

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO DEPOSITING A METAL ON A SURFACE

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED of 222 Broadway and formerly of 195 Broadway, New York City, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The invention relates to depositing a metal on a dielectric surface.

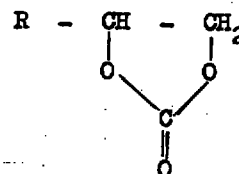
It is commonplace today to generate metallic patterns or deposits on electrically insulative or dielectric surfaces by means of electroless metal deposition techniques. Conventionally, aqueous sensitizer and/or activator solutions are employed wherein a catalytic activating metal is deposited on the surface which catalyzes electroless metal deposition from a suitable electroless metal deposition solution. Where the surface to be metallized is hydrophobic, as for example in the case of most organic polymeric substrate surfaces, it is often very difficult to achieve wetting thereof by the aqueous sensitizing and/or activating solutions thereby leading to electroless metal deposits which are discontinuous and/or have poor adhesion to the surface metallized.

A method of electrolessly metal depositing such hydrophobic surfaces with a continuous and adherent deposit is desired and needed.

The invention provides a method of depositing a metal on a dielectric surface which comprises treating the surface with a stable hydrosol formed by mixing and heating together in an acidic aqueous medium

- (1) a salt of a noble metal, and
- (2) an organic compound containing at least two oxygen atoms selected from the group consisting of

- (a) an organic carbonate having a structural formula of



where R is an alkyl radical or a hydrogen atom, (b) ethylene glycol and (c) 1, 3 dioxane, and exposing the treated surface to an electroless metal deposition solution so that the metal is catalytically deposited thereon.

The present embodiment of the invention will be discussed primarily in terms of electrolessly depositing Cu metal on a dielectric surface by means of an electroless metal deposition catalyst comprising a catalytic Pd species or a catalytic Ag species. However, it will be readily appreciated that other suitable metals may be used which are catalytically reduced from their respective ions by other catalytic activating metals (noble metals) such as Pt, Au, Ir, Os, Rh, Ru, or catalytic species thereof.

A suitable substrate is selected. For the production of electrical circuit patterns, suitable substrates are those which are generally electrically non-conductive. In general all dielectric materials are suitable substrates. Dielectric materials commonly employ a resinous material which may incorporate fibrous reinforcement. For instance, paper or cardboard, glass fibre or other fibrous material may be impregnated with a phenolic, epoxy or fluorohydrocarbon (e.g., polytetrafluoroethylene) resinous material and pressed or rolled to a uniform thickness. Ceramic substrates may likewise be selected.

A surface of the substrate, e.g., a polyimide substrate, a polytetrafluoroethylene substrate, is treated with a universal electroless metal deposition catalyst to render the surface capable of being electrolessly metal deposited by

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exposure to a suitable electroless metal deposition solution. By the use of the term "universal" is meant that the catalyst is one which is effective for the electroless deposition of a void-free and adherent metal deposit on a hydrophilic surface, e.g., a ceramic surface, as well as on a hydrophobic surface, e.g., an organic polymer surface, on a surface which is swelled thereby, e.g., a polyimide surface, or on a surface which is not swelled thereby, e.g., a polytetrafluoroethylene surface. Additionally, hydrophobic surfaces, e.g., polyimide or polytetrafluoroethylene surfaces, treated by the catalyst of the present embodiment of the invention, do not appear to be either wetted by the catalyst nor rendered hydrophilic by the catalyst.

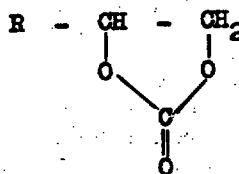
The universal catalyst is one which is capable of participating in an electroless metal deposition catalysis, either by initially existing as a catalytic noble metal (atomic) or by subsequently being converted into or forming a catalytic noble metal species (ionic and/or atomic). By the term "catalytic noble metal species" is meant a noble metal species, which serves as a reduction catalyst in an autocatalytic electroless metal deposition. For example, a universal catalyst comprising a catalytic palladium species is one which can initially exist (1) as a catalytic atomic species, i.e., catalytic palladium metal (Pd^0); (2) as a catalytic ionic species, i.e., Pd^{+2} ions, which is subsequently converted into catalytic palladium metal, as by reduction with a suitable reducing agent, e.g., formaldehyde, hydrazine, etc.; or (3) as both a catalytic palladium atomic species and a catalytic palladium ionic species.

The universal catalyst of the present invention comprises a stable hydrosol and is prepared by first mixing or combining together a noble metal salt, e.g., PdCl_2 , AgNO_3 , etc., and a suitable organic compound containing at least two oxygen atoms. The salt and the organic compound are mixed in an acidic aqueous medium, e.g., a 5 weight percent aqueous HCl solution. The resultant mixture is maintained at or heated to an elevated temperature, e.g., $65-75^\circ\text{C}$., for a sufficient period of time, e.g., 15-30 minutes at $65-75^\circ\text{C}$., whereby a stable hydrosol is formed. By a stable hydrosol is meant a hydrosol which is homogeneous in that there is no agglomeration of the colloidal particles contained therein and also there is no occurrence of a distinct liquid-liquid phase separation.

Suitable noble metal salts are those comprising salts of Pd, Pt, Ag, Au, etc., which are soluble in an acidic aqueous medium. Some typical salts include the

noble metal nitrates, halides, e.g., chlorides, bromides, fluorides, iodides, etc. The amount of the noble metal salt employed should be sufficient to deposit an adequate catalytic species concentration on the substrate surface whereby a continuous, void-free and adherent electroless metal deposit will be obtained. However, the amount of the noble metal salt should not be so large as to deposit too large a catalytic species concentration on the surface whereby the resultant electroless metal deposit will lose adhesiveness and result in poor adhesion to the surface being treated. Typically, for Pd salts, e.g., PdCl_2 , the amount employed ranges from 0.025 weight percent of the mixture to 0.075 weight percent of the mixture. A concentration of a Pd salt of less than 0.025 weight percent results in a spotty electroless metal deposit and a concentration of greater than 0.075 weight percent results in a deposit having poor adhesion.

Suitable organic compounds include liquid organic carbonates having a structural formula of



where R is a hydrogen atom or an alkyl radical such as CH_3 , C_2H_5 , etc. Preferred carbonates are ethylene carbonate ($\text{R}=\text{H}$) and propylene carbonate ($\text{R}=\text{CH}_3$). Other suitable organic compounds include ethylene glycol and 1, 3 dioxane. The preferred amount of the organic compound employed has been found to be at least 50 volume percent (e.g., 81 weight percent of propylene carbonate) of the resultant mixture. If less than 50 volume percent is employed, a spotty electroless metal deposition is obtained.

In order to obtain a stable hydrosol which functions as a universal catalyst, the aqueous medium must be acidic. That is, the mixing of the noble metal salt and the organic compound must be done in a water medium which has been acidified by a suitable acid, e.g., HCl, H_2SO_4 , etc. Additionally, the pH of the resultant mixture should be controlled to prevent the formation of a discontinuous electroless metal deposit and to preserve the stability of the resultant hydrosol, as by preventing flocculation from occurring therein. It has been found that a pH ranging from 0.3 up to but less than 4.0 is preferred. If the pH is less than 0.3 a discontinuous electroless metal deposit may be obtained. If the pH is 4.0 or greater, than the hydrosol becomes

unstable and a noble metal hydrous oxide or other oxygen containing species thereof precipitates therefrom and electroless metal deposition with the use thereof will not take place.

The concentration of both the noble metal salt and the organic compound employed as well as the pH maintained depend upon the particular compounds selected whereby a stable catalytic hydrosol is obtained. In this regard, such concentrations and pH maintenance are known or are easily ascertained experimentally by one skilled in the art.

The mixture is heated at temperatures above room temperature (25°C.) ranging up to the boiling point of the mixture for a period sufficient to form the stable hydrosol. The stable hydrosol is typically characterized by a dark coloured sol which does not change colour upon additional heating, i.e., the colour of the resultant sol remains constant with time at a particular temperature. Typically, the mixture is heated at 65—75°C. for a period of time ranging preferably from 15 minutes to 30 minutes but may range from 15 minutes to several hours whereby a stable hydrosol is obtained.

The time and temperature parameters for forming a stable hydrosol are interdependent and variations in the temperature will require variations in the time whereby a stable catalytic hydrosol will be obtained. The various parameters and their interaction between one another are known or can be easily ascertained by one skilled in the art.

The colloidal particles contained in the hydrosol are thought to be a hydrous oxide of the noble metal which has been complexed in some manner with the organic compound. However, the exact species contained in the hydrosol are not known.

The surface of the substrate is then treated with the universal catalyst, employing any conventional technique such as spraying, spin coating, dipping, etc., whereby the surface is catalyzed by forming thereon a layer or coat of the hydrosol, which layer or coat is capable of participating in an electroless metal deposition catalysis. Preferably, the substrate surface is immersed in the hydrosol at the elevated temperature of its formation, e.g., 65—75°C., for a short period of time, e.g., typically one minute, whereafter it is removed therefrom.

The hydrosol treated substrate surface may then be water rinsed and is then treated, as for example by immersion, with a suitable electroless metal deposition solution, wherein, sequentially, (1) a catalytic noble metal species, e.g., Pd metal, is formed if not already present, and (2) an

electroless metal ion, e.g., Cu^{+2} , is reduced to the metal, e.g., Cu^0 , and catalytically deposited on the surface to form an electroless metal deposit. A suitable electroless metal deposition solution comprises a metal ion, e.g., Cu^{+2} , which is catalytically reduced to its corresponding metal, e.g., Cu^0 , by a suitable reducing agent, e.g., formaldehyde, in the presence of a catalytic noble metal species such as a noble metal. A suitable reducing agent is one which (1) is capable of reducing a noble metal ionic species to a catalytic noble metal species such as a noble metal and (2) is capable of reducing the electroless metal ions to the corresponding electroless metal. The electroless metal deposit may then be further built up or electro-plated in a standard electroplating bath.

It is to be noted that the various typical electroless and electroplating solutions and the plating conditions and procedures are well known in the art and will not be elaborated herein. Reference in this regard is made to *Metallic Coating of Plastics*, William Goldie, Electrochemicals Publications, 1968.

It is also to be noted that the invention may be employed for selective metallization whereby a metal pattern is obtained. Conventional masking and lithographic techniques, well known in the art, may be employed to obtain such metal patterns used for example in the production of electrical circuit patterns on a non-conductive substrate.

EXAMPLE I

An electroless metal deposition catalyst (hydrosol) was prepared in the following manner. Three hundred ml. (366 grams) of propylene carbonate was heated to a temperature in the range of 65—75°C. One hundred ml. (100 grams) of deionized water was added to the heated propylene carbonate and the mixture was maintained at 65—75°C. until a homogenous solution comprising 75 volume percent propylene carbonate was obtained (60—90 minutes). Twenty-five grams of an aqueous solution comprising 0.5 weight percent PdCl_2 and 0.5 weight percent HCl was added to the aqueous propylene carbonate solution maintained at 65—75°C. The solution had a pH of 2. After 15 minutes the solution turned from an initial red colour to a constant dark brown colour and a stable hydrosol formed.

A plurality of hydrophobic substrates were then treated with the resultant hydrosol. The substrates were (1) a polyimide substrate; (2) a polytetrafluoroethylene substrate; (3) a polyethylene terephthalate substrate; (4) a polypropylene substrate; and (5) a rubber-

modified epoxy substrate. Each of the substrates was immersed in a bath comprising the hydrosol and maintained at 65–75°C. for one minute and then removed. Each substrate was then water rinsed for one minute and then immersed in a commercially obtained electroless metal plating bath comprising cupric sulphate, formaldehyde, a complexer and caustic. A 5–8, inch continuous and adherent electroless copper deposit was obtained on the substrate.

The following observations were made:

(1) the hydrosol did not wet any of the substrates as evidenced by beading of the hydrosol on the surfaces upon removal from the hydrosol bath;

(2) the hydrosol swelled the polyimide film as determined by a weight gain thereof;

(3) the hydrosol did not swell the polytetrafluoroethylene substrate; and

(4) the hydrosol did not render any of the substrate surfaces hydrophilic as evidenced by the beading of water on the surfaces after rinsing therewith.

EXAMPLE II

The procedure of Example I was repeated except that the hydrosol was prepared from a 50 volume percent (81 weight percent) aqueous propylene carbonate solution. The solution had a pH of 2. Substantially the same results as of Example I were obtained, except that the resultant electroless deposit exhibited a somewhat lower adhesion.

EXAMPLE III

For comparison purposes, the procedure of Example I was repeated except that the hydrosol was prepared from a 12 volume percent aqueous propylene carbonate solution. The solution had a pH of 2. A discontinuous metallization was obtained.

EXAMPLE IV

The procedure of Example I was repeated except that the PdCl_2 was added in the form of an aqueous solution containing 0.16 weight percent H_2SO_4 . The pH of the reaction mixture and hydrosol was about 2. Substantially the same results were obtained.

EXAMPLE V

A. The procedure of Example I was repeated except that 0.075 weight percent PdCl_2 was contained in the hydrosol. Substantially the same results were obtained.

B. For comparison purposes, the procedure of Example I was repeated except that less than 0.025 weight percent of PdCl_2 was contained in the hydrosol. A discontinuous metallization was obtained.

C. For comparison purposes, the procedure of Example I was repeated except that one weight percent of PdCl_2 was contained in the hydrosol. A copper deposit was obtained which did not adhere to the surfaces of the substrates.

EXAMPLE VI

Again for comparison purposes the procedure of Example I was repeated except that the pH of the hydrosol was 4.0. A stable hydrosol was not obtained as evidenced by agglomeration. Also the mixture obtained did not catalyze any of the surfaces as evidenced by no metallization upon subsequent immersion in the electroless metal deposition bath for 10 minutes.

EXAMPLE VII

The procedure of Example I was repeated except that sufficient crystalline AgNO_3 solution was added to the aqueous propylene carbonate solution to form a mixture containing one weight percent AgNO_3 . The pH of the mixture was about 2. Substantially the same results of Example I were obtained.

EXAMPLE VIII

The procedure of Example I was repeated except that a 75 volume percent (78.54 weight percent) aqueous ethylene carbonate solution was employed. Substantially the same results were obtained.

EXAMPLE IX

The procedure of Example I was repeated except that a 75 volume percent (79 weight percent) aqueous 1,3 dioxane solution was employed. Substantially the same results were obtained.

EXAMPLE X

The procedure of Example I was repeated except that a 75 volume percent aqueous ethylene glycol solution was employed. Substantially the same results were obtained.

EXAMPLE XI

For comparison purposes, the procedure of Example I was repeated except that 0.3 gram of PdCl_2 was added to propylene carbonate at 65–75°C. The solution was acidified to a pH of 2. No metallization on any of the substrates was obtained.

WHAT WE CLAIM IS:—

1. A method of depositing a metal on a dielectric surface which comprises treating the surface with a stable hydrosol formed by mixing and heating together in an acidic aqueous medium

modified epoxy substrate. Each of the substrates was immersed in a bath comprising the hydrosol and maintained at 65–75°C. for one minute and then removed. Each substrate was then water rinsed for one minute and then immersed in a commercially obtained electroless metal plating bath comprising cupric sulphate, formaldehyde, a complexer and caustic. A 5–8_μ inch continuous and adherent electroless copper deposit was obtained on the substrate.

The following observations were made:

(1) the hydrosol did not wet any of the substrates as evidenced by beading of the hydrosol on the surfaces upon removal from the hydrosol bath;

(2) the hydrosol swelled the polyimide film as determined by a weight gain thereof;

(3) the hydrosol did not swell the polytetrafluoroethylene substrate; and

(4) the hydrosol did not render any of the substrate surfaces hydrophilic as evidenced by the beading of water on the surfaces after rinsing therewith.

EXAMPLE II

The procedure of Example I was repeated except that the hydrosol was prepared from a 50 volume percent (81 weight percent) aqueous propylene carbonate solution. The solution had a pH of 2. Substantially the same results as of Example I were obtained, except that the resultant electroless deposit exhibited a somewhat lower adhesion.

EXAMPLE III

For comparison purposes, the procedure of Example I was repeated except that the hydrosol was prepared from a 12 volume percent aqueous propylene carbonate solution. The solution had a pH of 2. A discontinuous metallization was obtained.

EXAMPLE IV

The procedure of Example I was repeated except that the PdCl₂ was added in the form of an aqueous solution containing 0.16 weight percent H₂SO₄. The pH of the reaction mixture and hydrosol was about 2. Substantially the same results were obtained.

EXAMPLE V

A. The procedure of Example I was repeated except that 0.075 weight percent PdCl₂ was contained in the hydrosol. Substantially the same results were obtained.

B. For comparison purposes, the procedure of Example I was repeated except that less than 0.025 weight percent of PdCl₂ was contained in the hydrosol. A discontinuous metallization was obtained.

C. For comparison purposes, the procedure of Example I was repeated except that one weight percent of PdCl₂ was contained in the hydrosol. A copper deposit was obtained which did not adhere to the surfaces of the substrates.

EXAMPLE VI

Again for comparison purposes the procedure of Example I was repeated except that the pH of the hydrosol was 4.0. A stable hydrosol was not obtained as evidenced by agglomeration. Also the mixture obtained did not catalyze any of the surfaces as evidenced by no metallization upon subsequent immersion in the electroless metal deposition bath for 10 minutes.

EXAMPLE VII

The procedure of Example I was repeated except that sufficient crystalline AgNO₃ solution was added to the aqueous propylene carbonate solution to form a mixture containing one weight percent AgNO₃. The pH of the mixture was about 2. Substantially the same results of Example I were obtained.

EXAMPLE VIII

The procedure of Example I was repeated except that a 75 volume percent (78.54 weight percent) aqueous ethylene carbonate solution was employed. Substantially the same results were obtained.

EXAMPLE IX

The procedure of Example I was repeated except that a 75 volume percent (79 weight percent) aqueous 1,3 dioxane solution was employed. Substantially the same results were obtained.

EXAMPLE X

The procedure of Example I was repeated except that a 75 volume percent aqueous ethylene glycol solution was employed. Substantially the same results were obtained.

EXAMPLE XI

For comparison purposes, the procedure of Example I was repeated except that 0.3 gram of PdCl₂ was added to propylene carbonate at 65–75°C. The solution was acidified to a pH of 2. No metallization on any of the substrates was obtained.

WHAT WE CLAIM IS:—

1. A method of depositing a metal on a dielectric surface which comprises treating the surface with a stable hydrosol formed by mixing and heating together in an acidic aqueous medium



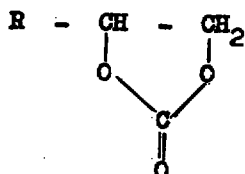
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- (1) a salt of a noble metal, and
(2) an organic compound containing at least two oxygen atoms selected from the group consisting of
5 (a) an organic carbonate having a structural formula of



where R is an alkyl radical or a hydrogen atom, (b) ethylene glycol, and (c) 1,3 dioxane and exposing the treated surface to an electroless metal deposition solution so that the metal is catalytically deposited thereon.

2. A method as claimed in claim 1, wherein the organic carbonate comprises either ethylene carbonate or propylene carbonate.

3. A method as claimed in claim 1 or claim 2, wherein the amount of the organic carbonate comprises at least 50 volume percent of the mixture.

4. A method as claimed in any one of claims 1—3, wherein the mixture is heated to a temperature from 25°C. up to the

boiling point of the mixture for a period of time sufficient to form the stable hydrosol.

5. A method as claimed in claim 4, wherein the mixture is heated to a temperature of from 65—75°C.

6. A method as claimed in claim 5, wherein the mixture is heated from 15 to 30 minutes.

7. A method as claimed in any one of the preceding claims, wherein whenever the noble metal is palladium the noble metal salt is added in an amount of from 0.025 to 0.075 weight percent of the mixture.

8. A method as claimed in any one of the preceding claims wherein the hydrosol is used at a pH of from 0.3 up to but less than 4.0.

9. A method of depositing a metal on a dielectric surface as claimed in claim 1, and substantially as hereinbefore described with reference to Examples I, II, IV, V(A), and VII to X.

10. An article when treated by the method according to any one of claims 1—9.

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