

Description

The present invention relates to a sensitizing agent for electroless plating and to a method for sensitizing substrates with the agent.

Electroless plating, such as electroless copper plating, is widely applied in the field of printed circuit boards to form circuits on electrically insulative substrates such as plastic laminated boards and the like. In this case, the substrate to be electroless-plated is subjected to sensitization, i.e. treatment to form catalytic nuclei for electroless plating thereon, before immersing in an electroless plating bath. For instance, copper ions in the bath are deposited as metallic copper around these catalytic nuclei and grow into copper films, thus forming circuits. To sensitize electrically insulative substrates, fine particles of metallic palladium, silver, copper, or nickel which act as catalytic nuclei for electroless plating are formed on the surfaces of the substrates. As an example, palladium particles for this purpose, according to the prior art, are produced by the following reaction:—



PdCl_2 — SnCl_2 — HCl sensitizing systems are described in US—A—3,011,920, US—A—3,960,573 and US—A—3,696,544.

The PdCl_2 — SnCl_2 — HCl sensitizing system contains many impurities particularly Sn and Cl and strongly acidic, therefore, apparatus exposed thereto are damaged and the pink-ring phenomenon, of inner layer circuits in multilayer circuit boards, occurs.

The pink-ring phenomenon of inner layer circuits occurs as follows:

Multilayer printed circuit boards are produced from circuits formed by etching copper-clad laminated sheets, the resulting inner layer circuit sheets and prepregs (products of impregnating base materials such as paper and glass fabrics with thermosetting resins, followed by drying them) are superposed alternately one over another; the top layer is overlaid with a copper foil or a laminate clad with copper on one side; the whole laminate is heated and pressed into a single body; the copper on the top layer is processed to form a circuit corresponding to the pattern of the inner layer circuit; through-holes are formed by perforating layers (including parts of the inner layer circuits) at required positions; and a metal layer is formed on the inner wall of each through-hole by electroless plating. In this process, the surfaces of the inner layer circuits are coated with copper oxide (usually 1—3 μm thick) so as to enhance the adhesion between each inner layer circuit and the prepreg facing it. The inner wall of each through-hole is sensitized before the electroless plating. When the PdCl_2 — SnCl_2 — HCl sensitizing system is used for the sensitization, portions of the oxide coat exposed to the through-holes will dissolve in

hydrochloric acid, and hydrochloric acid will diffuse into the interface between the surface of the inner layer circuit and the prepreg resin layer, thus causing delamination thereof. This is the pink-ring phenomenon. When this phenomenon occurs, the bond strength and the insulation resistance are reduced.

An object of the present invention is to provide a sensitizing agent for electroless plating which causes minimum damage to exposed apparatus and no pink-ring phenomenon.

Another object of the invention is to provide a method for sensitizing such substrates with the agent.

According to the invention there is provided a sensitizing agent for electroless plating which consists of (i) water or alcohol and (ii) a solution of at least one compound of palladium (II), silver (I), copper (I), copper (II), or nickel (II) dissolved in an amide, the concentration of the metal compound in the agent being 0.01 to 1.0% by weight and the agent having a pH of 11 to 13.

Suitable amides for use in the present invention include formamide, dimethylformamide, diethylformamide, dimethylacetamide, dimethylarylamide, and mixtures of these amides.

Suitable compounds of palladium (II), silver (I), copper (I), copper (II), and nickel (II) for use in the invention include chlorides, fluorides, bromides, iodides, nitrates, sulfates, oxides, sulfides, and mixtures of these compounds. Of these compounds, the chlorides are particularly preferred.

The metal compounds are dissolved in the above-mentioned amide, and the solution is diluted with water or alcohol to make up a sensitizing agent having a compound concentration of 0.01 to 1.0% by weight and a pH of 11 to 13, preferably 11.5 to 12.5. It is considered that the above compound, dissolved in the above amide, may form a complex with the amide.

When substrates, such as plastic laminated boards, ceramic boards, plastic molded articles and plastic films, which are intended to be plated are dipped in the sensitizing agent and then soaked in a reducing solution, metallic nuclei of palladium, silver, copper, and/or nickel are formed on the substrate surfaces.

Suitable reducing solutions for use herein are aqueous or alcoholic solutions of reducing substances such as formaldehyde, stannous chloride, sodium borohydride (NaBH_4), grape sugar, and the like. The concentration thereof is desirably from 0.01 to 10%, preferably from 0.1 to 1% by weight, and the pH is desirably from 3 to 14.

The above reducing substances may be used alone or in combination with one or another with a stabiliser having buffer action, for example, methanol for formaldehyde, hydrochloric acid for stannous chloride, or sodium hydroxide for sodium borohydride.

Electroless plating is effected on immersing the substrate, on which nuclei, for instance of palladium, have been thus formed for plating, in an electroless plating bath, which may be a

commonly used electroless plating solution of for instance copper or nickel.

The sensitizing effect can be further improved by a pretreatment of the substrate to be plated before it is immersed in the sensitizing agent defined above. For this pretreatment, it is possible to use 0.1 to 10% aqueous hydrogen peroxide; aqueous hydrogen peroxide having the same concentration and adjusted with sulfuric acid to pH 3—6; hydrochloric acid of pH 3—6; sulfuric acid of pH 3—6; a 0.1 to 10% solution of an epoxy resin of the bisphenol A type in water, alcohol, or methyl ethyl ketone; and the above-mentioned reducing solution.

Instead of immersing it in the sensitizing agent for electroless plating and the reducing solution, the substrate may be sprayed with these solutions.

Example 1

A glass-epoxy laminated board (1.6 mm thick) copper-clad on both sides which had previously been dipped in an aqueous solution of a mixture of sodium hydroxide, potassium chlorite, and sodium phosphate to form an oxide coat on each copper surface, was drilled to form through-holes and then immersed for 5 minutes in a sensitizing solution prepared by diluting a 2.0% by weight concentration solution of PdCl_2 in formamide, with water to a PdCl_2 concentration of 0.1% and pH 12.5. After removing the liquid, the board was immersed with agitation in a 1% solution of sodium borohydride in 1% aqueous NaOH for 5 minutes, then immersed in an electroless plating solution CUST-201 (tradename, made by Hitachi Chemical Co., Ltd.) for 20 minutes, and rinsed with water. As a result of the electroless copper plating, copper was uniformly deposited on the inner walls of the through-holes in the glass-epoxy laminated board and no chemical attack of the oxide coats covering the copper surfaces was observed.

Example 2

The same glass-epoxy laminated board clad with copper on both sides (1.6 mm thick) as used in Example 1 was coated with the oxide as in Example 1, drilled to form through-holes, and rinsed.

The board was then treated with a 1.0% solution of NaBH_4 in 0.1% aqueous NaOH for 30 seconds.

A sensitizing agent was prepared by diluting a 1% solution of PdCl_2 in formamide with an 0.3% aqueous NaOH solution to a PdCl_2 concentration of 0.05% and pH 12. The board was immersed in this sensitizing agent and agitated well for 5 minutes. After removing the liquid, the board was treated with a 1.0% reducing solution of NaBH_4 in 0.1% aqueous NaOH for 3 minutes, then immersed in an electroless copper plating solution, CUST-201 (the same as used in Example 1) for 20 minutes, and rinsed with water. As a result of this electroless copper plating, copper was uniformly deposited on the walls of the through-

holes in the board and no chemical attack of the oxide films covering the copper surfaces was observed.

According to the present invention, the following effects can be achieved:

(1) The damage of the apparatus exposed to the sensitizing agent for electroless plating is reduced since the pH of the solution is in the range of 11 to 13.

(2) Uniform plating can be accomplished.

(3) No chemical attack of the inner layer circuits of multilayer printed circuit boards occurs.

Claims

1. A sensitizing agent for electroless plating which consists of (i) water or alcohol and (iii) a solution of at least one compound of palladium (II), silver (I), copper (I), copper (II) or nickel (II) dissolved in an amide, the concentration of the metal compound in the agent being 0.01 to 1.0% by weight and the agent having a pH of 11 to 13.

2. A sensitizing agent according to claim 1, wherein the amide is at least one selected from formamide, dimethylformamide, diethylformamide, dimethylacetamide, and dimethylacrylamide.

3. A sensitizing agent according to claim 1 or claim 2, wherein the metal compound is at least one selected from chlorides, fluorides, bromides, iodides, nitrates, sulfates, oxides, and sulfides of the metal.

4. A sensitizing agent according to any one of claims 1 to 3 wherein the pH of the agent is 11.5 to 12.5.

5. A method for sensitizing a substrate to be electroless-plated, which comprises treating the substrate with a sensitizing agent, according to any one of claims 1 to 4, followed by treating the substrate with a reducing solution.

6. A method according to claim 5, wherein the substrate is a plastic laminated board, ceramic board, plastic molded article or plastic film.

7. A method according to claim 5 or claim 6 wherein the reducing solution is an aqueous or alcoholic solution of at least one reducing substance selected from formaldehyde, stannous chloride, sodium borohydride and grape sugar.

8. A method according to any one of claims 5 to 7, wherein the concentration of the reducing substance in the reducing solution is 0.01 to 10% by weight.

9. A method according to claim 8 wherein the concentration of the reducing substance in the reducing solution is 0.1 to 1% by weight.

10. A method according to any one of claims 5 to 9 wherein the pH of the reducing solution is 3 to 14.

Patentansprüche

1. Sensibilisierungsmittel für stromloses Plattieren, dadurch gekennzeichnet, daß es aus (i) Wasser oder Alkohol und (iii) einer Lösung mindestens einer Verbindung von Palladium (II), Sil-

commonly used electroless plating solution of for instance copper or nickel.

The sensitizing effect can be further improved by a pretreatment of the substrate to be plated before it is immersed in the sensitizing agent defined above. For this pretreatment, it is possible to use 0.1 to 10% aqueous hydrogen peroxide; aqueous hydrogen peroxide having the same concentration and adjusted with sulfuric acid to pH 3—6; hydrochloric acid of pH 3—6; sulfuric acid of pH 3—6; a 0.1 to 10% solution of an epoxy resin of the bisphenol A type in water, alcohol, or methyl ethyl ketone; and the above-mentioned reducing solution.

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The same glass-epoxy laminated board clad with copper on both sides (1.6 mm thick) as used in Example 1 was coated with the oxide as in Example 1, drilled to form through-holes, and rinsed.

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Claims

1. A sensitizing agent for electroless plating which consists of (i) water or alcohol and (iii) a solution of at least one compound of palladium (II), silver (I), copper (I), copper (II) or nickel (II) dissolved in an amide, the concentration of the metal compound in the agent being 0.01 to 1.0% by weight and the agent having a pH of 11 to 13.

2. A sensitizing agent according to claim 1, wherein the amide is at least one selected from formamide, dimethylformamide, diethylformamide, dimethylacetamide, and dimethylacrylamide.

3. A sensitizing agent according to claim 1 or claim 2, wherein the metal compound is at least one selected from chlorides, fluorides, bromides, iodides, nitrates, sulfates, oxides, and sulfides of the metal.

4. A sensitizing agent according to any one of claims 1 to 3 wherein the pH of the agent is 11.5 to 12.5.

5. A method for sensitizing a substrate to be electroless-plated, which comprises treating the substrate with a sensitizing agent, according to any one of claims 1 to 4, followed by treating the substrate with a reducing solution.

6. A method according to claim 5, wherein the substrate is a plastic laminated board, ceramic board, plastic molded article or plastic film.

7. A method according to claim 5 or claim 6 wherein the reducing solution is an aqueous or alcoholic solution of at least one reducing substance selected from formaldehyde, stannous chloride, sodium borohydride and grape sugar.

8. A method according to any one of claims 5 to 7, wherein the concentration of the reducing substance in the reducing solution is 0.01 to 10% by weight.

9. A method according to claim 8 wherein the concentration of the reducing substance in the reducing solution is 0.1 to 1% by weight.

10. A method according to any one of claims 5 to 9 wherein the pH of the reducing solution is 3 to 14.

Patentansprüche

1. Sensibilisierungsmittel für stromloses Platieren, dadurch gekennzeichnet, daß es aus (i) Wasser oder Alkohol und (iii) einer Lösung mindestens einer Verbindung von Palladium (II), Sil-



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be Kupfer (I), Kupfer (II) oder Nickel (II) gelöst in einem Amid, besteht, wobei die Konzentration der Metallverbindung in dem Mittel 0,01 bis 1,0 Gew.-% beträgt und das Mittel einen pH von 11 bis 13 hat.

2. Sensibilisierungsmittel nach Anspruch 1, dadurch gekennzeichnet, daß das Amid mindestens ein Amid ausgewählt aus Formamid, Dimethylformamid, Diethylformamid, Dimethylacetamid und Dimethylacrylamid ist.

3. Sensibilisierungsmittel nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Metallverbindung mindestens eine Metallverbindung ausgewählt aus Chloriden, Fluoriden, Bromiden, Iodiden, Nitraten, Sulfaten, Oxiden und Sulfiden des Metalls ist.

4. Sensibilisierungsmittel nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der pH des Mittels 11,5 bis 12,5 ist.

5. Verfahren zur Sensibilisierung eines Substrats, das stromlos plattiert werden soll, dadurch gekennzeichnet, daß man das Substrat mit einem Sensibilisierungsmittel nach einem der Ansprüche 1 bis 4 behandelt und anschließend das Substrat mit einer reduzierenden Lösung behandelt.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das Substrat eine mit Kunststoff laminierte Tafel, eine Keramiktafel, ein Kunststoffkörper oder ein Kunststofffilm ist.

7. Verfahren nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß die reduzierende Lösung eine wäßrige oder alkoholische Lösung mindestens einer reduzierenden Substanz ausgewählt aus Formaldehyd, Zinn(II)chlorid, Natriumborhydrid und Traubenzucker ist.

8. Verfahren nach einem der Ansprüche 5 bis 7, dadurch gekennzeichnet, daß die Konzentration der reduzierenden Substanz in der reduzierenden Lösung 0,01 bis 10 Gew.-% ist.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß die Konzentration der reduzierenden Substanz in der reduzierenden Lösung 0,1 bis 1 Gew.% ist.

10. Verfahren nach einem der Ansprüche 5 bis 9, dadurch gekennzeichnet, daß der pH der reduzierenden Lösung 3 bis 14 ist.

Revendications

1. Agent de sensibilisation pour dépôt non électrolytique, constitués de (i) de l'eau ou un alcool et (iii) une solution d'au moins un composé de palladium (II), argent (I), cuivre (I), cuivre (II) ou nickel (II), dissous dans un amide, la concentration du composé métallique dans l'agent étant de 0,01 à 1,0% en poids et l'agent présentant un pH de 11 à 13.

2. Agent de sensibilisation conforme à la revendication 1, dans lequel l'amide est au moins un amide choisi parmi le formamide, le diméthylformamide, le diéthylformamide, le diméthylacétamide et le diméthylacrylamide.

3. Agent de sensibilisation conforme à la revendication 1 ou à la revendication 2, dans lequel le composé métallique est au moins un composé choisi parmi les chlorures, fluorures, bromures, iodures, nitrates, sulfates, oxydes et sulfures du métal.

4. Agent de sensibilisation conforme à l'une quelconque des revendications 1 à 3, dans lequel le pH de l'agent est de 11,5 à 12,5.

5. Procédé de sensibilisation d'un substrat destiné à recevoir un dépôt non électrolytique, qui comprend le traitement du substrat avec un agent de sensibilisation conforme à l'une quelconque des revendications 1 à 4, suivi par le traitement du substrat avec une solution réductrice.

6. Procédé conforme à la revendication 5, dans lequel le substrat est un panneau stratifié de matière plastique, un panneau de céramique, un article moulé en matière plastique ou un film de matière plastique.

7. Procédé conforme à la revendication 5 ou à la revendication 6, dans lequel la solution réductrice est une solution aqueuse ou alcoolique d'au moins une substance réductrice choisie parmi le formaldéhyde, le chlorure stanneux, le borohydrure de sodium et le sucre de raisin.

8. Procédé conforme à l'une quelconque des revendications 5 à 7, dans lequel la concentration de la substance réductrice dans la solution réductrice est de 0,01 à 10% en poids.

9. Procédé conforme à la revendication 8, dans lequel la concentration de la substance réductrice dans la solution réductrice est de 0,1 à 1% en poids.

10. Procédé conforme à l'une quelconque des revendications 5 à 9, dans lequel le pH de la solution réductrice est de 3 à 14.

