PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO METAL DEPOSITION

(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 organised 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 a method of depositing a metal on a surface and more particularly, to a method of selectively depositing a metal on a surface of an electrically non-conducting substrate.

There is a growing need in various devices and circuit applications for an inexpensive process which will produce adherent conducting circuit patterns on a non-conductor surface. Most of the processes used for metallic pattern generation involve a photographic step. Pattern resolution may be good but most methods are often slow, involving many process steps, and are relatively expensive.

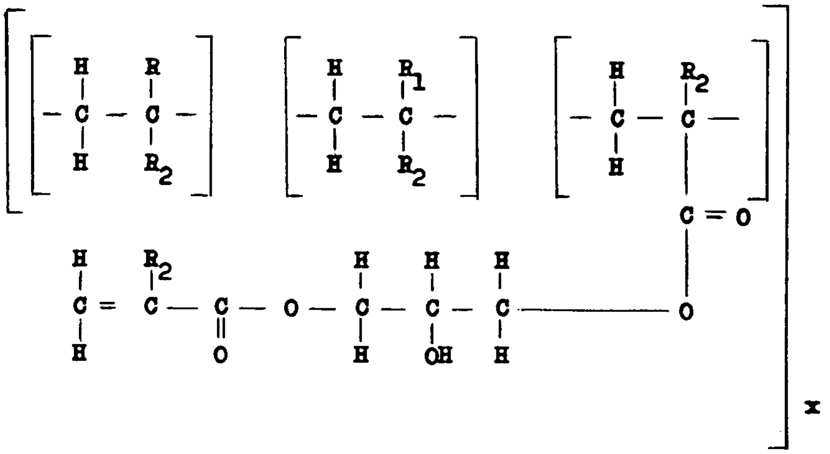
A conventional method for producing macro circuit patterns employs a copper-clad insulator board coated with a photoresist material which is photoexposed and chemically processed to selectively remove copper, leaving a desired circuit pattern. This method is effective but wasteful of copper and chemicals. The high cost of this method has encouraged research and development toward new techniques for metallic pattern generation on a non-conductor surface.

An electroless metal-deposition process is especially attractive for metallic pattern generation since it is only necessary to produce a pattern of a suitable catalyst on a substrate and metal deposition will occur only on that pattern. However, conventional electroless metal techniques usually involve separate sensitizing and activating steps which are followed by a photoresist masking step prior to immersion in an electroless deposition solution. This plurality of steps and the sequency required thereof is time consuming and expensive. Also, where a substrate has a through-hole, additional electroless deposition conditioning steps are often required and add to the expense of manufacture.

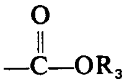
A method for selective metal deposition which eliminates one or more conventional steps is therefore needed and desired.

The invention provides a method of depositing a metal on a dielectric surface of a substrate, which method comprises:

(a) selectively polymerizing on the surface a photopolymerizable composition, comprising an addition polymer containing a plurality of units of the formulae



where R and R_1 are each a member taken from the group consisting of —CN,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR_3$$

and pyrrolidone, R_3 is an alkyl group of 1 to 18 carbons, R_2 is a member selected from the group consisting of H and CH_3, and x is a positive integer of 100 to 1000, to form a polymerized coating thereof on the surface to delineate an uncoated portion of the surface conforming to a desired metallic pattern, capable of retaining a noble metal species thereon;

(b) treating the surface with a solution comprising a noble metal ion to selectively deposit said noble metal ion on the said uncoated portion of the surface, the noble metal ion not being retained on the polymerized coating; and

(c) exposing the treated surface to an electroless metal deposition solution to selectively deposit a metal on the said uncoated portion of the surface.

The present invention will be more readily understood by reference to the following drawing taken in conjunction with the detailed description, wherein:—

Fig. 1 is an isometric view of a portion of a typical substrate;

Fig. 2 is an isometric view of the portion of Fig. 1 which has been coated with a polymerizable compound and selectively exposed to a source of radiation;

Fig. 3 is an isometric view of the portion of Fig. 2 which has been solvent treated; and

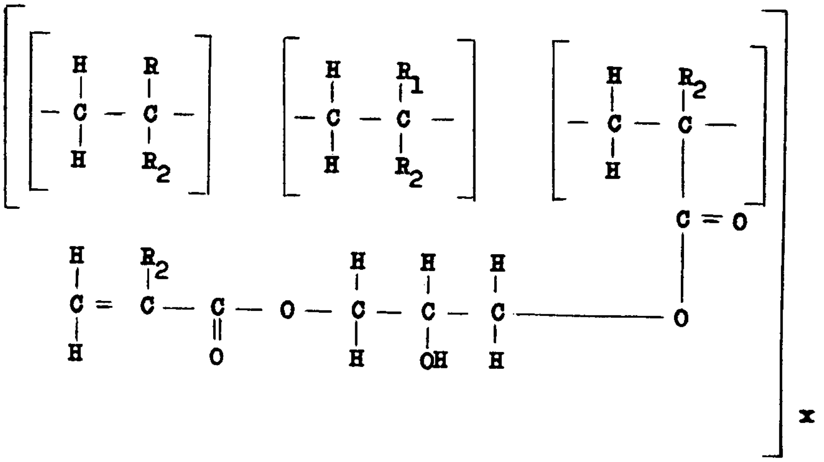
Fig. 4 is a partial isometric view of a portion of the substrate of Fig. 3 having a deposited metal pattern thereon.

The present embodiment of the invention will be discussed primarily in terms of selectively depositing Pd and Cu on a surface of an electrically insulative substrate utilizing conventional lithographic techniques. It will be readily appreciated that the idea is equally applicable to depositing other suitable metals, which are catalytically reduced from their respective ions by catalytic activating metals (Pt, Pd, Ag, Au, etc.). It will also be appreciated that the selective deposition may be carried out utilizing any conventional printing technique as well as brushing and stencilling techniques.

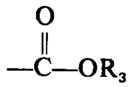
Referring to Fig. 1, a suitable substrate 70 is selected. For the production of electrical circuit patterns, suitable substrates are those which are generally electrically non-conductive. In general, all dielectric materials are suitable substrates. Dielectric materials commonly employed comprise a resinous material. If desired, the resinous material 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. Illustratively, substrate 70 is provided with a plurality of through-holes 71 which are drilled or punched in substrate 70 using any conventional technique known in the art.

Substrate 70 may then be cleaned or degreased employing techniques well known in the art. Referring to Figs. 1 and 2, surface 72 of substrate 70 is treated with a suitable photopolymerizable composition to form a coat or layer 73.

Suitable photopolymerizable compositions include the polymerizable polymeric esters disclosed in U.S. Patent Specification No. 3,418,295 and in U.S. Patent Specification No. 3,469,982. Such polyesters contain a plurality of units of the formula



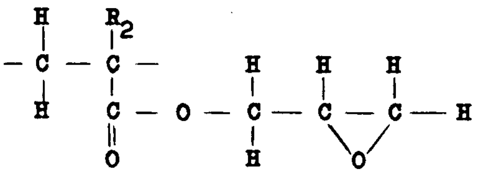
where R and R_1 are each a member taken from the group consisting of —CN,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR_3$$

and pyrrolidone, R_3 is an alkyl group of 1 to 18 carbon atoms, R_2 is a member selected from the group consisting of H and CH_3 and x is a positive integer of 10 to 1000. These polyesters are made by reacting in an inert organic solvent solution:

(1) a vinyl addition polymer having a wholly carbon chain of atoms and extralinear glycidyl ester groups in recurring intralinear units of the formula



of said chain of atoms, where R_2 is a number selected from the group consisting of H and CH_3, with

(2) acrylic or methacrylic acid in an amount sufficient to react with all the said glycidyl groups present from 10% to 100%, in the polymer to form an acrylic or methacrylic acid ester therewith, in the presence of

(3) an organic tertiary amine esterification catalyst, and

(4) an addition polymerization inhibitor; and recovering the polymeric ester containing extralinear acrylic ester groups from the solution.

The preferred addition polymers of (1) above are copolymers of unsaturated glycidyl esters with polymerizable vinyl compounds, namely compounds having a terminal methylene group attached through a double bond to the adjacent carbon atom. These materials include the copolymers of unsaturated glycidyl compounds formed with acrylic and methacrylic acid esters and nitriles, e.g., methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate and propyl, isopropyl, sec-butyl, tert.-butyl, amyl, hexyl, heptyl, etc., acrylate and methacrylate, acrylonitrile, and vinyl esters, e.g., vinyl acetate, vinyl propionate, vinyl butyrate, vinyl isobutyrate, and vinyl valerate. The preferred glycidyl monomers are glycidyl acrylate and glycidyl methacrylate.

Some suitable polymerization inhibitors include copper metal, cuprous salts, cupric salts, phenyl-α-naphthylamine, 2,2 methylene-bis (4-ethyl-6-tertiary butyl phenol) and N,N'-di-2-naphthyl-p-phenylenediamine.

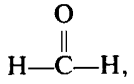
Typically, the photopolymerizable composition is dissolved in a suitable solvent, e.g., a chlorinated hydrocarbon such as methylene chloride, carbon tetrachloride, etc., in a concentration of 10 to 50% solids, and is then applied to surface 72 using any conventional means. The applied solution is then dried to form layer 73. A suitable mask 74 is placed contiguous to polymerizable composition layer 73. Mask 74 is a positive mask, i.e., has areas 76 which are opaque to a desired radiation to which positive mask 74, and, ultimately, layer 73, is destined to be exposed, which areas correspond to a desired electroless metal-deposited pattern. Positive mask 74 has areas 77 which are capable of transmitting therethrough the desired radiation to which positive mask 74 and layer 73 is destined to be exposed. It should be noted that alternatively separate masking areas may be applied to layer 73 utilizing standard materials and techniques known in the art.

A radiation source 78, e.g., an actinic radiation source, is placed above mask 74 and directed thereat. Radiation is transmitted through areas 77 of mask 74 to expose areas of polymerizable composition layer 73 thereto. The thus exposed areas of layer 73 underlying and corresponding to areas 77 of mask 74 are polymerized. Generally, about a 30 second exposure to a carbon arc source is sufficient.

After exposure, layer 73 is developed by treating, e.g., by immersion, spraying, etc. substrate 70 with a liquid which is a solvent for the unexposed polymerizable composition, comprising areas underlying and corresponding to areas 76 of mask 74. The solvent is one in which the exposed polymerized composition of layer 73, underlying and corresponding to areas 77 of mask 74, is essentially insoluble. Chlorinated hydrocarbon solvents, e.g., methylene chloride, carbon tetrachloride, 1,1-dichloroethane and 1,1,2-trichloroethylene are quite suitable solvents. Referring to Figs. 2 and 3, upon devlopment, the areas of layer 73 underlying and corresponding to areas 76 of mask 74 are removed to delineate both and exposed substrate surface pattern 79, including the walls of the through-holes 71, and a polymerized surface pattern 81. Exposed surface pattern 79 has the ability to initially retain a noble metal ion thereon to some degree, even upon rinsing of its surface with an inert agent, e.g., water. On the other hand, polymerized surface pattern 81 has the ability, relative to pattern 79, to initially repel a noble metal ion or conversely has the inability, relative to pattern 79, to initially retain a noble metal ion thereon.

Substrate 70 is then treated, e.g., by immersion or spraying, with a solution containing a dissolved salt of a noble metal, e.g., a salt of Pd, Pt, Ag, Au, etc., and is then rinsed with water. Surprisingly, activating metal ions are retained only on pattern 79 and not on pattern 81. The noble metal deposited substrate 70 may then be treated with a suitable reducing agent, e.g., a solution containing Sn^{+2} ions, formaldehyde, etc. A suitable reducing agent is one which will reduce a noble metal ion to a catalytic noble metal, i.e., a metal capable of functioning as a reduction catalyst in an autocatalytic process. Such suitable reducing agents are well known in the art or can be easily ascertained experimentally. The noble metal ions, e.g., Pd^{+2}, contained on pattern 79 are reduced by the reducing agent to a catalytic metal, e.g., Pd°, to form a catalytic metal-deposited pattern. The catalytic metal-deposited pattern may then be water rinsed and is then subjected to a conventional electroless metal deposition solution, e.g., by immersion therein, wherein an electroless metal ion, e.g., Cu^{+2}, Ni^{+2}, is reduced to the metal, e.g., Cu°, Ni° and deposited on surface pattern 79 to form an electroless metal deposit 82 as shown in Fig. 4.

Alternatively, the noble metal ion-deposited substrate 70 may be directly treated with a suitable electroless metal deposition solution when the latter contains a reducing agent, wherein sequentially the noble metal ion, e.g., Pd^{+2}, is reduced to the metal, e.g., Pd°, by the reducing agent contained therein, e.g.,



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H,$$

H_2N-NH_2, etc., and the electroless metal ion, e.g., Cu^{+2}, is catalytically reduced to the metal, e.g., Cu°, to form electroless metal deposit 82.

The electroless metal deposit 82 may be built up to a desired thickness by prolonged exposure to the electroless metal deposition solution or alternatively may be further built up by being electroplated in a standard electroplating bath.

The fact that polymerized pattern 81 does not initially retain a noble metal species without some preliminary treatment thereof is surprising. This is especially surprising and unexpected since if the developed substrate 70 is treated initially with a sensitizing species, e.g., Sn^{+2}, followed by treatment with an activating metal species or noble metal ion, e.g., Pd^{+2}, metallization will occur over the entire surface of substrate 70, including patterns 79 and 81, upon subsequent exposure to an electroless metal deposition solution. The same is true if the so-called "one-step activators" are employed which contain a tin species therein. One such typical colloidal one-step activator, revealed in U.S. Patent Specification No. 3,011,920 contains stannous chloride, palladium chloride and aqueous hydrochloric acid. Another typical one-step activator is revealed in U.S. Patent Specification No. 3,532,578 which comprises acid-palladium metal-stannous chloride sols.

It is to be noted that the various typical electroless and electroplating solutions and 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, Electrochemical Publications, 1968.

After the electroless metal deposition or the electrodeposition is carried out, the polymerized pattern 81 may be removed, if desired, by treatment with a suitable solvent such as methylene chloride followed by mechanical scrubbing thereof, if needed.

In another manner, the photopolymerizable composition can be selectively applied to surface 72 of substrate 70 (Fig. 1), e.g., as by printing, and then exposed to a source of suitable radiation to form polymerized pattern 81 and exposed surface pattern 79 (Fig. 3). The process of treating the resultant patterned substrate 70 for electroless metal deposition there-on is then carried out as described above.

EXAMPLE I

A copper-clad epoxy-polyester substrate having a through-hole therein was etched with ammonium persulfate (1.5 lbs./gal.) to remove the copper therefrom. An exposed epoxy-polyester surface of the etched substrate was coated with a photopolymerizable composition, commercially obtained, comprising poly (methyl methacrylate/acrylonitrile/acrylated glycidyl acrylate). The coated substrate surface was then selectively exposed to a source of actinic radiation for 50 seconds to polymerize the coating composition so exposed thereto. The selectively exposed substrate surface was then developed by immersion in a bath comprising 1,1,1-trichloroethane whereby unexposed portions of the coating composition (unpolymerized portions) were removed to delineate an exposed surface pattern (including the walls of the through-hole) and a polymerized composition coating pattern. The patterned surface was then immersed in an aqueous solution comprising 0.05 weight percent $PdCl_2$ for 2 minutes at 23°C. and then sprayed with a conventional electroless metal deposition solution, commercially obtained, comprising cupric sulphate and formaldehyde. An electroless copper deposit of approximately 5_{μ} inches was obtained only on the exposed substrate surface (including the walls of the through-hole) and not on the surface of the polymerized composition coating.

EXAMPLE II

For comparison purposes, the procedure of Example I was repeated except that the pattern delineated surface (developed surface) was first sensitized with an aqueous solution comprising 3.5 weight percent $SnCl_2$ and 1.0 weight percent $SnCl_4$. The sensitized surface was then immersed in the $PdCl_2$ solution. A blanket electroless copper deposition was obtained on the entire patterned surface. A spotty, poorly adherent electroless deposit was obtained on the surface of the polymerized composition coating.

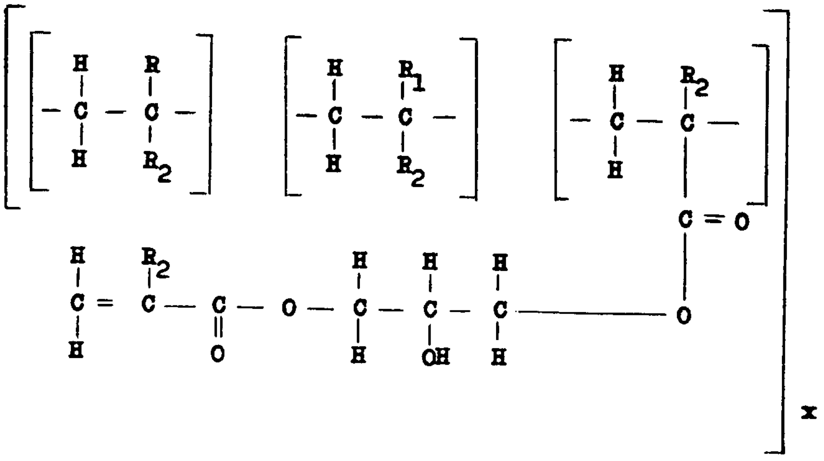
EXAMPLE III

For comparison purposes, the procedure of Example I was repeated except that the pattern-delineated surface (developed surface) was treated with a one-step activator, commercially obtained, comprising colloidal palladium metal and a protective colloid comprising a stannic oxide colloid. Again a blanket metallization of the entire substrate surface was obtained. A spotty, poorly adherent electroless-copper deposit was obtained on the surface of the polymerized composition coating.

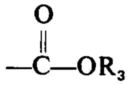
WHAT WE CLAIM IS:—

1. A method of depositing a metal on a dielectric surface of a substrate, which method comprises:

(a) selectively polymerizing on the surface a photopolymerizable composition comprising an addition polymer containing a plurality of units of the formula



where R and R_1 are each a member taken from the group consisting of —CN,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OR_3$$

and pyrrolidone, R_3 is an alkyl group of 1 to 18 carbons, R_2 is a member selected from the group consisting of H and CH_3, and x is a positive integer of 10 to 1000, to form a polymerized coating thereof on the surface to delineate an uncoated portion of the surface conforming to a desired metallic pattern, capable of retaining a noble metal species thereon;

(b) treating the surface with a solution comprising a noble metal ion to selectively deposit said noble metal ion on the said uncoated portion of the surface, the noble metal ion not being retained on the polymerized coating; and

(c) exposing the treated surface to an electroless metal deposition solution to selectively deposit a metal on the said uncoated portion of the surface.

2. A method as claimed in claim 1, wherein the inverted pattern is produced by coating the surface with the composition and treating the coated surface to polymerize the composition.

3. A method as claimed in claim 2, wherein the coated surface is selectively exposed to a source of light to polymerize the composition, and the selectively exposed coated surface is treated with a solvent to remove unpolymerized portions of said composition to delineate the uncoated portion of the surface.

4. A method as claimed in any one of the preceding claims, whereby the noble metal ion pattern is treated either by:

a) contacting the said noble metal ion pattern with an electroless metal plating solution containing a reducing agent capable of acting as a reducing agent for both the noble metal ion and for the metal ion of the metal to be plated, the so-reduced noble metal acting as a catalyst in the reduction of the metal ion to a respective metal, or

b) first contacting the treated surface with an agent capable of reducing the noble metal ion to a noble metal and then contacting the so produced noble metal pattern with an electroless metal plating solution of a desired metal to deposit the metal on the noble metal pattern.

5. A method as claimed in any one of the preceding claims, wherein the noble metal ion is Pd^{+2}.

6. A method of selectively depositing electroless coating metal on a surface of a dielectric substrate substantially as hereinbefore described with reference to and illustrated in Figs. 1—4 of the accompanying drawings.

7. An electroless coating metal deposition produced by the method according to any one of the preceding claims.

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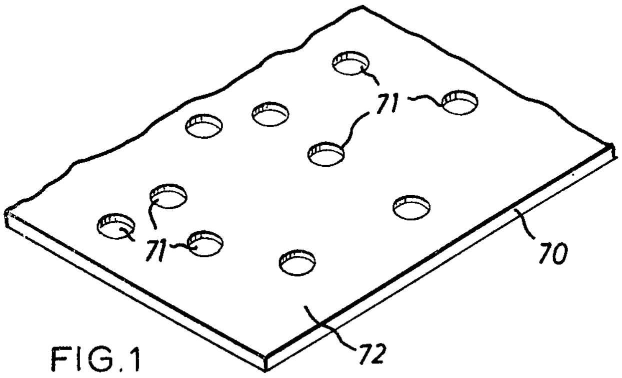

FIG.1

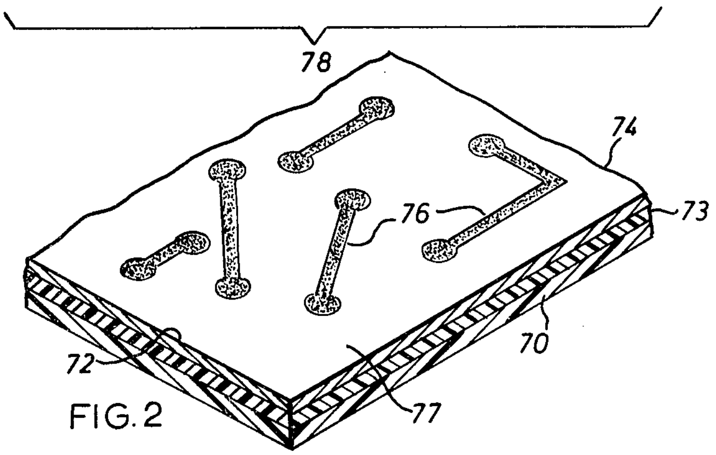

FIG.2

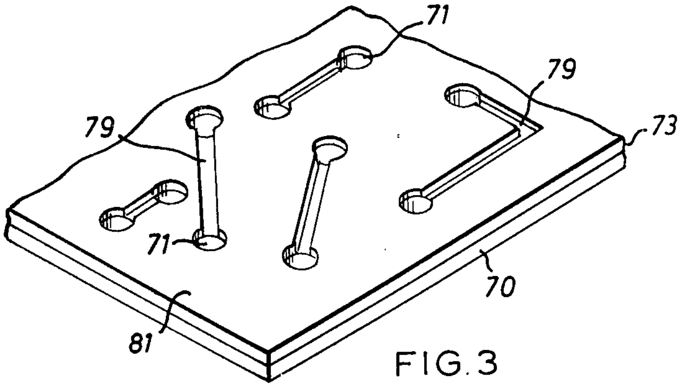

FIG. 3

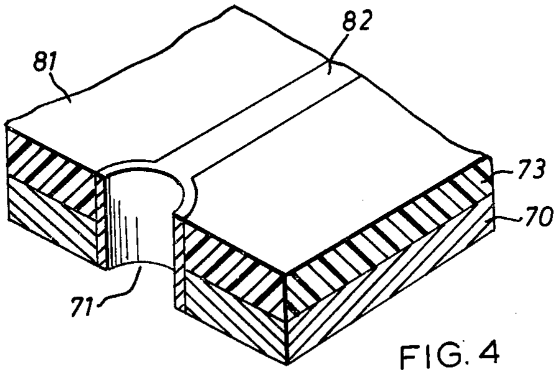

FIG. 4