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(54) **Activating a substrate for electroless plating.**

(57) A dielectric surface is conditioned for electroless plating of a conductive metal thereon by contacting the surface with a colloid of a precious metal and tin and then contacting the surface with a salt of ethylene diamine tetraacetic acid and/or of diethylene triamine pentaacetic acid.

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ACTIVATING A SUBSTRATE FOR ELECTROLESS PLATING

The present invention is concerned with conditioning or activating a substrate for electroless plating and is particularly concerned with treating a dielectric substrate to activate the substrate for the electroless deposition of a conductive metal thereon. This conditioning can be in the holes and/or on the surfaces of the substrate. The present invention finds particular applicability for the manufacture of printed circuit cards and boards. However, the present invention is applicable wherever a metal is to be deposited on a dielectric substrate such as providing decorative coatings and magnetic devices.

In the manufacture of printed circuit cards and boards, a dielectric sheet material is employed as the substrate. A conductive circuit pattern is provided on one or both of the major surfaces of the substrate.

A conductive pattern can be formed on the surface of the substrate using a variety of known techniques. These known techniques include the subtractive technique where a layer of copper is etched to form the desired circuit pattern, the EDB (electroless direct bond) technique where copper is electrolessly plated directly on the surface of the substrate in the desired pattern, the peel-apart technique where the desired circuit pattern is plated up from a thin layer of peel-apart copper and the technique whereby a thin conductive layer is electrolessly deposited and is then built up to the desired thickness by electroplating.

In any of these techniques, connections between layers are made by means of plated through holes. In plating such holes, copper must be plated directly on the dielectric substrate (on the walls of the holes). Furthermore, if one uses the EDB technique, plating occurs directly on the surface of the substrate.

Since the dielectric substrate is nonconductive, in order to plate on the substrate (either on the walls of the holes or on the surface of the substrate) the substrate must be seeded or catalyzed prior to the deposition of metal onto the substrate.

Among the more widely employed procedures for catalyzing a substrate is the use of a suspension of a Pd-Sn colloid. The colloid is a metallic core of a combination of a Pd and a small amount of Sn. The metallic core is stabilized and kept in suspension by a surrounding layer of adsorbed Sn (II) and associated counter-ions (such as Cl^- and OH^-). The noncatalytic surfaces are immersed in the colloidal suspension to deposit the catalytic material. Once the colloid is on the surface, the tin no longer plays a role. The tin in the colloid covers the Pd and detracts from the catalytic activity of the Pd. Accordingly, an accelerator is often used with the colloidal activator in order to remove tin from the activated surface.

Some of the more common accelerators are solutions of very very high or very low pH and/or are complexing agents for tin ions. Examples of such accelerators are HCl , NaOH , NH_3 , NH_4BF_4 , NH_4HF_2 , and HBF_4 . The known accelerators are often overly aggressive, tending to also remove the previously deposited metal, such as copper, in the internal planes of the substrate.

Disclosure of the Invention

The present invention provides for improved activation of a precious metal catalyst for electroless plating thereon. The accelerator employed in accordance with the present invention is non-corrosive and does not tend to remove metal already present. Also, the accelerator employed is effective over a wide pH range.

The process of the present invention is directed to treating a dielectric surface to render it catalytic for the deposition of metal thereon. The process includes contacting the surface with a colloid of a precious metal and tin to provide a layer of the precious metal and tin on the surface. The surface containing the layer is contacted with at least one material selected from the group of salts of ethylene diamine tetraacetic acid, and/or of diethylene triamine pentaacetic acid. Mixtures of these materials can be used when desired. This treatment increases the catalytic activity of the layer for the electroless deposition.

The process of the present invention is applicable to treating or conditioning a wide variety of dielectric (non-conductor) substrates. Dielectric substrates described in the prior art, including thermoplastic and thermosetting resins and glass, may be treated in accordance with the present invention.

Typical thermosetting polymeric materials include epoxy, phenolic-based materials and polyamides. The

dielectric materials may be molded articles of the polymers containing fillers and/or reinforcing agents such as glass-filled epoxy or phenolic-based materials. Examples of some phenolic-type materials include copolymers of phenol, resorcinol and cresol. Examples of some suitable thermoplastic polymeric materials include polyolefins such as polypropylene, polysulfones, polycarbonates, nitrile rubbers and ABS polymers.

The present invention can be used to treat at least one of the major surfaces of the substrate as well as the plated through holes or vias and/or blind holes in the substrate, when present.

Prior to the initiation of the process of the present invention for treating the dielectric substrate, the holes, if present in the circuit board, are made and the dielectric with the holes is suitably cleaned and preconditioned.

The preconditioning can include enhancement of the adhesion of the deposit to the substrate, for example, by physical means such as sand and/or vapor blasting and/or chemical methods such as solvent swelling. A typical solvent is N-methyl pyrrolidone. The substrate can also be pretreated with a sulfochromic acid composition.

According to a preferred aspect of the present invention, prior to treatment with the precious metal-tin colloid, the substrate is treated with an aqueous solution containing a multifunctional ionic polymer, as disclosed in US-A-4478883. However, the present invention

does not require and is not dependent upon this treatment with an ionic polymer.

The polymer is a multifunctional ionic material in that it must contain at least two active or available ionic functional moieties of the opposite polarity of the overall charge on the precious metal colloid. The polymers are at least water-miscible and are preferably water-soluble or at least soluble in the water compositions employed in the present invention. For a negatively charged colloid, the ionic moieties are cationic moieties such as quaternary phosphonium and quaternary ammonium groups. Polymers containing at least two ionic moieties are commercially available and need not be described herein in any great detail. Examples of commercially available multifunctional cationic polymers are Reten 210, Reten 220 and Reten 300, available from Hercules, description of which can be found in "Water-Soluble Polymers", Bulletin VC-482A, Hercules Incorporated, Wilmington, Delaware 19899, disclosure of which is incorporated herein by reference.

Reten 210 is in powder form and is a copolymer of acrylamide and betamethacryloxyethyltrimethylammonium methyl sulfate having a Brookfield viscosity of a 1% solution of 600-1000 cps.

Reten 220 is in powder form and is a copolymer of acrylamide and betamethacryloxyethyltrimethylammonium methyl sulfate having a Brookfield viscosity of a 1% solution of 800-1200 cps.

Reten 300 is a liquid and is a homopolymer of betamethacryloxyethyltrimethylammonium methyl sulfate having a Brookfield viscosity of a 1% solution of 300-700 cps.

The molecular weight of the Reten polymers is usually relatively high and varies from about 50,000 to about 1,000,000 or more. These high molecular weight polymers are solid products and their main chemical backbone structure is polyacrylamide. The cationic Reten (positive charge) is obtained by attaching to the polyacrylamide various tetraalkyl ammonium compounds. These quaternary ammonium groups provide the number of positive charges of the polymer.

In the preferred aspects of the present invention, the ionic polymer is employed as a dilute aqueous solution of about 0.01 to about 1% by weight and preferably, about 0.05 to about 0.5% by weight of the copolymer. The aqueous solution also usually contains an inorganic acid, such as HCl, to provide a pH of about 1 to about 7 and preferably a pH of about 2 to about 3. The use of a pH of about 2 to about 3 is preferred in order to obtain a relatively low viscosity for the polymer solution to facilitate application of the polymer. The viscosity drastically increases when the pH is above about 4 to 5. The acid is usually present in amounts of about 2 to about 10% by weight.

The treatment with the ionic polymer is generally about 1 to about 10 minutes and preferably about 1 to 2 minutes.

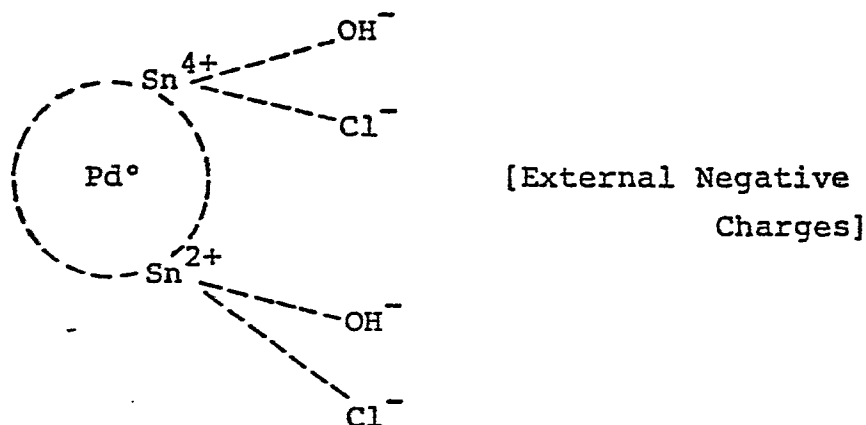
The multifunctional polymer provides a surface being of a polarity opposite from that associated with the catalyst particles to be subsequently applied to the substrate. This difference in polarity provides for electrostatic attraction of the catalyst particles. Although this treatment with the polymer provides for improved coverage of the colloid on the surface, it is a preferred, but not required step of the present invention.

After the substrate is contacted with the ionic polymer composition, the substrate is rinsed, such as with deionized water, to remove any excess polymer not adsorbed by the substrate.

Next, the substrate is activated by contact with a composition containing a catalytic composition capable of initiating the electroless plating process. The compounds contain a metal which can directly provide the catalytic sites or can serve as a precursor which leads to the catalytic sites. The metal present may be in the elemental form, an alloy, or compound or mixtures thereof. The preferred metal catalysts are precious metals such as palladium and platinum.

The most preferred catalyst is palladium. A typical colloidal palladium composition is prepared from about 1.2 to 2.5 g/l of a palladium salt which is preferably PdCl_2 , about 80 to 150 g/l of a stannous salt which is preferably $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and about 100 to 150 ml/l of an acid which is preferably 37% HCl and about 150-200 g/l of NaCl . The composition can also contain a wetting agent such as FC-95. The most preferred composition contains about 1.5 g/l of PdCl_2 , about 100 g/l of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, about 100 ml/l of 37% HCl , about 175 g/l of NaCl , and about 0.11 g/l of FC-95. The composition is generally used at about normal room temperature. It is believed that the palladium particles in the solution have associated therewith a negative charge as the pendant charge extending outward therefrom. In

particular, it is believed that the following occurs in the palladium chloride solution:



Accordingly, with a palladium-stannous catalyst system, the ionic polymer is a cationic polymer (positively charged).

Although the above procedure is preferred, it is understood that the present invention is applicable to any activation procedure using tin-stabilized colloidal activators alone or in combination with other activating procedures.

After deposition of the colloid catalyst, the substrate is preferably rinsed with deionized water.

The substrate is then treated with a salt of ethylene diamine tetraacetic acid and/or of diethylene triamine pentaacetic acid to accelerate the catalytic activity of the precious metal by removing the tin protective layer therefrom. The salts include alkali metal salts such as sodium and potassium, and ammonium salts. The preferred treatment is with salts of ethylenediamine tetraacetic acid.

The preferred compounds employed are disodium ethylenediamine tetraacetic acid and tetrasodium ethylenediamine tetraacetic acid. The extent of the ionization of the acid can be varied by changing the pH of the solution.

The treatment is preferably with an aqueous solution of the compound being a pH of at least about 4.5 and preferably about 4.5 to about 12 and therefore the salts are preferably soluble in water. The solution used contains at least about 0.05 molar and up to the solubility limit of, and preferably about 0.1 molar to the solubility limit of the salt of the ethylene diamine tetraacetic acid and/or of the ethylene triamine pentaacetic acid.

The treatment with the acceleration components is usually about 1/2 minute to about 5 minutes and preferably about 1 minute.

After this treatment, the substrate is preferably rinsed by contacting it with water and essentially deionized water. The substrate is then preferably dried by heating at about 73°C for 15 minutes and then at about 160°C for about 1 hour under vacuum before undergoing any required photoprocesses prior to electroless plating. It is not necessary to dry the substrate prior to electroless plating if no photoprocesses are required. It is essential that the tin is removed prior to the drying since such step tends to convert the tin into SnO_2 , which is extremely difficult to remove. In addition, it is desirable to remove the tin prior to the plating bath itself since contamination of the bath by the tin should be avoided. Also, a superior deposit is obtained when the substrate is covered with the most active catalyst and when

plating begins immediately upon immersion in the electroless plating bath.

Next, a metal such as copper, nickel, cobalt, and gold or alloys thereof selected for the desired application is deposited by an electroless plating technique. Mixtures can be employed when desired.

The metal is coated to the desired thickness. The preferred metal for printed circuit boards is copper. Suitable copper electroless plating baths and their method of application are disclosed in U.S. Patent Nos. 3,844,799 and 4,152,467.

The copper electroless plating bath is generally an aqueous composition which includes a source of cupric ion, a reducing agent, a complexing agent for the cupric ion and a pH adjuster. The plating baths also preferably include a cyanide ion source and a surface active agent.

The cupric ion source generally used is cupric sulfate or a cupric salt of the complexing agent to be employed. When employing cupric sulfate, it is typical to use amounts from about 3 to about 15 g/l and more typically, from about 8 to about 12 g/l. The most common reducing agent employed is formaldehyde which typically is used in amounts from about 0.7 to about 7 g/l and more typically, from about 0.7 to about 2.2 g/l. Examples of some other reducing agents include formaldehyde precursors or derivatives such as paraformaldehyde, trioxane, dimethyl hydantoin and glyoxal; borohydrides such as alkali metal borohydrides (sodium and potassium borohydride) and substituted borohydrides such as sodium trimethoxyborohydride; and boranes such as amineboranes (dimethyl amine borane,

isopropyl amine borane and morpholine borane). Hypophosphite reducing agents can also be used for electroless Cu plating.

Examples of some suitable complexing agents include Rochelle salts, ethylene diamine tetraacetic acid, the sodium (mono-, di-, tri-, and tetra-sodium) salts of ethylene diamine tetraacetic acid, gluconic acid, gluconates, triethanol amine, glucono (gamma)-lactone, modified ethylene diamine acetate such as N-hydroxyethyl ethylene diamine triacetate. In addition, a number of other suitable cupric complexing agents are suggested in U.S. Patent Nos. 2,996,408; 3,075,855; 3,075,856; and 2,938,805. The amount of complexing agent is dependent upon the amount of cupric ions present in the solution and is generally from about 20 to about 50 g/l, or in a 3-4 fold molar excess.

The copper plating bath can also contain a surfactant which assists in wetting the surface to be coated. A satisfactory surfactant is, for instance, an organic phosphate ester available under the trade designation "Gafac RE-610". Generally, the surfactant is present in amounts from about 0.02 to about 0.3 g/l. In addition, the pH of the copper bath is also generally controlled, for instance, by the addition of a basic compound such as sodium hydroxide or potassium hydroxide in the desired amount to achieve the desired pH. The preferred pH of the electroless copper plating bath is between 11.6 and 11.8.

The copper plating bath can also contain a cyanide ion and typically contains about 10 to about 25 mg/l to provide a cyanide ion concentration in the bath within the range of 0.0002 to 0.0004 molar. Examples of some cyanides which can be employed are the alkali metal,

alkaline earth metal, and ammonium cyanides. In addition, the plating baths can include other minor additives as is well known in the prior art.

The copper plating baths employed typically have a specific gravity within the range of 0.060 and 1.080. In addition, the temperature of the bath is preferably maintained between 70° and 80°C and most preferably between 70° and 75°C. For a discussion of the preferred plating temperatures coupled with the preferred cyanide ion concentrations, see U.S. Patent No. 3,844,799.

Also, the O₂ content of the bath can be maintained between about 2 ppm and 4 ppm and preferably about 2.5 to 3.5 ppm, as discussed in U.S. Patent No. 4,152,467. The O₂ content can be controlled by injecting oxygen and an inert gas into the bath.

The overall flow rate of the gases into the bath is generally from about 1 to about 20 SCFM per 1000 gallons of bath and more usually from about 3 to about 8 SCFM per 1000 gallons of bath.

The following non-limiting examples are presented to further illustrate the present invention:

Example 1

An epoxy substrate is immersed into a bath of about 0.05 grams of Reten per 100 ml of a 2% HCl aqueous solution for about 3 minutes. The substrate is then rinsed with deionized water. Next, the coated substrate is immersed in a bath prepared from about 1.5 grams per liter of PdCl₂, about 100 grams per liter of SnCl₂·2H₂O and about 100 milliliters per liter of 37% HCl, about 175 grams per liter of NaCl, and about 0.11

grams per liter of FC-95 at normal room temperature for about 5 minutes. The substrate is rinsed in deionized water. The substrate is then contacted for about 1 minute with a 0.12 molar solution of tetrasodium salt of ethylenediamine tetraacetic acid having a pH of 11.7.

The substrate is rinsed in deionized water and then immersed in a copper electroless additive plating bath for about 10 minutes. The electroless plating bath contains about 10 grams per liter of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 35 grams per liter of ethylene diamine tetraacetic acid, 10 milligrams per liter sodium cyanide, and 2 milliliters per liter of 37% aqueous HCHO . The pH is 11.7 by the addition of NaOH and the temperature of the bath is $73^\circ \pm 5^\circ\text{C}$. The O_2 content of the bath is maintained at about 2.5 to 3.5 ppm. The gas flow rate is about 12 SCFM. In addition, the plating racks are continuously agitated during the plating.

The substrate, after plating, has a continuous copper film thereon.

Example 2

Example 1 is repeated except that the acceleration composition employed is a 0.13 molar solution having a pH of about 4.5 and containing about 1.9×10^{-3} molar of monosodium ethylene diamine tetraacetic acid; about 0.125 molar of disodium ethylene diamine tetraacetic acid and about 2.6×10^{-3} molar of trisodium ethylene diamine tetraacetic acid. The results obtained are similar to those of Example 1.

CLAIMS

1. A process for treating a dielectric surface to render it catalytic for the electroless deposition of metal thereon which comprises:

contacting the surface with a colloid of a precious metal and tin to provide a layer of the precious metal and tin on the surface; and

contacting the surface containing said layer with an agent selected from the group of salts of ethylene diamine tetraacetic acid or of diethylene triamine pentaacetic acid or mixtures thereof in order to accelerate and activate the layer to render it catalytic for said electroless deposition.

2. The process of claim 1 wherein said agent is applied as an aqueous solution having a pH of at least about 4.5.

3. The process of claim 1 wherein said agent is applied as an aqueous solution having a pH of about 4.5 to about 12.

4. The process of claim 1 wherein said agent is applied as an aqueous solution containing at least about 0.05 molar of the agent.

5. The process of claim 1 wherein said agent is applied as an aqueous solution containing about 0.1 to the solubility limit of the agent.

6. The process of claim 1 wherein said agent is a salt of ethylene diamine tetraacetic acid.

7. The process of claim 1 wherein said salt is an alkali metal salt.
8. The process of claim 1 wherein said salt is a sodium salt.
9. The process of claim 1 wherein the treatment with said agent is for about 1/2 to about 5 minutes.
10. The process of claim 1 wherein said precious metal is palladium.
11. The process of claim 1 wherein prior to contact with said colloid, the substrate is contacted with a composition containing a multifunctional ionic polymer material containing at least two available ionic moieties, wherein said ionic moieties are of a charge opposite from the charge associated with the particles of the colloid to be subsequently applied to the substrate.
12. The process of claim 1 wherein said multifunctional ionic polymer material is a multifunctional cationic polymer material.
13. The process of claim 1 wherein said multifunctional ionic polymer material is a copolymer of acrylamide and ammonium quaternary compound.
14. The process of claim 1 wherein subsequent to contacting with said agent, the substrate is heated in order to dry the substrate.

15. A process for plating a substrate with a conductive metal which comprises treating a dielectric substrate to render it catalytic by a process as claimed in any one of claims 1 to 14 and thereafter contacting the treated substrate with an electroless plating bath containing a conductive metal therein.

16. The process of claim 15 wherein said conductive metal is selected from the group of nickel, copper, cobalt, gold, alloys thereof and mixtures thereof.