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METHOD OF COPPER PLATING BY CHEMICAL REDUCTION

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This invention relates to electroless plating by the deposition of metals by chemical reduction. More particularly the invention relates to improvement in the deposition of copper from chemical reduction plating solutions.

The chemical reduction process for plating has several advantages over conventional metal electroplating methods. Chemical reduction plating provides a deposit of substantially uniform thickness over articles having complex shapes and other irergularities such as small recesses and apertures. Even the remote surfaces in such recesses may be uniformly plated by the chemical reduction process in contrast with conventional electroplating methods where the plating of such recesses is a practical impossibility. Known prior chemical reduction processes, however, all employ soluble metallic compounds which are exceptionally light-sensitive and therefore easily reduced. It will be appreciated that the ease of reduction of such light-sensitive compounds renders the process difficult to control. Generally in order to achieve control it is necessary to carry out the processes under darkroom conditions or to include other additives in the plating solution which increase the solubility of the compounds and thus reduce the light sensitivity thereof. Attempts to increase the solubility of metallic compounds in aqueous solutions have not been markedly successful and such solutions have, in general, failed to produce a good plate.

It is therefore an object of the instant invention to provide an improved method for plating suitable surfaces with copper by a controllable chemical reduction process.

According to the invention a chemical reduction plating solution is employed in which an insoluble compound of copper is included. Since an insoluble copper compound is employed, the plating reaction is not adversely affected by light and greater control of the plating process is thus obtained. The insoluble compound is reduced by including in the plating solution a soluble compound which forms a soluble complex with the insoluble compound. This complex is then reducible upon a suitable surface by the action of a reducing agent.

Examples of metals and alloys which may be coated or plated with copper by the practice of the present invention include steel, iron, ferrous alloys, nickel, cobalt, gold, silver, platinum, copper, copper base alloys, magnesium, and aluminum. It will be understood that superior copper plating results when the surface of the article to be coated is thoroughly cleaned. Hence, in most instances it is desirable to employ conventional plating pretreatments, such as buffing, abrading, or acid etching prior to chemical reduction plating.

In the practice of a specific embodiment of the invention an improved copper deposit or plating is obtained by immersing an article having a surface to be plated into an aqueous solution in contact with water-insoluble cupric oxide and containing, a reducing agent such as sodium hypophosphite, and a chelating or complexing agent such as ammonium sulfate or ammonium chloride. The purpose of the complexing agent is to maintain a relatively small portion of the copper in solution in a water-soluble copper complex while permitting a relatively large portion of the copper in the water-insoluble copper oxide to remain out of solution as a copper reserve in contact with the aqueous plating solution. The reduction plating is continued until a predetermined thickness of plating is obtained or until the copper ion content in the solution and the reserve supply of copper oxide are substantially exhausted. The function of the chelating or complexing agent is to continuously form a soluble complex with the insoluble copper compound and to continuously hold the copper in solution in a controlled concentration until reduced to the metallic state. During the plating process the plating solution bath is maintained at a temperature in the range of from about 50° C. to about 110° C. At the higher temperature the plating rate is increased and becomes more difficult to control. Chelating or complexing agents suitable in the chemical reduction plating processes of the instant invention are ammonium sulfate and ammonium chloride. The reducing agent is preferably the hypophosphite radical which may be introduced as an alkali metal hypophosphite such as sodium or calcium hypophosphite, ammonium hypophosphite, or as hypophosphorous acid.

A chemical reduction plating solution in accordance with the present invention is formed by adding the insoluble copper compound and the soluble chelating or complexing agent to water. The amount of insoluble copper compound is determined by the amount necessary to deposit a desired thickness of copper on a particular surface which amount can, of course, be calculated for a particular article. The ratio of the chelating or complexing agent to the insoluble copper compound is not critical. However, it will be understood that if an ion ratio of greater than about 5 to 1 chelating agent to insoluble compound is employed, the copper ion is held so strongly in solution by the chelating agent that its reduction therefrom becomes difficult and the plating process becomes less controllable. Likewise employing a ratio of less than about 0.025 to 1 chelating agent to insoluble compound results in an extremely low rate of plating or no plating at all since there is an insufficient amount of chelating agent to form a significant amount of soluble complex. The hypophosphite reducing agent is then added to the solution, the quantity being determined by the amount of copper to be reduced. In general it is advisable to provide an excess amount of hypophosphite radical to accommodate side reactions and to maintain the plating reaction during the final reduction stages. It has been found that excellent results are obtainable when an ion ratio of hypophosphite radical to insoluble copper compound of 0.5–40 to 1 is employed.

The following are illustrative examples of initial plating bath compositions and conditions in accordance with the present invention wherein the quantities, where applicable, are expressed in terms of grams per litre:

Example 1

CuO	2.0
$NaH_2PO_2.H_2O$	5.0
$(NH_4)_2SO_4$	5.0
Temperature, ° C.	93.0
pH	3.1
Work load (cm.^{2}/cm.^{3})	0.25
Average plating rate (mgs./cm.^{2}/hr.)	45.6

Example 2

CuO	3.0
$NaH_2PO_2.H_2O$	10.0
NH_4Cl	0.1
Temperature, ° C.	93.0
pH	3.0
Work load (cm.^{2}/cm.^{3})	0.25
Average plating rate (mgs./cm.^{2}/hr.)	136.0

Example 3

CuO	3.0

$NaH_2PO_2.H_2O$	40.0
NH_4Cl	0.1
Temperature, ° C.	93.0
pH	3.0
Work load (cm.^{2}/cm.^{3})	0.25
Average plating rate (mgs./cm.^{2}/hr.)	160–175

Example 4

CuO	3.0
$NaH_2PO_2.H_2O$	1.25
NH_4Cl	0.1
Temperature, ° C.	93.0
pH	3.0
Work load (cm.^{2}/cm.^{3})	0.25
Average plating rate (mgs./cm.^{2}/hr.)	30.0

The acidity of the solutions in the above examples was adjusted by the addition of a few drops of concentrated H_2SO_4 so that the solutions had a pH value of about 3.0.

It will thus be understood from the foregoing description and examples of the invention that an improved method of plating copper by chemical reduction has been provided in which the reduction action is not sensitive to light and is more controllable whereby an improved plating of copper is obtained. It should be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited since changes and alterations therein may be made which are within the intended scope of the invention as defined in the claims appended.

What is claimed is:

1. The method of copper plating comprising the step of contacting the surface to be plated with an acidic plating solution at a temperature in the range of from about 50° to about 110° C., consisting essentially of a dissolved ammonium salt, a dissolved hypophosphite reducing agent, dissolved copper ions, and an undissolved-copper ion-containing compound in contact with the plating solution, the ion ratio of said hypophosphite ion to the undissolved copper ion being in the range of from about 0.5 to about 40, and the ion ratio of the ammonium ion of the dissolved ammonium salt to the undissolved copper ion being in the range of from about 0.025 to about 5.

2. The method according to claim 1, wherein the undissolved copper compound is copper oxide.

3. The method according to claim 2, wherein the plating solution is maintained at a pH of about 3.

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