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[54] COPPER STRIKE BATH AND METHOD FOR COATING ELECTROLESSLY PLATED ARTICLES

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[51] **Int. Cl.**[2] **C25D 3/40;** C25D 5/00
[58] **Field of Search** .... 204/52 Y, 38 B, 38 E; 106/1

[56] **References Cited**

FOREIGN PATENTS OR APPLICATIONS

94,652 6/1960 Netherlands .... 204/52 Y

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[57] **ABSTRACT**

A copper strike electroplating bath comprising tetrapotassium pyrophosphate, potassium cyanide and cuprous cyanide. The strike is especially useful for plating on electroless metal deposits such as nickel.

6 Claims, No Drawings

COPPER STRIKE BATH AND METHOD FOR COATING ELECTROLESSLY PLATED ARTICLES

This invention pertains to an electrolyte bath suitable for deposition of copper; more particularly, this invention is directed to an electrolyte bath for the deposition of a copper strike; still further, this invention pertains to a copper cyanide electrolyte bath suitable for producing a copper strike especially useful for deposition on thin film, passive and electroless metal deposits such as nickel.

BACKGROUND OF THE INVENTION

In the art of electrolytically depositing various metals, it has been very important that good adhesion is obtained between the substrate and the electrolytically deposited metal. A good adhesion is essential when passive electrolyte deposits are being produced by a technique known as electroless nickel or copper deposition.

According to electroless nickel deposition, thin film, passive electroless metal deposits are obtained by appropriately causing to react on the surface a catalyst, which is on the surface of the substrate, a very light deposit of metal, such as, by immersion in a bath containing the metal in solution. The film, which is formed on the substrate, is then exposed to a strike which co-operates especially well with the thin film deposit so that the subsequent layers of metals sought to be deposited will adhere between the electroless deposit and the electrolytic deposit.

Furthermore, it is well known that in order to produce tightly adhering deposits on an organic substrate, such as a polyimide film, polyimide-amide film, etc., a catalyst must furnish a sufficiently tight bond with the substrate so that the metal from the electroless bath would deposit on the surface sufficiently tightly with a good bond between the substrate and the metal in the electroless bath. As it can well be appreciated, the adhesion between the catalyst and the metal deposited from the electroless and electrolyte bath is fairly critical and numerous proposals have been made to solve the adhesion problem.

In addition, in order to improve the adhesion between the electroless metal and the electrolytically deposited metal without affecting the catalyst to electroless metal bond, various baths known as "strike" baths have been used to achieve a deposit for subsequent immersion of the substrate in another bath for electrolytical deposition of the metal sought to be deposited. Often the metal which is being deposited on the "strike" is a noble metal, i.e., gold or silver.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been discovered that a copper cyanide bath of a particular combination of elements is eminently suitable for use with thin film, passive electroless metal deposits such as nickel to achieve a deposit of a "strike" of good quality. The novel bath displays an ability to "strike" deposit copper on the surface and cover the electroless metal e.g. nickel deposit immediately with copper.

As it covers the electroless nickel metal deposit, the strike also provides very good adhesion. In addition, the strike deposit builds up to nominal thickness such as from 2 to 10 microinches of copper thereby reducing the electrical resistance in the substrate for subsequent

additional plating operations, such as the electrolytic plating operations previously mentioned above.

As can well be appreciated, not every electrolyte bath is a good bath for obtaining a "strike." Thus, the particular combination of the elements in the invention herein have been found to be suitable for the purpose of achieving the "strike" effect especially between the copper strike and the passive, electroless nickel deposit without being necessarily useful for some other purpose.

The term "strike" is defined as a deposit sufficient to cover the underlying deposit and improve its conductivity by means of a thin (1 to 15 microinch) layer of the "strike" metal.

In accordance with the invention, the following embodiment is illustrative of the same and is illustrated by the following solution made up as a 1 liter solution useful as a strike electrolyte.

TABLE I

ELECTROLYTE SOLUTION

Solution Make Up	gr/liter	Range gr/liter
a. Tetrapotassium Pyrophosphate $K_4P_2O_7.3H_2O$*	120	90 – 150
b. Potassium Cyanide KCN**	12.3	4 – 17
c. Cuprous Cyanide CuCN	8.2	

*Ratio of b. to c. is 2:1 to 4:1 by weight
**Proportionate to c. in the indicated ratio

With reference to the above disclosed bath, it has been used for the deposition of a strike of a thickness from 2 to 10 microinches on a Kapton H film having a nickel or cobalt deposit thereon. These deposits have been prepared as follows.

A Kapton polyimide polymer film of a thickness of 3 mils is immersed from 1 to 3 minutes in an aqueous solution of equal parts of 25% sodium hydroxide, by weight, 85% hydrazine hydrate, by weight, and triethanol amine 10% solution by weight. Thereafter the film is sprayed or immersion rinsed with cold water, followed by immersion into a 1%, by weight, palladium chloride aqueous hydrochloric acid solution, wherein palladium chloride is of a concentration of 0.1 to 1 gram per liter and hydrochloric acid is 5 to 10 milliliters per liter. In addition, a stannous chloride (10 grams per liter) and hydrochloric acid (40 milliliters per liter) solution may be used in conjunction with the palladium chloride solution as a catalyst, immersed in cold water, and dried at 100°C for 2 minutes. The surface accepts nickel or cobalt from one of the following:

Nickel Chloride	80 gm/l
Sodium Citrate	100 gm/l
Ammonium Chloride	50 gm/l
Sodium Hypophosphite	10 gm/l
Bath Temp.: 180°F	
Nickel Chloride Hexahydrate	20 gm/l
Ethylene Diamine (98%)	45 gm/l
Sodium Hydroxide	40 gm/l
Sodium Borohydride	0.67 gm/l
Bath Temp.: 180°F	
Cobalt Chloride Hexahydrate	30 gm/l
Sodium Citrate Pentahydrate	35 gm/l
Ammonium Chloride	50 gm/l
Sodium Hypophosphite, Monohydrate	20 gm/l
Bath Temp.: 180°F	
Cobalt Sulphate Heptahydrate	24 gm/l
Ammonium Sulphate	40 gm/l
Sodium Hypophosphite	20 gm/l
Sodium Citrate	80 gm/l
Sodium Lauryl Sulphate	0.1 gm/l
Bath Temp.: 180°F	

The above treated film when immersed in the above nickel or cobalt solution deposited nickel or cobalt in thicknesses which were sufficient for additive, semi-additive, or subtractive plating. These deposits were then covered with the copper strike.

Besides the Kapton (polyimide) film, poly imideamides and poly (parabanic acid) polymers may be used. The last two are of the polyimide polymer type family. Poly (parabanic acid) polymers are described in U.S. Pat. Nos. 3,547,897; 3,591,562 and 3,661,859, the disclosures of which are incorporated by reference herein. The polyimides and polyimide-amides are described in Lee et al., *New Linear Polymer*, McGraw-Hill, N.Y., N.Y. (1967) pp. 171 et seq.

To obtain the strike deposit on the nickel or cobalt deposits, the above bath was used under the following operating conditions.

TABLE II

Operating conditions	range	optimum
Temperature	120° – 140°F	130°
Sp Gravity (25°C)	14° – 22°Be	18°Be
pH (25°C) electrolitically	6.8 – 7.2	7.0
Anodes		High purity copper
Agitation	Vigorous	
ASF (Amperes per square foot)	10 – 30	about 15

As part of operating said bath, continuous filtration is necessary to remove any precipitates and impurities and to prevent auto-decomposition of the bath.

As obtained from the above bath, the strike deposit was tested by a Scotch tape adhesion test and the total electroless and strike deposit by adhesion test known in the industry as a 90° peel test and it was found that the adhesion was very satisfactory both for the strike-electroless adhesion by the Scotch tape test and the 90° peel test for the total deposit. The last test also indicates that the "strike" bath does not affect the adhesion of the electroless metal to the substrate.

According to the above-identified method, the following substrates of which an electroless and strike coating are deposited are: polyimides; polyimides-amides; poly (parabanic acid); polyester film (Mylar film); polyethylene film, etc.

The above strike covered deposits which are electroplated are used such as in printed circuit boards, circuits for integrated circuit chip attachment used in hand held calculators, etc.

What is claimed is:

1. A method for depositing a strike electrolytically on a substrate the steps comprising: depositing on a substrate an electroless layer of metal by catalyzed deposition or by immersion deposition; exposing said electroless layer on said substrate between an anode and a cathode in a bath which is at a pH of about 6.8 to 7.2 and of a composition which comprises: tetrapotassium pyrophosphate $K_4P_2O_7.2H_2O$ from about 90 to 150 grams per liter; potassium cyanide from about 4 to 17 grams per liter; and cuprous cyanide wherein the ratio of potassium cyanide to cuprous cyanide is from 2:1 to 4:1 by weight; impressing a current between said anode and said cathode to electrolytically cause the deposition of copper from said solution onto said substrate having said electroless or immersion deposited layer; and building upon said electroless or immersion deposit a tightly adhering layer of high purity copper in a thickness of 2 to 10 micro inches.

2. An aqueous bath for depositing electrolytically a copper strike on an immersed body having a metal deposit thereon, the copper strike bath being at about a pH of 6.8 to 7.2 and consisting essentially of the following components: tetrapotassium pyrophosphate $K_4P_2O_7.3H_2O$ from 90 to 150 grams per liter; (a) potassium cyanide from 4 to 17 grams per liter; and (b) cuprous cyanide, wherein the ratio of a to b is 2:1 to 4:1, by weight.

3. A method for depositing a copper strike electrolytically on a substrate having an electroless or immersion deposited layer as a conductive layer the steps of the method comprising inserting the substrate as a cathode in a bath which is at about a pH of 6.8 to 7.2 and consisting essentially of tetrapotassium pyrophosphate $K_4P_2O_7.3H_2O$; (a) potassium cyanide; and (b) cuprous cyanide, wherein the ratio of a to b is 2:1 to 4:1, by weight, impressing a current between an anode and said cathode to electrolyze said bath and cause a deposition of copper from said solution unto said substrate and building upon said substrate a tightly adhering layer of high purity copper in a thickness of 2 to 10 microinches.

4. The process as defined in claim **3** wherein the temperature of the bath is from 120° to 140°F and the pH of the bath at 25°C is from 6.8 to 7.2.

5. The process as defined in claim **3** wherein the bath is vigorously agitated and the current is impressed between the anode and cathode between at 10 to 30 ASF of said cathode.

6. The process as defined in claim **3** wherein the specific gravity of the bath at 25°C, is 14° to 22°Be.

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