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ELECTROLESS GOLD PLATING BATH AND PROCESS

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U.S. Cl. 106—1 17 Claims

ABSTRACT OF THE DISCLOSURE

A gold chemical plating bath is provided for depositing gold on a catalytic surface which is an aqueous solution having a pH of 1.5 to 5 and contains as essential ingredients a soluble gold compound and an alkali metal cyanoborohydride as the reducing agent. Optional, but preferred, ingredients are a chelating agent and an organic monovalent or divalent sulfur compound. Plating is preferably carried out at a temperature of 80 to 90° C.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to gold plating and more particularly to electroless gold plating baths and processes for the deposition of gold from such baths.

Prior art

A variety of applications for gold coatings exist in the electronics industry, where gold is specified because of its corrosion resistance and oxidation resistance. A substantial proportion of the gold deposited in these applications is applied by electrodeposition; however, this method of application is often difficult or impossible where the areas to be plated are discrete and isolated.

Where electroplated gold is difficult or impossible, electroless gold processes have been employed. There have been a number of electroless gold processes described in the art and W. Goldie in "Metallic Coating of Plastics," vol. I, Middlesex, England, Electrochemical Publications Ltd., 1968, pp. 99–103, describes a number of processes. For instance, the original approach to electroless gold was to use formaldehyde as the reducing agent. With gold cyanide plating solutions, sodium hypophosphite has been used as a reducing agent with citrates used as a complexing agent. Hydrazine, N,N-diethylglycine, citric acid and tartaric acid have also been used. However, some have considered some of these processes not to be true electroless gold processes (R. F. Bunshah, Techniques of Materials Preparation and Handling, part 3, pp. 1372–74, 1968) but to be immersion or displacement gold processes which are limited in the thickness and electrical resistance of the gold deposit obtained.

Recently in the art there has appeared another electroless gold process using an alkali metal borohydride or dimethylamine borane as the reducing agent in a bath prepared using potassium gold cyanide, potassium cyanide and potassium hydroxide, see Y. Okinaka, Plating, pp. 914–920 (1970). In British Pat. No. 1,058,915, gold is deposited by reducing a soluble gold salt with sodium borohydride or an amine borane. Cyanides can be added to enhance bath life. The major disadvantage of these processes, as well as those mentioned previously is that the plating rate is too slow to make them commercially attractive. Usually, the plating rate will be under 5 microns per hour.

SUMMARY OF THE INVENTION

According to the present invention there is provided a gold chemical plating bath comprising an aqueous

solution having a pH within the range of about 1.5 to 5, said solution containing as essential ingredients a soluble gold compound and an alkali metal cyanoborohydride.

There is also provided a process of chemically plating a catalytic surface with gold comprising contacting said surface with an aqueous solution having a pH within the range of about 1.5 to 5 at a temperature within the range of 25° C. up to the boiling point of the solution, said solution containing as essential ingredients a soluble gold compound and an alkali metal cyanoborohydride.

DETAILED DESCRIPTION OF THE INVENTION

Plating is accomplished by initially forming an aqueous plating solution having a pH of 1.5 to 5, preferably 2 to 4, which contains a soluble gold compound and an alkali metal cyanoborohydride. Gold can then be chemically deposited in uniform layers from such a solution on articles which have catalytic surfaces. There are preferred concentrations of the components in the solution in addition to temperature of operation and other factors which lead to optimum plating conditions. However, it is to be understood that gold can be plated chemically from a simple aqueous solution by reducing gold ions on a catalytic surface where the reduction is brought about by an alkali metal cyanoborohydride.

The term "catalytic surface" refers to the surface of any object which contains in whole or in part a material which promotes on its surface the reduction of gold ions. Such surfaces are readily known to those skilled in the art and include iron, steel, nickel, copper, silver, cobalt, platinum and palladium metals. Surfaces of glass, ceramics and plastics are, in general, noncatalytic but are rendered catalytic by known sensitization techniques or by bonding foils of catalytic metals to the noncatalytic surfaces.

An alkali metal cyanoborohydride is used in the solution as the gold ion reducing agent. Sodium cyanoborohydride is commercially available and, thus, is preferred although potassium cyanoborohydride is also suitable. The concentration of the cyanoborohydride in the aqueous solution is important to the rate of plating, but not determinative as to operativeness since the presence of minute amounts permits the plating of gold. High concentrations of cyanoborohydride such as a saturated aqueous solution also permit plating. As a practical matter, it is preferred to use the cyanoborohydride at a concentration of 0.1 to 10 grams per liter. A most preferred concentration is 0.1 to 5 grams per liter, and, generally, 0.25 to 2 grams per liter is adequate.

Gold ions are introduced into the aqueous solution by adding a desired amount of water-soluble gold salt such as the sulfate, chloride, acetate, formate or alkali metal gold cyanide. The concentration of the gold ions in solution is not critical and may vary over a wide range. As a practical matter, as little as possible should be used as long as an adequate plating rate is maintained. The rate of plating is slightly increased with increases in the concentration of gold ions. An initial concentration of from 0.02 to 0.5 gram mole per liter of salt is preferred.

While not an essential ingredient, it is preferred that the aqueous solution contain a chelating agent to tie up trace amounts of undesirable materials or impurities and also to buffer the pH. Chelating agents for electroless plating baths are well known and any one or a combination may be used. Among suitable chelating agents are citric acid, tartaric acid, glycolic acid and their alkali metal salts. The borates are also useful chelating agents. The amount added is essentially 1 mole for each mole of gold ion present in solution.

Another optional ingredient which can be added to the solution to increase its shelf life and stability is an organic monovalent or divalent sulfur compound. Suitable divalent compounds are disclosed in U.S. Pat. 3,234,031 issued to Eberhard Zirngiebl and Henry Gunter on Feb. 8, 1966. Only small amounts of sulfur compound need be added. For example, 0.001 to 5 grams per liter can be used, but usually there is no improvement to be gained from the higher concentrations. Thus, it is preferred to use a concentration of 0.01 to 1 gram per liter.

In conducting the actual plating operation to deposit gold on a catalytic surface, it is preferred to operate the bath at a temperature of 80 to 95° C., since the rate of plating increases with temperature. While this range is preferred, plating will occur at lower or higher temperatures; thus, the temperature can range between 25° C. up to the boiling point of the solution, but will usually be above 40° C.

The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

An aqueous plating bath was prepared containing 7 g./l. potassium gold cyanide and 30 g./l. citric acid, and 2 g./l. sodium cyanoborohydride. The pH of the bath was 3.5. It was found that above pH 5 there was no reduction to gold and below pH 1.5 the bath was unstable. The bath was used to plate copper and nickel foil (2.54 cm. x 7.62 cm.) at 90° C. The plating rate was constant at 0.1 mil/hour over a test period of 6 hours. There was gas evolution from the work piece observed and there was a weight increase of 58 mg. during the test period. A ceramic chip sensitized with palladium according to known procedures was also plated and was checked for electrical resistance during the plating operation. The electrical resistance was reduced from 127 ohms per square to 0.4 ohm per square after a coating of 0.1 mil in thickness was applied. Similar baths were prepared with 1,4 and 5 g./l. of sodium cyanoborohydride, respectively, and similar results were obtained.

EXAMPLE 2

An aqueous plating bath of pH 4 was prepared containing 10 g./l. gold chloride and 30 g./l. tartaric acid, and 2 g./l. sodium cyanoborohydride. A copper foil (2.54 cm. x 7.62 cm.) was plated in the bath at 90° C. with a plating rate of 0.05 mil/hour over a test period of 6 hours. The weight increase was 30 mg. Similar baths were prepared with 1,4 and 5 g./l. of sodium cyanoborohydride, respectively, and similar results were obtained.

EXAMPLE 3

An aqueous plating bath of pH 3.5 was prepared containing 10 g./l. potassium gold cyanide, 30 g./l. citric acid, 0.01 g./l. thiodiglycolic acid, and 2 g./l. sodium cyanoborohydride. Copper foil (2.54 cm. x 7.62 cm.) was plated as in Example 1 and gold was deposited on the copper with no decomposition of the baths after continuously plating over a period of 24 hours. Similar baths were prepared with 1,4 and 5 g./l. of sodium cyanoborohydride, respectively, and similar results were obtained. Similar results were obtained when 0.01 g./l. of mercapto acetic acid was used in place of the thiodiglycolic acid in the bath containing 2 g./l. sodium cyanoborohydride.

What is claimed is:

1. A gold chemical plating bath comprising an aqueous solution having a pH within the range of about 1.5 to 5, said solution containing as essential ingredients a water-soluble salt of gold and an alkali metal cyanoborohydride.

2. The chemical plating bath of claim **1** wherein the water-soluble gold salt is present at a concentration of 0.02 to 0.5 mole per liter.

3. The chemical plating bath of claim **2** wherein the water-soluble gold salt is an alkali metal gold cyanide or a gold salt of a mineral or aliphatic acid.

4. The chemical plating bath of claim **3** wherein the alkali metal cyanoborohydride is sodium cyanoborohydride.

5. The chemical plating bath of claim **1** wherein the alkali metal cyanoborohydride is present at a concentration of 0.1 to 10 grams per liter.

6. The chemical plating bath of claim **2** wherein the alkali metal cyanoborohydride is present at a concentration of 0.1 to 5 grams per liter.

7. The chemical plating bath of claim **6** wherein the water-soluble gold salt is an alkali metal gold cyanide or a gold salt of a mineral or aliphatic acid.

8. The chemical plating bath of claim **7** wherein the alkali metal cyanoborohydride is sodium cyanoborohydride present at a concentration of 0.25 to 2 grams per liter.

9. A process of chemically plating a catalytic surface with gold comprising contacting said surface with an aqueous solution having a pH within the range of about 1.5 to 5 at a temperature within the range of 25° C. up to the boiling point of the solution, said solution containing as essential ingredients a water-soluble salt of gold and an alkali metal cyanoborohydride.

10. The process of claim **9** wherein the temperature is within the range of 80 to 95° C.

11. The process of claim **1** wherein the water-soluble gold salt is present at a concentration of 0.02 to 0.5 mole per liter and the alkali metal cyanoborohydride is present at a concentration of 0.1 to 10 grams per liter.

12. The process of claim **11** wherein the catalytic surface is the surface of a metal object.

13. The process of claim **12** wherein the alkali metal cyanoborohydride is sodium cyanoborohydride present at a concentration of 0.1 to 5 grams per liter.

14. The process of claim **12** wherein the surface of a metal object is of iron, steel, nickel, copper, silver cobalt, platinum and palladium.

15. The process of claim **11** wherein the solution additionally contains a chelating agent.

16. The chemical plating bath of claim **6** wherein the solution additionaly contains chelating agent and from 0.001 to 5 grams per liter of at least one organic monovalent or divalent sulfur compound as a bath stabilizer.

17. The chemical plating bath of claim **16** wherein the chelating agent is citric acid, tartaric acid, and glycolic acid.

References Cited

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LORENZO B. HAYES, Primary Examiner

U.S. Cl. X.R.

117—47 A, 130 E, 130 B, 160

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,697,296 Dated October 10, 1972

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 36, "claim 1" should be -- claim 10 --.

Column 4, line 37, "0.02 o 0.05" should be -- 0.02 to 0.05 --.

Column 4, line 51, "additionaly" should be -- additionally --.

Signed and sealed this 29th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents