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3,457,089

ELECTROLESS COPPERPLATING

Charles R. Shipley, Jr., and Michael Gulla, Newton, Mass.,
assignors to Shipley Company, Inc., Newton, Mass., a
corporation of Massachusetts

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U.S. Cl. 106—1

10 Claims

ABSTRACT OF THE DISCLOSURE

The disclosure describes an improved electroless copper plating solution which includes a soluble alkaline alcohol for improving stability.

Background of the invention

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

Electroless copper deposition refers to the chemical reductive plating of copper over active surfaces in the absence of external electric current. Such processes and compositions useful therein are known and are in substantial commercial use. They are disclosed in a number of prior art patents, for example, U.S. Patent No. 3,011,920, issued Dec. 16, 1961.

Known electroless copper deposition solutions comprise four ingredients dissolved in water. These are (1) a source of cupric ions, usually copper sulphate, (2) formaldehyde as reducing agent therefore, (3) alkali, generally an alkali metal hydroxide and usually sodium hydroxide, sufficient to provide the required alkaline solution in 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 patent, and also in U.S. Patents Nos. 2,874,072; 3,075,856; 3,119,709 and 3,075,855.

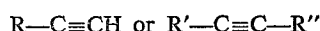
The above compositions containing both an oxidizing and a reducing agent present in the same solution, have limited stability and tend to trigger with reduction of substantially all the copper in the solution. Consequently, it is customary to include stabilizers in the composition which provide resistance against triggering and which increase the range of usable concentration and temperature without destroying the capacity of the solutions for depositing copper by reduction at catalytic surfaces in contact therewith.

Summary of the invention

In accordance with the present invention it has been discovered that electroless plating solutions of the above type can be substantially improved in stability and other properties by the inclusion therein of effective amounts of a soluble lower alkine alcohol in which the acetylenic group, and particularly such a group containing an active hydrogen atom, is believed to be the effective portion.

Description

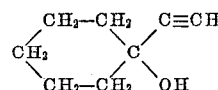
The alkine alcohols useful according to this invention have the following formulas:



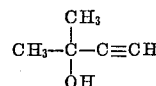
wherein each of R, R', and R'' individually are a lower monovalent hydroxy-alkyl, cyclohydroxy-alkyl, or hydroxy-alkyl ether radical, said alkine alcohol being soluble in the alkaline electroless copper solution. Useful examples include the following:

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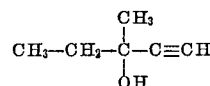
(1) Ethynyl cyclohexanol



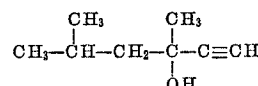
(2) Methyl butynol



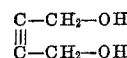
(3) Methyl pentynol



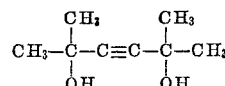
(4) Dimethyl hexynol



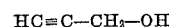
(5) 2-butyne-1,4-diol



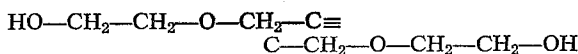
(6) Dimethyl hexynediol



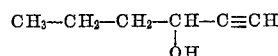
(7) Propargyl alcohol



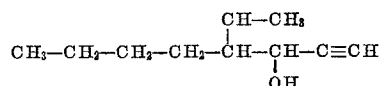
(8) Bis-hydroxyethyl butynediol ether



(9) Hexynol



(10) Ethyl octynol



The above alcohols are used in quantities which are effective to improve stability or otherwise improve the performance of the solution but in quantities that are not so great as to prevent deposition. Generally useful quantities are between 2.5 and 2000 parts per million of total solution weight and the preferred range is from about 25 to 150 parts per million.

The preferred example according to this invention is as follows:

CuSO ₄ ·5H ₂ O	g	7.5
NaOH	g	5.0
HCHO	g	2.5
Rochelle salts	g	12.0
Methyl butynol	p.p.m.	25 to 150
Water, to make 1 liter.		

In the above formulations, other well known complexing agents and sources of cupric ion may be employed. For example, those disclosed in the above cited patents can be employed.

Concentrations of the above ingredients are not critical and are generally in the ranges previously known to be useful in electroless coppering solutions. Sufficient copper must be employed to provide a useful deposit and sufficient alkali to provide the high pH required, generally from about 10 to 14. Sufficient formaldehyde must be

employed to serve as a reducing agent for the copper in the presence of a catalytic surface and sufficient complexing agent used to prevent precipitation of copper in the alkali solution during storage and use. Generally, the known concentrations most useful for these are given in the following table.

TABLE.—CONCENTRATIONS

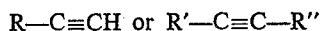
Cu ⁺⁺ -----	mols/liter--	0.02 to 0.12	
Alkali -----	mols/liter--	0.17 to 1.15	
HCHO -----	mols/mol Cu ⁺⁺ --	2 to 20	10
Complexer -----	mols/mol Cu ⁺⁺ --	1.1 to 5	

The use of the alkine alcohols as herein described is believed to be effective through the acetylenic group to hold impurities such as cuprous materials in deactivated form. The hydroxyl group is believed to render the alcohol soluble in basic solution. Other solubilizing substituents can be used but hydroxy radicals are preferred.

It should be understood that the foregoing description is for the purpose of illustration and that the invention includes all modifications within the scope of the appended claims.

We claim:

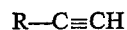
1. In an autocatalytic electroless copper solution having, in basic aqueous solution, a source of cupric ions, formaldehyde, and a complexing agent sufficient to render said cupric ions soluble in basic solution, the improvement wherein said solution also contains as stabilizer an alkine alcohol having one of the following formulas:



wherein each of R, R' and R'' are lower monovalent hydroxy-alkyl, cyclo-hydroxy-alkyl, or hydroxy-alkyl ether radicals, said alcohol being soluble in said basic aqueous solution and being present in an effective amount sufficient to prevent copper deposition in contact with a catalytic surface.

2. An electroless copper solution according to claim 1 wherein said alcohol is present between about 2.5 and 2000 parts per million by weight of said solution.

3. An electroless copper solution according to claim 1 wherein said alcohol has the formula



and wherein the OH radical on said R radical is attached to the carbon atom thereof adjacent the acetylenic group.

4. An electroless copper solution according to claim 3 wherein said alcohol is present in an amount between about 2.5 and 2000 parts per million of solution weight.

5. An electroless copper solution according to claim 1 wherein said alcohol is methyl butynol.

6. An electroless copper solution according to claim 1 wherein said alcohol is methyl pentynol.

7. An electroless copper solution according to claim 1 wherein said alcohol is dimethyl hexynol.

8. An electroless copper solution according to claim 1 wherein said alcohol is hexynol.

9. A process for autocatalytic electroless copper deposition which comprises contacting a catalytic surface with a solution according to claim 2.

10. A process for autocatalytic electroless copper deposition which comprises contacting a catalytic surface with a solution according to claim 4.

References Cited

UNITED STATES PATENTS

30	3,326,700	6/1967	Zeblisky.
	3,361,580	1/1968	Schneble et al.

JULIUS FROME, Primary Examiner

35 L. HAYES, Assistant Examiner

U.S. Cl. X.R.

117—130, 160

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION 30463

Patent No. 3,457,089 Dated July 22, 1969

Inventor(s) Charles R. Shipley, Jr. and 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 claim 1, line 12, the term "sufficient" should be changed to --insufficient--.

Signed and sealed this 19th day of September 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents