidic materials there may be mentioned inorganic acids such as hydrochloric acid, hydrobromic acid, phosphoric acid and the like, or organic acids, especially weak acids such as formic acid, citric acid, acetic acid, tartaric acid, gluconic acid, and the like. These may be employed singly or in combination. Additionally, they may be employed as partially neutralized materials using alkaline reactants such as ammonium or alkali metal hydroxides and carbonates such as ammonium, sodium or potassium hydroxides, ammonium carbonate and the like.

Where it is desired to utilize alkaline materials to raise the pH, such alkaline materials as are mentioned above are suitable. Sodium hydroxide or potassium hydroxide are preferred but the particular ones used are within the discretion of the plater. Whether acidic or basic materials are added, the actual amounts of buffering materials should be such as to obtain the desired pH. These amounts will therefore vary depending upon the particular system used.

It has also been observed that the amount of thallium used is somewhat related to the pH of the solution. For example, at lower pH's the higher range of thallium is preferred whereas somewhat less thallium is desired for the higher pH's within the ranges stated.

As suitable sources of thallium there may be mentioned the soluble thallous and thallic salts such as the sulfides, chlorides, nitrates, fluosilicates and the like.

The electrolytic solution may contain other materials as desired such as conducting salts and the like, which may also act in the capacity of buffering materials. For example, it is suitable to provide one or more of the sulfate, sulfamate, formate, acetate, citrate, lactate, tartrate, fluoroborate, borate, or phosphate ions, or the like. These may be provided in the form of a suitable metal salt. When used, suitable results are obtained at levels ranging from 10 to 500 g. of the salt per liter of plating solution. Of course, if the desired pH in the bath is obtained inherently from such materials it may be unnecessary to add additional buffering and conducting materials. Additionally, the use of these salts, and others is desirable when an alloy of electrodeposited gold is sought such as is obtained by adding from 0–100 g./l. of alum to produce a 24 karat gold alloy.

The electrolytic solutions of the present invention are utilized in the electroplating process at current densities suitably in the range of 1 to 200 and preferably 2 to 10 amperes per square foot. The temperature of operation is preferably elevated, of the order of 100° to 180° F. Higher or lower temperatures may be employed if desired. For example, temperatures in range of from 50° to 180° F. are suitable.

The following examples are given to illustrate specific embodiments of the invention.

EXAMPLE I

A 24 karat gold plating electrolyte solution is formulated by dissolving the indicated materials in sufficient water to make 1 liter of solution.

Gold [as $KAu(CN)_2$]	12 grams
$Na_2H\ PO_4$	60 grams
Thallium (as Tl_2SO_4)	20 milligrams

The pH was adjusted to about 10.5. A header consisting of a cap having several small leads extending therefrom is plated at a temperature of around 140° F. at a current density of around 5 amps. per square foot. A smooth semibright 24 karat lemon-yellow gold deposit is obtained on the header. The deposit is uniformly distributed over the cap and small wire leads of the transistor header.

When the above procedure is followed without the thallium addition, a gold deposit results which has a bronze-orange matte surface and is nonuniform in thickness.

EXAMPLE II

The procedure of Example I is followed utilizing an electrolyte made from the following materials in sufficient water to make 1 liter of solution.

Gold [as $KAu(CM)_2$]	24 grams
$Na_2H\ PO_4$	60 grams
Trisodium citrate	60 grams
Thallium (as Tl_2SO_4)	140 milligrams

The pH of the solution was adjusted to 10.0. The plating is conducted at a temperature of around 150° F. at a current density of around 6 amps. per square foot yielding a 24 karat lemon-yellow gold deposit. The deposit is smooth and semibright, has a uniform gold thickness and exhibits good characteristics of attachability to gold-silicon dies.

Following the above procedure, but without the thallium addition, a bronze-orange matte deposit results which is nonuniform in thickness.

EXAMPLE III

The procedure of Example I is followed utilizing an electrolyte made from the following materials in sufficient water to make 1 liter of solution.

Gold [as $KAu(CN)_2$]	8 grams
Phosphoric acid	50 grams
Ammonium hydroxide	to pH 9.0
Thallium (as Tl_2SO_4)	15 milligrams

The plating is conducted at a temperature of around 150° F. at a current density of around 2 amps. per square foot yielding a 24 karat lemon-yellow gold deposit. The deposit is smooth and semibright, is uniform in thickness and exhibits good characteristics of attachability to gold-silicon dies.

Following the above procedure, but without the thallium addition, a bronze-orange matte deposit results which is nonuniform in thickness.

EXAMPLE IV

The procedure of Example I is followed utilizing an electrolyte made from the following materials in sufficient water to make 1 liter of solution.

Gold [as $KAu(CN)_2$]	16 grams
Diammonium citrate	50 grams
Potassium chrome alum	20 grams
Thallium (as Tl_2SO_4)	75 milligrams

The pH of the solution was adjusted to 10. The plating is conducted at a temperature of around 140° F. at a current density of around 5 amps. per square foot yielding a 24 karat lemon-yellow gold deposit. The deposit is smooth and semibright, is uniform in thickness and exhibits good characteristics of attachability to gold-silicon dies.

Following the above procedure, but without the thallium addition, a bronze-orange matte deposit results which is nonuniform in thickness.

What is claimed is:

1. An aqueous electrolytic cyanide-gold plating solution comprising a gold cyanide complex, from 1 to 140 milligrams of thallium per liter of plating solution and sufficient conducting and buffering materials to provide a pH in said solution of at least 6.5.

2. The solution of claim **1** wherein the gold cyanide ion is provided by way of the potassium or sodium gold cyanide double salt.

3. The solution of claim **2** wherein the conducting and buffering compounds comprise ammonium hydroxide, potassium hydroxide, sodium hydroxide or ammonium carbonate.

4. The solution of claim **1** wherein the pH is in the range of from 7 to 13.

5. The solution of claim **1** wherein the thallium is present at a level of from 3 to 50 milligrams per liter of solution.

6. The solution of claim **1** wherein there is additionally present from 0 to 100 grams of alum per liter of solution.

7. The process for plating gold which comprises electrolyzing the solution defined in claim **1**.

8. The process of claim **7** wherein the electrolysis is carried out at a current density of from about 1 to about 200 amps per square foot.

9. The process according to claim **8** wherein the electrolysis is carried out at a temperature in the range of from 100° to 180° F.

10. The process of claim **9** wherein the pH of the electrolytic solution is between 7 and 13.

* * * * *