

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

**0 375 179  
A2**

12

**EUROPEAN PATENT APPLICATION**

21 Application number: 89312444.6

51 Int. Cl.<sup>5</sup>: **C25D 3/38, C25D 5/30,  
C25D 5/28**

22 Date of filing: 29.11.89

30 Priority: **21.12.88 US 289993**

43 Date of publication of application:  
**27.06.90 Bulletin 90/26**

84 Designated Contracting States:  
**DE FR GB**

71 Applicant: **International Business Machines Corporation**  
**Old Orchard Road**  
**Armonk, N.Y. 10504(US)**

72 Inventor: **Mahmoud, Issa Said**  
**10500 Settlers Trail**  
**Austin Texas 78750(US)**

74 Representative: **Burt, Roger James, Dr.**  
**IBM United Kingdom Limited Intellectual**  
**Property Department Hursley Park**  
**Winchester Hampshire SO21 2JN(GB)**

54 **Copper plating process for difficult to plate metals.**

57 An acid copper plating bath and process for using with electropositive metals such as aluminium and tungsten is described, wherein the bath contains sulphuric acid, copper sulphate, in solution with levelling, wetting and brightening agents.

**EP 0 375 179 A2**

## COPPER PLATING PROCESS FOR DIFFICULT TO PLATE METALS

The present invention relates to an electroplating bath composition suitable for electroplating extremely electropositive metals such as aluminium and tungsten.

Strongly electropositive metals such as aluminium and tungsten are quite difficult to electroplate. Such metals have a strong affinity for atmospheric oxygen. This characteristic creates an ever present compacted oxide layer at the metal surface. Such a layer forms within seconds after a fresh surface of these metals is exposed to oxygen. The oxide layer renders plating these metals very difficult; and if plating occurs, in many cases, the adhesion is quite poor.

Conventional techniques for plating such metals include extensive surface pre-treatment. In the case of tungsten, parts to be plated are often transferred from tank to tank while under electrical bias, thereby creating a safety hazard due to the possibility of electrical shock. Additionally, conventional plating processes for these metals generate significant amounts of harsh waste, such as hydrofluoric acid.

Thus, a better process and plating bath chemistry is desirable for plating these difficult to plate metals. U.S. Patent 3,769,179 to Durose et al, U.S. Patent 4,242,181 to Malak and 3,923,613 to Immel, exemplify the prior art of copper plating; the first two particularly, as applied to the printed circuit manufacturing industry.

The present invention provides a process including a bath formulation for depositing copper on difficult to plate metals such as aluminium and tungsten. The bath formulation of the present invention is an acid copper bath and includes additives for specific purposes.

The process of the present invention requires no surface preparation or etching prior to plating, thereby reducing the amount of chemical waste attendant to the process. Further, the present invention provides for oxide removal from difficult to plate metals in the plating tank so that there is minimal opportunity for new oxide to form on clean surfaces, thereby enabling the establishment of excellent metallic bonds between the electrodeposited copper and base metal.

The inventive process provides higher yields, better adhesion while minimizing the cost associated with waste treatment.

The preferred aqueous plating solution contains sulphuric acid, 0.5-0.75 moles per litre; hydrated copper sulphate, 0.3-0.5 moles per litre; urea, 1-2 grammes per litre; a wetting agent, 1-2 millilitres per litre; sulphonic acid, 1-2 grammes per litre; and deionized water, 800-1000 millilitres.

More particularly, the preferred solution composition includes 0.5 mol. copper sulphate, 0.4 mol. sulphuric acid, 1 gramme urea, 1 gramme Beta-phenylethylsulfate (an ester of a sulphonic acid) and sufficient water to make one litre of solution. Preparation of the bath is preferably carried out as follows. About 700 millilitres of deionised or distilled water is measured into a 2000 ml beaker, to which is added the above bath constituents in the order listed with continuous agitation. Subsequently enough water is added to make one litre of solution which is then filtered to remove any undissolved reagents.

Urea is included for its properties as a levelling agent. Sulphonic acid is used for its brightening properties. Sulphonic acids of the ester type, particularly of the tosyl and mesyl types, are well suited for use in the present plating bath solution. Suitable wetting agents include cationic surfactants such as sodium lauryl sulphate.

The bath is prepared by adding all of the chemicals in the order listed to the deionized water. The solution is mixed and filtered if need be to remove any undissolved particles. Metals to be plated are first cleaned to remove soil, dirt and other surface contaminants, then rinsed in deionized water. The metals are then placed in the plating tank containing the prepared bath.

Preferably, the parts remain in the plating solution for 2 to 3 minutes before a negative bias is applied to commence electroplating of copper. However, it has been noted that in some difficult cases, if the parts are given a positive bias for 30 to 60 seconds before the negative bias is applied, particularly stubborn, naturally grown oxide layers may be removed.

Normal plating process parameters include a bath temperature in the range of 20-30 degrees Celsius, at a current density of 108-216 amperes per square metre (10-20 amperes per square foot) With continuous, strong agitation. The duration of the plating step is variable, depending on the desired copper thickness.

The sulphuric acid concentration in the plating bath is sufficient for removing the oxide layers during the 2-3 minute soak before introduction of current. No extensive surface preparation or etching is required before plating, thereby reducing the number of steps and the amount of chemical waste generated and the cost attendant thereto.

The following examples are illustrative of the various aspects of the invention.

### Example 1

Aluminium and tungsten workpieces were cleaned in a mild alkaline cleaner and then plated in the following solution:

Sulphuric acid, 75 grammes/litre  
Copper sulphate, 72 grammes/litre  
Urea (levelling agent), 1 gramme/litre  
Sulphonic acid (brightener), 1 gramme/litre  
Sodium lauryl sulphate surfactant, 1 gramme/litre  
Deionized water, 1 litre

The workpieces were immersed in this solution for 2-3 minutes prior to biasing. Plating was carried out at room temperature and at 108 amperes per square metre (10 amperes per square foot) for 20 minutes. The copper deposits were smooth and free of defects such as skip plating. Testing for adhesion strength by both cross-cut and quench method showed no adhesion failures.

#### Example 2

Another example of this invention was carried out in a similar manner as Example 1, except the amount of sulphuric acid was reduced to 50 grammes/litre. Again the quality and adhesion of the copper deposit were similar to Example 1.

#### Example 3

Another experiment was carried out as in Examples 1 and 2, except that the concentration of sulphuric acid was further reduced to 30 grammes/litre. Subsequent adhesion testing showed failures at more than 25% of the tested areas.

#### Example 4

In another example the conditions were as in Example 1 except that the amount of copper sulphate was 50 grammes/litre. The electrodeposits were smooth, free of skip plating and had excellent adhesion.

#### Example 5

Coupons of tungsten which showed slight blue colour (tungsten oxide) were cleaned and then plated as in Example 1. Subsequent adhesion testing showed poor adhesion. However, when the coupons were first positively biased for 1 minute, then plated in the negative bias, the plated coupons showed good adhesion.

While the invention has been described having reference to a particular preferred embodiment,

those having skill in the art will appreciate the various changes and detail will be made without departing from the spirit and scope of the invention as claimed.

#### Claims

1. A process for copper plating electropositive metals comprising the steps of:

preparing a bath containing  
0.5 to 0.75 moles per litre sulphuric acid,  
0.3 to 0.5 moles per litre hydrated copper sulphate,  
1 to 2 grammes per litre, urea,  
1 to 2 millilitres per litre, wetting agent,  
1 to 2 grammes per litre, brightening agent, and  
800 to 1000 millilitres deionized water;  
soaking parts to be plated in the bath; and  
electrodepositing copper from the bath,  
at a temperature of about 20 to 30 degrees Celsius,  
at a current density of 108 to 216 amperes per square metre (10-20 amperes per square foot),  
with continuous agitation.

2. The process of Claim 1 wherein the soaking step is 2 to 3 minutes in duration.

3. The process of Claim 1 wherein the soaking step lasts for 30 to 60 seconds, under the influence of a positive bias.

4. The method of Claim 1 wherein the preparing step includes: mixing of bath components in the order set forth on Claim 1, in deionized water; and  
filtering the bath solution.

5. The method of Claims 1,2,3 or 4 wherein: the wetting agent is sodium lauryl sulphate; and the brightening agent is a tosyl or mesyl sulphonic acid.

6. An acid copper plating bath for electropositive metals consisting essentially of:  
0.5 to 0.75 mols per litre sulphuric acid,  
0.3 to 0.5 mols per litre hydrated copper sulphate,  
1 to 2 grammes per litre, levelling agent,  
1 to 2 millilitres per litre, wetting agent,  
1 to 2 grammes per litre, brightening agent, and  
800 to 1000 millilitres deionized water.

7. The bath of Claim 6 wherein the wetting agent is a cationic surfactant.

8. The bath of Claim 6 wherein the brightening agent is sulphonic acid.

9. The bath of Claims 6, 7, or 8 wherein the levelling agent is urea.

10. An aqueous acid copper electroplating bath composition for strongly electropositive metals such as aluminium and tungsten comprising:  
sulphuric acid, 30-50 grammes/litre;  
hydrated copper sulphate, 50-72 grammes/litre;  
urea, 1 gramme/litre;

sulphonic acid, 1 gramme/litre; and  
cationic surfactant, 1 gramme/litre.

5

10

15

20

25

30

35

40

45

50

55

4