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METHOD OF ELECTROLESS DEPOSITION OF METALS WITH IMPROVED SENSITIZER

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ABSTRACT OF THE DISCLOSURE

Method for autocatalytically electrolessly plating a dielectric surface with a metal such as nickel, cobalt or copper comprising sensitizing the surface with an improved sensitizing solution comprising both divalent tin ion and tetravalent tin ion, the solution having a pH less than about 1.5, treating the sensitized surface with a catalyzing solution to provide catalytic nucleating centers, and plating the metal on the catalyzed surface. The improved sensitizing solution permits plating on smooth, dense, water repellent plastic surfaces such as Teflon, Lucite, silicone rubbers and Mylar.

BACKGROUND OF THE INVENTION

Certain metals can be plated on non-metallic surfaces by an autocatalytic electroless process in which the surface is first treated with a sensitizing solution, then with an activating solution which precipitates nucleating centers. In this way ceramics and many synthetic resins can be provided with coatings of nickel or copper, for example, which may or may not be later covered with a heavier layer of metal by electroplating.

The sensitizing solution most commonly used in the past contains Sn^{+2} ions generally formed from the salt stannous chloride. This material has proved to be quite satisfactory for electroless plating of metals on most non-metallic materials. However, there are certain plastics, such as Teflon, Lucite and silicone rubbers, as well as certain commercial photoresists, which cannot be satisfactorily plated by this method. The reason for the difficulty appears to be that these materials are unusually smooth and non-porous and are not readily wetted by aqueous solutions of stannous salts. As a result, when one attempts to deposit metal autocatalytically on one of these materials with no surface roughening, using conventional stannous salt sensitizers and conventional activators, such as palladium chloride, plating is spotty and otherwise non-uniform.

It should be noted that, in general, those who have used acidic solutions of stannous salts as electroless plating sensitizers, have tried to keep the tin ion in the divalent state by methods such as keeping metallic tin or other reducing agents such as sugars in the shelf stock solutions.

OBJECTS OF THE INVENTION

One object of the present invention is to provide an improved method of autocatalytically electrolessly depositing metals on certain non-metallic substrates which are difficult to "wet."

Another object of the invention is to provide an improved sensitizing solution for autocatalytically electrolessly depositing metals on non-metallic substrates.

DESCRIPTION OF PREFERRED EMBODIMENTS

It has now been found, unexpectedly, that if stannic ion is added to conventional acid sensitizing solutions containing stannous ion, and the resulting solution is used to treat difficult-to-plate non-metallic surfaces, in the usual way, these sensitized surfaces (after the usual activation

treatment) can readily be given uniform metal coatings by conventional autocatalytic electroless plating solutions. The improved method appears to be applicable to the deposition of any metal that has previously been deposited autocatalytically. These metals include nickel, cobalt, copper, platinum, gold and palladium and combinations of these.

In order to show comparisons between use of sensitizing solutions containing, effectively, only stannous ion, with solutions containing stannous and controlled amounts of stannic ion, some experimental examples are given below.

Example I

Substrate: smooth Teflon plate with no mechanical or chemical roughening.

Procedure: after the Teflon plate was chemically cleaned with a detergent solution it was immersed in a sensitizing solution comprising $SnCl_2$ having the concentration of 6.4×10^{-2} moles/liter, an HCl content of 0.19 mole, and varying amounts of $SnCl_4$.

The treated plate was removed from the sensitizing bath, rinsed and immersed in an activating bath of $PdCl_2$ containing 1 g. of $PdCl_2$ and 1 cc. conc. HCl per liter (remainder water). After a few seconds in the activating bath, the plate was again removed and rinsed, after which it was immersed in a nickel-depositing bath at 25° C. having the following composition:

In one liter of solution:

Dimethylamine borane—1.5 g.
$NiSO_4.6H_2O$—25 g.
$Na_4P_2O_7.10H_2O$—50 g.
NH_4OH (58% conc.)—25 cc.
Water—remainder.

The plate is permitted to remain in the plating bath until either a good uniform plating is obtained or it is apparent that no further deposit is being obtained on unplated areas. This is usually a few minutes.

The following table shows the effect of adding varying amounts of $SnCl_4$ solution to a conventional $SnCl_2$ sensitizing solution. In this case, the $SnCl_4$ stock solution was prepared by dissolving crystalline material in water and permitting the solution to stand for about one week at room temperature before using. It has been found that an aging effect, not fully understood, occurs in this solution. Less of the aged solution is required to impart the improved wetting to the sensitizer. The aging effect may be due to an hydrolysis reaction taking place.

Conc. of $SnCl_4$ (moles/liter): [1]	Plating results
0	Practically no wetting or plating.
2.5×10^{-4}	Spotty plating.
5.0×10^{-4}	Do.
7.5×10^{-4}	Do.
1.25×10^{-4}	Do.
2.0×10^{-3}	Good plating.
2.5×10^{-3}	Do.
3.25×10^{-3}	Do.
3.75×10^{-3}	Do.

[1] In the sensitizing bath which also contained 6.4×10^{-2} moles/liter of $SnCl_2$.

NOTE.—As the amount of $SnCl_4$ was increased, coverage of plating became better ni gradual increments. There was actually no abrupt change from "spotty" to "good."

Example II

With all conditions and treating and plating solutions remaining the same as in Example I except the proportion of stannic ion, Mylar tape coated with AZ–1350, a positive acting photoresist, was plated with nickel from

the same nickel-boron bath. In this case, when the concentration of stannic ion was above zero and up to 7.5×10^{-5} moles/liter, only patchy plating was obtained. Above about 1.25×10^{-4} moles/liter good plating was obtained although this increase in coverage was again gradual. With no stannic ion added, only little plating was obtained.

Example III

In another test run using a nickel-boron plating bath, as described in Example I, on AZ–1350 photoresist, the sensitizing solution was made up by adding varying amounts of powdered $SnCl_4\cdot5H_2O$ (reagent grade) to freshly prepared $SnCl_2$ solution. The stock solution from which the stannous ion solution was prepared comprised 214 gms. $SnCl_2\cdot2H_2O$ (Baker reagent grade) and 290 cc. conc. HCl. The actual solution used for the run contained 6.4×10^{-2} molar concentration of Sn^{+2} ion and an HCl content of 0.19 M.

Patchy plating was obtained with molar concentrations of Sn^{+4} ion below about 0.86×10^{-2}. Above about 0.86×10^{-2} molar, satisfactory, uniform plating resulted.

Activation procedure was the same as in Example I.

Example IV

With conditions otherwise the same as in Example III, the molar concentrations of Sn^{+2} ion used was increased to 12.8×10^{-2} molar and the HCl to 0.38 M. Patchy plating on AZ–1350 photoresist from the same nickel-boron plating bath was obtained using molar concentration of Sn^{+4} ion below about 10.4×10^{-2} molar. Good, uniform plating was obtained above about 10.4×10^{-2} molar.

Example V

Copper was deposited on a smooth Teflon substrate using the following procedure. After cleaning the substrate, it was immersed in a sensitizer solution containing Sn^{+2} and Sn^{+4} ions as set forth below, treated with a $PdCl_2$ activating solution as in the previous examples, and then immersed in a copper plating bath. The copper plating bath had the following composition.

		Per liter
$CuSO_4\cdot5H_2O$	gms.	7.5
Ethylene diaminetetra-acetic acid (E.D.T.A.) (40% solution of the sodium salt)	gms.	36.5
NaOH	gms.	20.0
NaCN	gm.	0.1
HCHO (37% solution)	ml.	40
Water to make 1000 ml.		

The sensitizing solution contained Sn^{+2} ion 6.4×10^{-2} molar and had an HCl content of 0.19 molar. To this was added varying amounts of stannic chloride solution that had been aged for a minimum of one week.

Conc. of Sn^{+4} ion (molar):	Plating results
0	Incomplete coverage.
7.5×10^{-4}	Do.
1.5×10^{-3}	Do.
2.0×10^{-3}	Do.
2.5×10^{-3}	Do.
3.25×10^{-3}	Do.
4.0×10^{-3}	Do.
5.0×10^{-3}	Good coverage.
6.5×10^{-3}	Do.
7.25×10^{-3}	Do.

(Gradual increase in plating coverage with increasing amounts of Sn^{+4} ion.)

Example VI

Using the same copper-depositing bath as in Example V and Sn^{+2} ion concentration of 6.4×10^{-2} moles, an experimental run was made to see if the quality of the plating was affected by using increasingly high ratios of Sn^{+4} ion to Sn^{+2} ion, with the following results. The substrate used was Teflon.

Conc. of Sn^{+4} ion (molar):	Plating results
8.0×10^{-3}	Good.
1×10^{-2}	Do.
2×10^{-2}	Do.
3×10^{-2}	Do.
4×10^{-2}	Do.
5×10^{-2}	Do.
6×10^{-2}	Borderline.
7×10^{-2}	Patchy.
8×10^{-2}	Do.

It was therefore concluded that, in each case, there is likely to be an upper limit to the amount of Sn^{+4} ion in relation to Sn^{+2} ion but this will differ with different plating solutions, different substrates and other conditions.

Although a preferred way to add the Sn^{+4} ion is by a solution which has been aged, since less tin (+IV) is required using this procedure, there are other ways in which stannic ion may be generated. One of these is by adding agents capable of oxidizing the Sn^{+2} ion to Sn^{+4} ion, such as iodine or permanganates, for example. Another method is by exposing the Sn^{+2} solution to U.V. light for a period of time. By merely heating the Sn^{+2} solution in air, some of the Sn^{+2} ion is converted to Sn^{+4}. In practice, the addition of Sn^{+4} ion is preferred because the amount can be more accurately controlled and can conveniently be used in production facilities.

For further information on other previously-known stannous chloride sensitizing solutions to which stannic ion can be added as described herein, see, for example, "Metallic Coating of Plastics" by William Goldie, Electrochemical Publications Limited, London (1968) Chapter 5.

In the examples given above, the pH of the solutions was generally below one and the solutions were clear. At pH values around 1.5 the solutions become turbid. It is therefore preferred that the pH value be kept below about 1.5 and, more preferably, below one.

In the present method it is believed that the improved results are due to the presence of a complex of Sn^{+2} and Sn^{+4}.

In general, a molar ratio of divalent tin ion to tetravalent tin ion between about 1:1 and 1000:1 has been found to be operative.

Although stanic chloride is given as an example of a suitable tin compound to use to add Sn^{+4} ion in the present invention, it will be understood that other soluble stannic compounds can be used.

The improved method of the present invention is also of particular interest in the making of printed circuit boards; especially boards having small-diameter through holes which must be plated with metal. Materials commonly used for printed circuit substrates are phenolic resin-impregnated fibrous materials, epoxy resin-impregnated boards and glass fiber-epoxy resin boards. The boards are usually laminates of several thin sheets. The improved sensitizers described herein wet these materials very well. The sensitizers wet so efficiently that very small diameter through holes, usually very difficult to plate electrolessly with previously used Sn^{+2} sensitizers, can now be plated very well. The improvement is due not only to the increased wetting ability of the present sensitizers but also due to the fact that they are not degraded by air agitation. Agitation of the bath is necessary to cause solutions to flow through the holes. Air agitation adversely affects Sn^{+2} sensitizers.

What is claimed is:

1. A method for electrolessly plating a surface with a metal comprising the steps of

sensitizing the surface with a sensitizing solution made by mixing separate sources of divalent tin ion and tetravalent tin ion in a molar ratio from about 1:1 to about 1000:1, the solution having a pH lower than about 1.5, the tetravalent tin ion being prepared as a separate solution of a stannic salt which is aged

for a time before combining it with the source of divalent tin ion,

treating the sensitized surface with a catalyzing solution so as to provide catalytic nucleating centers thereon, and

plating said metal on the catalyzing surface by contacting the surface with an electroless metal plating bath.

2. A method according to claim 1 in which said surface is a smooth, dense, difficultly wettable plastic.

3. A method according to claim 2 in which said surface is Teflon.

4. A method according to claim 1 in which said metal is nickel.

5. A method according to claim 1 in which said metal is copper.

6. A method according to claim 1 in which said surface is a phenolic resin impregnated fibrous material.

7. A method according to claim 1 in which said surface is an epoxy resin-impregnated material.

8. A method according to claim 1 in which said surface is a glass fiber-epoxy board.

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