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3,383,224

ELECTROLESS COPPER DEPOSITION

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ABSTRACT OF THE DISCLOSURE

An electroless copper solution comprising a source of cupric ions, hydroxyl radicals, formaldehyde and a hydroxy alkali substituted dialkylene triamine complexing agent alone or in combination with other known complexing agents. The use of the triamine complexing agent provides rapid and even deposition of copper over a wide range of operating conditions. The deposited copper coating is excellent in appearance and of high conductivity.

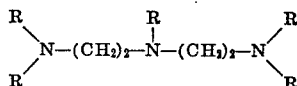
This invention relates to the electroless deposition of copper and has for its principal object the provision of improved copper plating solutions and deposition methods employing the same.

Electroless copper deposition refers to the chemical plating of copper over active surfaces by chemical means and in the absence of external electric current. Such processes and compositions useful therewith are known and are in substantial commercial use. They are disclosed in a number of prior art patents, for example United States Patent 3,011,920, issued Dec. 16, 1961.

Known electroless copper deposition solutions comprises basically four ingredients dissolved in water. These are (1) a source of cupric ions usually copper sulphate, (2) formaldehyde as reducing agent therefor, (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.

Numerous complexing agents for use in such compositions are known. The above-mentioned patent discloses the use of tartrates in the form of Rochelle salts, salicylates are disclosed in United States Patent No. 2,874,072, acid substitution diamines and triamines in United States Patents Nos. 3,075,856 and 3,119,709 and alkanolamines in United States Patent No. 3,075,855. Other known complexers are citrates, glycerin and lactones.

In accordance with the present invention, a new complexing agent has been discovered which when used alone or in admixture with other complexing agents provides substantial advantages. These new additives are hydroxy-alkyl substituted dialkylene triamines having the following structure.



wherein at least three of said R radicals, taken individually, are



and not more than 2 of said R groups, taken individually, are $-(\text{CH}_2)_2\text{OH}$, $-\text{CH}_2\text{COOH}$, $-\text{C}_2\text{H}_4\text{COOH}$ or inert organic radicals such as lower alkyl or lower dialkyl ethers having from 1 to 4 carbon, inclusive. Inert as used above means that the radicals do not react in the copper solution and neither contribute to nor detract from the

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complexing activity of the molecule. Substantially pure pentahydroxypropyl diethylene triamine wherein all of said R radicals are $-(\text{CH}_2)_3\text{OH}$ is preferred.

The principal advantages provided by the instant invention are as follows:

(1) A very rapid rate of deposition providing, for most applications, a sufficient deposit in about ten minutes.

(2) Even and rapid coverage of the surface to be plated. The plating commences immediately and within one minute parts are generally completely covered with copper without voids.

(3) A wide range of operating temperature, at least about 45° F. to 100° F.

(4) A wide range of useful concentration, the deposition rate being substantially independent of concentration within broad limits.

(5) While commencing deposition at a rapid rate, the rate rapidly falls so that a predetermined amount of copper can be deposited and additional deposition time is of little effect. This considerably lessens the time control required for consistent performance in production.

(6) Replenishment or addition of components to replace those consumed is facilitated with minimum requirements for analysis. The amount of active ingredients consumed per square foot of surface plated is relatively independent of deposition time and replenishment requirements can be calculated on a per square foot plated basis without need for frequent analysis.

(7) The product is useful for an extremely wide range of plating applications for copper and provides thicknesses of up to 70 millionths of an inch readily.

(8) The copper deposit is of excellent quality, both analytically and by appearance.

(9) The deposited copper has an extraordinarily high electrical conductivity greatly simplifying the usual operation of increasing the copper thickness by electroplating. Coatings of 40 millionths of an inch or more can be immediately electroplated with current densities of as high as 100 amps per square foot without harm or burning of the electroless copper plating. With most prior electroless compositions, initial electric plating had to be started below current densities of 40 amperes and slowly increased to the desired density. Good copper to copper bonds are obtained.

Illustrative examples of plating solutions according to this invention are given below wherein all parts are by weight except where otherwise indicated. Example 1 is currently preferred.

EXAMPLES

50	CuSO ₄ ·5H ₂ O	g	10
	Paraformaldehyde	g	9.3
	NaOH	g	25
	Water, to make 1 liter.		

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		Grams	Deposit Thickness *
60	Complexer, one of—		
1.	Pentahydroxypropyldiethylene triamine.	20	65
2.	Triamine, above	5	73
	Sodium tartrate	9.9	
3.	Triamine, above	5	80
	Delta-Gluconolactone	22.5	
4.	Triamine, above	15	73
	Sodium salicylate	6	

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*Thickness of deposit obtained in 10 minutes at 75° F., inches×10⁻⁴.

Copper sulfate is the source of copper ions and the NaOH provides the desired alkalinity, generally a pH of 10 or preferably higher. Other soluble copper salts and other alkali metal hydroxides can be employed.

While the above concentrations are preferred, concentration is not critical and usable amounts are within the limits generally known in the art. Sufficient copper must be employed to provide a useful deposit and sufficient alkali to provide the high pH required. 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 alkaline solution. Generally, the limits of concentration of these ingredients is given in the following Table I.

TABLE I.—CONCENTRATIONS

Cu ⁺⁺ -----	mols/liter—	0.02 to 0.12
Alkali -----	do-----	0.17 to 1.25
HCHO -----	mols/mol Cu ⁺⁺ --	2 to 20
Complexer: total -----	do-----	1.1 to 5

Of which the

Triamine must be -----do----- 0.15 to 5

As indicated in examples and in Table I, sufficient total complexer must also be employed. Since one mol of complexer is required to complex one mol of copper, a slight excess or about 1.1 is required minimum. About 2 mols complexer per mol copper is preferred and greater amounts up to at least 5 mols may be employed although generally undesirable for economic reasons. The hydroxy triamine complexers herein disclosed can be used alone or in admixture with other complexers. About 0.15 mols triamine per mol copper is the approximate minimum to obtain the present advantages and more is preferred.

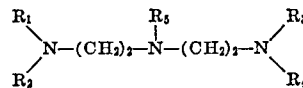
Compositions according to this invention are stable for extended deposition at temperatures of up to about 65° F. Above this temperature the stability without treatment may be less than desirable. If so, they can be stabilized by the addition of chemical stabilizers or by aerating them in accordance with the disclosure of U.S. Patent No. 2,938,805.

The novel solution herein disclosed can be applied to the surfaces to be plated in any suitable way. Most conveniently the surfaces are immersed in a tank containing the solution which can be heated or cooled to provide the desired temperature and to which aeration or stabilizers can be applied if desired. The solutions will plate onto a large variety of known catalytic metals or onto non-catalytic surfaces such as dielectrics pre-treated with known sensitizing substances.

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.

I claim:

1. For electroless plating of copper, an improved basic aqueous bath containing a source of cupric ions, hydroxyl radicals, formaldehyde and sufficient complexing agent to render said ions soluble in alkaline solution, wherein the improvement comprises using at least one complexing agent of the following substituted triamine



wherein at least three of said R₁, R₂, R₃, R₄ and R₅ radicals are —(CH₂)₃OH and no more than two are —(CH₂)₂OH, —CH₂COOH, —C₂H₄COOH or lower alkyl or lower dialkyl ethers having from 1 to 4 carbons, at least 0.15 mols of said triamine being present per mol of copper ions.

2. A bath according to claim 1 wherein said triamine is pentahydroxypropyl diethylene triamine.

References Cited

UNITED STATES PATENTS

2,329,512 7/1967 Shipley et al. ----- 106—1

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