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ELECTROLESS COPPER PLATING

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Int. Cl. C23c 3/02
U.S. Cl. 106—1 8 Claims

ABSTRACT OF THE DISCLOSURE

This invention is for an improved electroless copper plating solution containing as a stabilizer, a member selected from the group of iodobenzoic acid, amino methane sulfonic acid and mixtures thereof.

BACKGROUND OF THE INVENTION

1. Introduction

This invention relates to autocatalytic electroless deposition of copper and has for its principal object, provision for an improved copper plating solution and deposition methods employing the same.

2. Description of the Prior Art

Electroless copper plating refers to the chemical reductive plating of copper over an active surface in the absence of an external electric current. Such processes and compositions useful therefor are known and are in substantial commercial use. They are disclosed in a number of prior art patents, for example, U.S. Pats. Nos. 3,457,089 and 3,708,329.

Known electroless copper solutions comprise four ingredients dissolved in water. These are (1) source of cupric ions, usually copper sulfate, (2) formaldehyde as a reducing agent therefor, (3) alkali, generally alkali metal hydroxide and usually sodium hydroxide, sufficient to provide the required pH at which said compositions are effective and (4) a complexing agent for the copper sufficient to prevent its precipitation in alkaline solution. A large number of suitable complexing agents are known and are described, for example, in the above cited patents and also in U.S. Pats. Nos. 2,874,072; 3,075,855; 3,075,856; and 3,119,709. For electroless plating of copper over a substrate especially for the plating of a nonconductive substrate, it has been known for some time that chemically plated copper deposits of suitable thickness and adequate bond strength are commercially practical only if the substrate surface is properly catalyzed prior to metal deposition.

A common method for catalyzing a substrate prior to plating involves contact of the substrate with two solutions known in the art as a two-step catalyst. A process for metallizing utilizing this catalyst comprises contact of the substrate with a first aqueous solution of a reducing agent such as stannous chloride followed by contact with a second solution of a catalytic metal salt, typically palladium chloride, in hydrochloric acid. The reducing agent reduces the catalytic metal salt in situ on the substrate surface to the catalytic metal thereby providing a catalytic surface receptive to electroless metal deposition thereon. An alternative method for catalyzing a substrate prior to electroless metal deposition is also known and is disclosed and claimed in U.S. Pat. No. 3,011,920 incorporated herein by reference. In this method, a substrate is contacted with a colloidal catalytic solution formed by the admixture in acid solution of a catalytic metal salt, typically a palladium salt, a stannous salt and a hydrohalide acid. Colloidal metal particles are absorbed onto a substrate immersed in the catalyst solution and act as nucleating sites for the deposition of electroless metal thereon.

The above compositions containing both an oxidizing and a reducing agent present in the same solution have

limited stability and tend to trigger (spontaneously decompose) with reduction of substantially all copper in the solution. It is believed there are two types of mechanisms responsible for initiating triggering of the electroless copper solution. The first involves the introduction or presence in the bath of ions or metallic particles of catalytic metal. If initially ionic such as from the above described two-step catalyst, they are reduced by the bath to the metallic state. They then catalyze the plating reaction. For example Pd^{++}, as noted above, is often used in the two-step catalyst to catalyze surfaces to be copper plated. Some of the Pd^{++} ion is inevitably introduced into the copper plating bath. This ion is then reduced to metallic palladium which in turn catalyzes the copper plating reaction. After initiation of the reaction, sufficient metallic copper is produced by the plating solution to catalyze subsequent decomposition of the plating solution. The second mechanism believed to be responsible for spontaneous decomposition involves the formation in the solution during electroless plating of small amounts of metallic copper or cuprous oxide particles which catalyze the plating reaction in the solution rather than on the surface to be plated.

To avoid spontaneous decomposition of a plating bath, it is customary to include stabilizers in the composition which provide resistance against triggering and which increase the range of useful concentration and temperature of the solution without destroying the capacity of the solution for depositing copper by reduction on catalytic surfaces in contact therewith. Prior art stabilizing agents are disclosed in the aforesaid U.S. Pats. Nos. 3,457,089 and 3,708,329.

SUMMARY OF THE INVENTION

In accordance with the invention disclosed herein, an electroless copper plating solution is provided having a stabilizer selected from the group of iodobenzoic acid, amino methane sulfonic acid and mixtures thereof.

It is believed that the iodobenzoic acid stabilizer is a complexing agent for copper metal particles or cuprous oxide particles and the amino methanesulfonic acid is a palladium complexing agent.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Except for the stabilizers described above, the composition of the plating bath is conventional. The copper is included in the bath in the form of a salt such as copper sulfate. A complexing agent such as disodium ethylenediaminetetracetate and a reducing agent such as formaldehyde are also included in the solution as well as a complexing agent to provide a pH for the solution of at least 10. Other substances conventionally used in electroless copper plating solutions may also be included such as, for example, to improve the properties of the plating or increase the wetability of the surface being plated.

A typical electroless copper solution in accordance with the invention will have ingredients in the following concentration ranges:

	Preferred
Copper salt: 0.002 moles to saturation	0.02 to 0.12 moles.
Formaldehyde: 0.05 to 3.5 moles	0.1 to 1 moles.
Complexing agent: Minimum necessary to maintain copper in solution.	About 1 to 3 times the moles of cupric ion.
Free hydroxide: Sufficient to provide pH 10 or greater.	0.1 to 0.8 moles.
Stabilizer: 1 to 2,500 milligrams	100 to 1,000 milligrams.
Water: To 1 liter of solution	To 1 liter of solution.

It should be understood that the above concentration ranges are preferred, but not critical. Variations in the ranges are possible without departing from the scope of the invention. In most cases, additives may be added in an amount up to that amount that poisons the solution.

As noted above, the stabilizer in accordance with this invention is selected from the group of iodobenzoic acid (preferably o-iodobenzoic acid), amino methane sulfonic acid and mixtures thereof. The concentration of the stabilizing agents described above is not critical as these materials do not tend to poison the copper plating solution. Typically, the concentration can range from as little as 1 milligram to that amount that retards deposition, typically to as much as 2500 milligrams or more, though preferably the concentration of stabilizer varies between 10 and 1000 milligrams per liter of solution and most preferably from 25 to 100 milligrams per liter.

Measurements were carried out to show the stabilizing effect of the stabilizers of this invention in electroless copper plating solutions. For purposes of comparison, one particular bath composition was used throughout these experiments unless indicated otherwise. The composition of this bath was cupric sulfate pentahydrate 0.4 moles per liter, formaldehyde 0.24 moles per liter, Rochelle salts 0.12 moles per liter, sodium hydroxide 0.24 moles per liter, hydroxyethylcellulose as a leveling agent, 0.30 grams per liter and water to 1 liter of solution.

Electroless copper plating solutions vary somewhat erratically in their stability. This is due to the fact that initiation of the triggering mechanism of the bath is often due, in addition to the two main mechanisms described above, to the presence of impurities of dust particles in solution which are difficult to control or eliminate. Therefore, in order to obtain results which reflect the stabilizing influence of the added stabilizer, the decomposition of the palladium solution was deliberately initiated by adding small amounts of a solution of palladium chloride in dilute hydrochloric acid. The procedure was as follows: Samples containing 50 ml. of the plating solution were placed in 150 ml. beakers at room temperature. Thereafter, 10 drops of an initiator solution were added. The initiator solution was made by dissolving 5 grams of palladium chloride in 100 mls. of concentrated hydrochloric acid and diluting to 1 liter. Under these conditions, the plating solution without added stabilizer decomposed in about one to two minutes. Decomposition is that time after standing when there is either considerable plate-out of copper or foaming. The results where the stabilizers were added are shown in Table 1. The importance of the table is to show that the additives of the invention markedly improve stability under the drastic condition of this test. Under less drastic conditions, usually encountered in ordinary use, much longer decomposition times are found. The tables show the decomposition times for electroless copper plating bath as a function of stabilizer concentration for the stabilizers of the invention.

	Additive (amt., mg./l.)		
Example No.	o-Iodobenzoic acid	Amino methane sulfonic acid	Decomposition time (min.)
1	0	0	2
2	25	0	>240
3	50	0	>240
4	100	0	>240
5	500	0	>240
6	1,500	0	>240
7	0	25	20
8	0	50	35
9	0	100	40
10	0	500	35
11	0	1,500	30
12	50	50	>240
13	100	100	>240
14	500	500	>240
15	1,000	1,000	>240
16	50	1,000	>240
17	1,000	50	>240
18	50	25	>240

In the above examples, it should be noted that most of the decomposition times have been set forth to the nearest five minutes. The reason for this is that decomposition time is an indefinite and somewhat subjective measurement as it is not instantaneous, but rather initiates and becomes progressively worse over a period of time, typically taking from five to ten minutes for complete decomposition except in extreme cases. An attempt was made to record decomposition time at a point when the decomposition was severe, but there is considerable experimental error associated with this determination.

It should be understood that the stabilizers of this invention work equally well with other copper plating solutions such as the plating solution of Example 1 of U.S. Pat. No. 3,663,242 incorporated herein by reference.

To determine the effect of the aforesaid stabilizers on the plating properties of the bath and the functional properties of the copper deposits formed therefrom, the following plating sequence was follows:

1. Cut a phenolic board to a size measuring two inches by two inches.
2. Scrub clean with an abrasive cleaner. Rinse in cold water.
3. Treat for from one to three minutes with a non-ionic surfactant conditioner maintained at room temperature. Rinse in cold water.
4. Immerse for from three to four minutes in a sensitizing solution of colloidal palladium having a stannic acid protective colloid (catalyst 6F) maintained at room temperature. Rinse in cold water.
5. Immerse for from three to six minutes in dilute hydrochloric acid solution maintained at room temperature. Rinse in cold water.
6. Deposit electroless metal for a period of ten minutes.
7. Rinse and dry parts and observe properties of deposit.

The above plating procedure was employed for the formulations of above examples numbers 2, 4, 6, 8, 10, 12, 14 and 18. In all cases, deposits having good color and functional properties were obtained. It is noted that plating rate in certain of the examples was somewhat decreased, particularly in those examples where the amount of total stabilizer was 1000 milligrams per liter or more.

I claim:

1. In an electroless copper plating solution comprising a source of cupric ions, a reducing agent therefor, a complexing agent for said cupric ions and a pH adjustor to provide a minimum pH of at least 10, the improvement comprising a stabilizer for said solution selected from the group of iodobenzoic acid, amino methane sulfonic acid and mixtures thereof, said stabilizer being present in an amount sufficient to improve the stability of said copper plating solution.

2. The plating solution of claim 1 where the total concentration of stabilizer varies between 1 and 2500 milligrams per liter.

3. The plating solution of claim 1 where the concentration of stabilizer varies between 10 and 1000 milligrams per liter.

4. The plating solution of claim 1 where the concentration of stabilizer varies between 25 and 100 milligrams per liter.

5. The plating solution of claim 1 where the stabilizer is iodobenzoic acid.

6. The plating solution of claim 5 where the iodobenzoic acid is o-iodobenzoic acid.

7. The plating solution of claim 1 where the stabilizer is amino methane sulfonic acid.

8. The plating solution of claim 1 where the stabilizer is a mixture of iodobenzoic acid and amino methane sulfonic acid.

References Cited

UNITED STATES PATENTS

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LEWIS T. JACOBS, Primary Examiner

U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,846,138

DATED : November 5, 1974

INVENTOR(S) : Michael Gulla

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

In the Heading of the patent, following the name of the inventor, delete "assignor to the Webline Corporation, Charlotte, N.C." .

Signed and Sealed this

ninth Day of *December 1975*

[SEAL]

Attest:

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Attesting Officer

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