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(54) **ELECTROLESS COPPER PLATING COMPOSITIONS AND METHODS FOR ELECTROLESS PLATING COPPER ON SUBSTRATES**

(57) Stable electroless copper plating baths include imidazolium compounds to improve rate of copper deposition on substrates. The copper from the electroless plating baths can be plated at low temperatures and at high plating rates.

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## Description

Field of the Invention

**[0001]** The present invention is directed to electroless copper plating compositions and methods for electroless plating copper on substrates, wherein electroless copper plating has a high electroless copper plating rate at low temperatures and the electroless copper plating compositions are stable. More specifically, the present invention is directed to electroless copper plating compositions and methods for electroless plating copper on substrates, wherein electroless copper plating has a high electroless copper plating rate at low temperatures and the electroless copper plating compositions are stable, wherein the electroless copper plating compositions include imidazolium compounds or salts thereof.

Background of the Invention

**[0002]** Electroless copper plating baths are in widespread use in metallization industries for depositing copper on various types of substrates. In the manufacture of printed circuit boards, for example, the electroless copper baths are used to deposit copper on walls of through-holes and circuit paths as a base for subsequent electrolytic copper plating. Electroless copper plating also is used in the decorative plastics industry for deposition of copper on nonconductive surfaces as a base for further plating of copper, nickel, gold, silver and other metals, as required. Electroless copper baths which are in commercial use today contain water soluble divalent copper compounds, chelating agents or complexing agents, for example, Rochelle salts and sodium salts of ethylenediamine tetraacetic acid, for chelating the divalent copper ions, reducing agents, for example, formaldehyde, and formaldehyde precursors or derivatives, and various addition agents to make the bath more stable, adjust the plating rate and brighten the copper deposit.

**[0003]** It should be understood, however, that every component in the electroless copper bath has an effect on plating potential, and therefore, must be regulated in concentration to maintain the most desirable plating potential for particular ingredients and conditions of operation. Other factors which affect internal plating voltage, deposition quality and rate include temperature, degree of agitation, type and concentration of basic ingredients mentioned above.

**[0004]** In electroless copper plating baths, the components are continuously consumed such that the baths are in a constant state of change, thus consumed components must be periodically replenished. Control of the baths to maintain high plating rates with substantially uniform copper deposits over long periods of time is exceedingly difficult. In general, electroless copper plating rates of greater than 0.6 μm/5 min. are highly desirable but rarely achieved, especially at low electroless plating temperatures, such as below 40 °C. Consumption and replenishment of bath components over several metal turnovers (MTO) can also contribute to bath instability, for example, through the buildup of side products. Therefore, such baths, and particularly those having a high plating potential, i.e. highly active baths, tend to become unstable and to spontaneously decompose with use. Such electroless copper bath instability can result in nonuniform or discontinuous copper plating along a surface. For example, in the manufacture of printed circuit boards, it is important to plate electroless copper on the walls of through-holes such that the copper deposit on the walls is substantially continuous and uniform with minimal, preferably, no break or gaps in the copper deposit. Such discontinuity of the copper deposit can ultimately lead to mal-functioning of any electrical device in which the defective printed circuit board is included.

**[0005]** To address the foregoing stability issues, various chemical compounds categorized under the label "stabilizers" have been introduced to electroless copper plating baths. Examples of stabilizers which have been used in electroless copper plating baths are sulfur containing compounds, such as disulfides and thiols. However, many stabilizers lower electroless copper plating rates, and, also, at high concentrations can be catalyst poisons, thus reducing plating rates or inhibiting plating and compromising the performance of the plating bath. Low plating rates are detrimental to electroless copper plating performance. Electroless copper plating rate is also temperature dependent, thus when high stabilizer concentrations lower the rate, increasing the plating temperature can increase the rate. However, increasing the operating temperatures can decrease the stability of the electroless copper bath by increasing the buildup of byproducts as well as reducing bath additives by side reactions, thus negating some of the effects of increasing the stabilizer concentration. As a result, in most cases the amount of stabilizer used must be a careful compromise between maintaining a high plating rate and achieving an electroless bath that is stable over a long period of time. Rate acceleration in electroless copper plating is a key strategy for lowering working temperatures, lowering internal stress of copper deposits such as on flexible substrates and decreasing overall running costs of metallization.

**[0006]** Therefore, there is a need for an additive for electroless copper plating baths which enables a high rate of electroless copper plating at low temperatures to provide bright and uniform copper deposits on substrates.

Summary of the Invention

**[0007]** The present invention is directed to an electroless copper plating composition including one or more sources of copper ions, one or more imidazolium compounds, one or more complexing agents, one or more reducing agents,

and, optionally, one or more pH adjusting agents, wherein a pH of the electroless copper plating composition is greater than 7.

**[0008]** The present invention is also directed to a method of electroless copper plating including:

a) providing a substrate comprising a dielectric;

b) applying a catalyst to the substrate comprising the dielectric;

c) applying an electroless copper plating composition to the substrate comprising the dielectric, wherein the electroless copper plating composition comprises one or more sources of copper ions, one or more imidazolium compounds, one or more complexing agents, one or more reducing agents, and, optionally, one or more pH adjusting agents, wherein a pH of the electroless copper plating composition is greater than 7; and

d) electroless plating copper on the substrate comprising the dielectric with the electroless copper plating composition.

**[0009]** The imidazolium compounds enable increased electroless copper plating rates at low plating temperatures of less than or equal to 40 °C. The electroless copper plating compositions and methods of the present invention further enable good through-hole wall coverage, even at low plating temperatures. Low plating temperatures reduce consumption of electroless copper plating composition additives which occur by undesired side reactions or decompose, thus providing a more stable electroless copper plating composition, and lower the cost of operating the electroless copper plating process.

**[0010]** The electroless copper plating compositions of the present invention are stable over wide concentration ranges of the imidazolium compounds. A broad operating window for the imidazolium compounds concentration means that the imidazolium compounds concentrations do not need to be carefully monitored such that the performance of the electroless copper plating compositions do not substantially change regardless of how the composition components are being replenished and consumed.

Detailed Description of the Invention

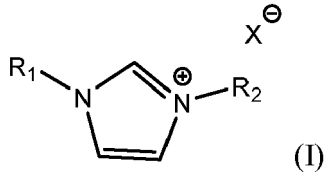
**[0011]** As used throughout this specification, the abbreviations given below have the following meanings, unless the context clearly indicates otherwise: g = gram; mg = milligram; mL = milliliter; L = liter; cm = centimeter; mm = millimeter; μm = micron; ppm = parts per million = mg/L; min. = minute; ° C = degrees Centigrade; g/L = grams per liter; DI = deionized; Pd = palladium; Pd(II) = palladium ions with a +2 oxidation state; Pd° = palladium reduced to its metal state vs. its ionic state; wt% = percent by weight; and $T_g$ = glass transition temperature.

**[0012]** All amounts are percent by weight, unless otherwise noted. All numerical ranges are inclusive and combinable in any order except where it is logical that such numerical ranges are constrained to add up to 100%.

**[0013]** The terms "plating" and "deposition" are used interchangeably throughout this specification. The terms "composition" and "bath" are used interchangeably throughout this specification. The term "alkyl", unless otherwise described in the specification as having substituent groups, means an organic chemical group composed of only of carbon and hydrogen and having a general formula: $C_nH_{2n+1}$. The term "average" is equivalent to the mean value of a sample. All amounts are percent by weight, unless otherwise noted. All numerical ranges are inclusive and combinable in any order except where it is logical that such numerical ranges are constrained to add up to 100%.

**[0014]** The electroless copper plating compositions of the present invention include one or more sources of copper ions, one or more imidazolium compounds, one or more complexing agents; one or more reducing agents; water; and, optionally, one or more pH adjusting agents, wherein a pH of the electroless copper plating composition is greater than 7.

**[0015]** Preferably, the one or more imidazolium compounds have a formula:




(I)

wherein $R_1$ is selected from the group consisting of linear or branched, unsubstituted ($C_1$-$C_{10}$)alkyl, linear or branched ($C_1$-$C_{10}$)alkoxy, linear or branched hydroxy($C_1$-$C_{10}$)alkyl, amino($C_1$-$C_{10}$)alkyl, benzyl, phenyl, carbobenzoxy, carbomethoxy, ($C_6$-$C_{10}$) heterocyclic nitrogen group and allyl; and $R_2$ is selected from the group consisting of linear or branched, unsubstituted ($C_1$-$C_{10}$)alkyl, linear or branched ($C_1$-$C_{10}$)alkoxy, linear or branched hydroxy(Ci-$C_{10}$)alkyl, ami-

no($C_1$-$C_{10}$)alkyl, benzyl, phenyl, carbobenzoxy, carbomethoxy and ($C_6$-$C_{10}$) heterocyclic nitrogen group; and $X^-$ is a counter anion. More preferably, $R_1$ is selected from the group consisting of linear or branched, unsubstituted ($C_2$-$C_4$)alkyl and benzyl; more preferably, $R_2$ is an alkyl selected from the group consisting of methyl and ethyl; and, most preferably, $R_1$ is selected from the group consisting of ethyl, butyl and benzyl, wherein the preferred is benzyl; and, most preferably, $R_2$ is methyl.

**[0016]** Preferably, $X^-$ is a halogen, hydroxide, acetate, formate, sulfate, alkylsulfate, such as methyl sulfate, hexafluorophosphate, tetrafluoroborate, tosylate, triflate, carbonate, hydrogencarbonate, bis(trifluoromethanesulfonyl)imide, phosphate, dimethyl phosphate, dicyanamide, bis(trifluoromethanesulfonyl)imide, trifluoro(trifluoromethyl)borate, or alkylsulfonate, such as methane sulfonate. More preferably, $X^-$ is a halogen selected from the group consisting of chloride, bromide, fluoride and iodide. More preferably, the halogens are selected from the group consisting of chloride and bromide, most preferably, the halogen is chloride.

**[0017]** Examples of the imidazolium compounds described above are 1-(2-methoxyethyl)-3-methylimidazolium chloride, 1-benzyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium chloride, 1-allyl-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, 1-hexyl-3-methylimidazolium chloride, 1-methyl-3-octylimidazolium chloride and 1-benzyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium acetate, 1-ethyl-3-methyimidazolium acetate, 1-butyl-3-methylimidazolium hydroxide and 1-butyl-3-methylimidazolium methane sulfonate.

The more preferred imidazolium compounds of the present invention are 1-benzyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride, wherein 1-benzyl-3-methylimidazolium chloride is the most preferred imidazolium compound.

**[0018]** The imidazolium compounds or salts thereof of the present invention are included in amounts of 0.5 ppm or greater, preferably, from 1 ppm to 50 ppm, more preferably, from 2 ppm to 30 ppm, even more preferably, from 2 ppm to 20 ppm, most preferably, from 5 ppm to 20 ppm.

**[0019]** Sources of copper ions and counter anions include, but are not limited to, water soluble halides, nitrates, acetates, sulfates and other organic and inorganic salts of copper. Mixtures of one or more of such copper salts can be used to provide copper ions. Examples are copper sulfate, such as copper sulfate pentahydrate, copper chloride, copper nitrate, copper hydroxide and copper sulfamate. Preferably, the one or more sources of copper ions the electroless copper plating composition of the present invention range from 0.5 g/L to 30 g/L, more preferably, from 1 g/L to 25 g/L, even more preferably, from 5 g/L to 20 g/L, further preferably, from 5 g/L to 15 g/L, and most preferably, from 10 g/L to 15 g/L.

**[0020]** Complexing agents include, but are not limited to, sodium potassium tartrate, sodium tartrate, sodium salicylate, sodium salts of ethylenediamine tetraacetic acid (EDTA), nitriloacetic acid and its alkali metal salts, gluconic acid, gluconates, triethanolamine, modified ethylene diamine tetraacetic acids, S,S-ethylene diamine disuccinic acid, hydantoin and hydantoin derivatives. Hydantoin derivatives include, but are not limited to, 1-methylhydantoin, 1,3-dimethylhydantoin and 5,5-dimethylhydantoin. Preferably, the complexing agents are chosen from one or more of sodium potassium tartrate, sodium tartrate, nitriloacetic acid and its alkali metal salts, such as sodium and potassium salts of nitirloacetic acid, haydantoin and hydantoin derivatives. Preferably, EDTA and its salts are excluded from the electroless copper plating compositions of the present invention. More preferably, the complexing agents are chosen from sodium potassium tartrate, sodium tartrate, nitriloacetic acid, nitriloacetic acid sodium salt, and hydantoin derivates. Even more preferably, the complexing agents are chosen from sodium potassium tartrate, sodium tartrate, 1-methylhydantoin, 1,3-dimethylhydantoin and 5,5-dimethylhydantoin. Further preferably, the complexing agents are chosen from sodium potassium tartrate and sodium tartrate. Most preferably, the complexing agent is sodium potassium tartrate (Rochelle salts).

**[0021]** Complexing agents are included in the electroless copper plating compositions of the present invention in amounts of 10 g/l to 150 g/L, preferably, from 20 g/L to 150 g/L, more preferably, from 30 g/L to 100 g/L, even more preferably, from 35 g/L to 80 g/L, and, most preferably, from 35 g/l to 55 g/L.

**[0022]** Reducing agents include, but are not limited to, formaldehyde, formaldehyde precursors, formaldehyde derivatives, such as paraformaldehyde, borohydrides, such sodium borohydride, substituted borohydrides, boranes, such as dimethylamine borane (DMAB), saccharides, such as grape sugar (glucose), glucose, sorbitol, cellulose, cane sugar, mannitol and gluconolactone, hypophosphite and salts thereof, such as sodium hypophosphite, hydroquinone, catechol, resorcinol, quinol, pyrogallol, hydroxyquinol, phloroglucinol, guaiacol, gallic acid, 3,4-dihydroxybenzoic acid, phenolsulfonic acid, cresolsulfonic acid, hydroquinonsulfonic acid, catecholsulfonic acid, tiron and salts of all of the foregoing reducing agents. Preferably, the reducing agents are chosen from formaldehyde, formaldehyde derivatives, formaldehyde precursors, borohydrides and hypophosphite and salts thereof, hydroquinone, catechol, resorcinol, and gallic acid. More preferably, the reducing agents are chosen from formaldehyde, formaldehyde derivatives, formaldehyde precursors, and sodium hypophosphite. Most preferably, the reducing agent is formaldehyde.

**[0023]** Reducing agents are included in the electroless copper plating compositions of the present invention in amounts of 0.5 g/L to 100 g/L, preferably, from 0.5 g/L to 60 g/L, more preferably, from 1 g/L to 50 g/L, even more preferably, from 1 g/L to 20 g/L, further preferably, from 1 g/L to 10 g/L, most preferably, from 1 g/L to 5 g/L.

**[0024]** A pH of the electroless copper plating composition of the present invention is greater than 7. Preferably, the

pH of the electroless copper plating compositions of the present invention is greater than 7.5. More preferably, the pH of the electroless copper plating compositions range from 8 to 14, even more preferably, from 10 to 14, further preferably, from 11 to 13, and most preferably, from 12 to 13.

**[0025]** Optionally, but preferably, one or more pH adjusting agents can be included in the electroless copper plating compositions of the present invention to adjust the pH of the electroless copper plating compositions to an alkaline pH. Acids and bases can be used to adjust the pH, including organic and inorganic acids and bases. Preferably, inorganic acids or inorganic bases, or mixtures thereof are used to adjust the pH of the electroless copper plating compositions of the present invention. Inorganic acids suitable for use of adjusting the pH of the electroless copper plating compositions include, for example, phosphoric acid, nitric acid, sulfuric acid and hydrochloric acid. Inorganic bases suitable for use of adjusting the pH of the electroless copper plating compositions include, for example, ammonium hydroxide, sodium hydroxide and potassium hydroxide. Preferably, sodium hydroxide, potassium hydroxide or mixtures thereof are used to adjust the pH of the electroless copper plating compositions, most preferably, sodium hydroxide is used to adjust the pH of the electroless copper plating compositions of the present invention.

**[0026]** Optionally, but preferably, one or more stabilizers can be included in the electroless copper plating compositions of the present invention. Stabilizers include, but are not limited to 2,2'-dipyridyl, and derivatives, 4,4'-dipyridyl, phenanthroline and phenanthroline derivatives, thiomalic acid, 2,2'dithiodisuccinic acid, mercaptosuccinic acid, cysteine, methionine, thionine, thiourea, benzothiazole, mercaptobenzothiazole, 2,2'-thiodiacetic acid, 3,3'-thiodipropionic acid, 3,3'-dithiodipropionic acid, thiosulfate, and glycols such as polypropylene glycol and polyethylene glycol.

**[0027]** Such optional stabilizers are included in the electroless copper plating compositions of the present invention in amounts of 0.1 ppm to 20 ppm, preferably, from 0.5 ppm to 10 ppm, more preferably, from 0.5 ppm to 5 ppm, most preferably from 0.5 ppm to 2 ppm.

**[0028]** Optionally, but preferably, one or more secondary accelerators can be included in the electroless copper plating compositions of the present invention. Such secondary accelerators include, but are not limited to, free nitrogen bases such as guanidine, guanidine derivatives, such as guanidine hydrochloride, pyridine and pyridine derivatives such as aminopyridine, di- and trialkylamines, such as trimethylamine and triethylamine, N,N,N',N'-Tetrakis(2-Hydroxypropyl)ethylenediamine, and ethylenediaminetetraacetic acid, and nickel(II) salts such as Nickel(II) sulfate. An example of a preferred secondary accelerator is guanidine hydrochloride.

**[0029]** Such secondary accelerators can be included in amounts of 0.1 ppm to 500 ppm, preferably, from 0.2 to 15 ppm, more preferably from, 0.3 ppm to 10 ppm, most preferably from 0.3 ppm to 5 ppm.

**[0030]** Optionally, one or more surfactants can be included in the electroless copper plating compositions of the present invention. Such surfactants include ionic, such as cationic and anionic surfactants, non-ionic and amphoteric surfactants. Mixtures of the surfactants can be used. Surfactants can be included in the compositions in amounts of 0.001 g/L to 50 g/L, preferably in amounts of 0.01 g/L to 50 g/L.

**[0031]** Cationic surfactants include, but are not limited to, tetra-alkylammonium halides, alkyltrimethylammonium halides, hydroxyethyl alkyl imidazoline, alkylbenzalkonium halides, alkylamine acetates, alkylamine oleates and alkylaminoethyl glycine.

**[0032]** Anionic surfactants include, but are not limited to, alkylbenzenesulfonates, alkyl or alkoxy naphthalene sulfonates, alkyldiphenyl ether sulfonates, alkyl ether sulfonates, alkylsulfuric esters, polyoxyethylene alkyl ether sulfuric esters, polyoxyethylene alkyl phenol ether sulfuric esters, higher alcohol phosphoric monoesters, polyoxyalkylene alkyl ether phosphoric acids (phosphates) and alkyl sulfosuccinates.

**[0033]** Amphoteric surfactants include, but are not limited to, 2-alkyl-N-carboxymethyl or ethyl-N-hydroxyethyl or methyl imidazolium betaines, 2-alkyl-N-carboxymethyl or ethyl-N-carboxymethyloxyethyl imidazolium betaines, dimethylalkyl betains, N-alkyl-β-aminopropionic acids or salts thereof and fatty acid amidopropyl dimethylaminoacetic acid betaines.

**[0034]** Preferably, the surfactants are non-ionic. Non-ionic surfactants include, but are not limited to, alkyl phenoxy polyethoxyethanols, polyoxyethylene polymers having from 20 to 150 repeating units and random and block copolymers of polyoxyethylene and polyoxypropylene.

**[0035]** Optionally, one or more grain refiner can be included in the electroless copper plating compositions of the present invention. Grain refiners include, but are not limited to, cyanide and cyanide containing inorganic salts such as potassium hexacyanoferrate, 2-mercaptobenthiazole, 2,2'-bipyridine and 2,2'-bipyridine derivatives, 1,10-phenanthroline and 1,10-phenanthroline derivatives, vanadium oxides such as sodium Metavanadate, and nickel salts such as nickel(II) sulfate. Grain refiners are included in amounts well known to those of ordinary skill in the art.

**[0036]** Preferably, the electroless copper plating composition of the present invention consists of one or more sources of copper ions, including corresponding anions, one or more imidazolium compounds having formula (I), one or more complexing agents, one or more reducing agents, water, optionally, one or more pH adjusting agents, optionally, one or more stabilizers, optionally, one or more grain refiners, optionally, one or more surfactants, and, optionally, one or more secondary accelerators, wherein a pH of the electroless copper plating composition is 10-13.

**[0037]** More preferably, the electroless copper plating composition of the present invention consists of one or more sources of copper ions, including corresponding anions, one or more imidazolium compounds having formula (I), one

or more complexing agents, one or more reducing agents, water, one or more pH adjusting agents, one or more stabilizers, optionally, one or more grain refiners, optionally, one or more surfactants, and, optionally, one or more secondary accelerators, wherein a pH of the electroless copper plating composition is 11-13.

**[0038]** Most preferably, the electroless copper plating compositions of the present invention consist of one or more sources of copper ions, including corresponding anions, one or more imidazolium compounds selected from the group consisting of 1-benzyl-3-methylimidazolium chloride, and 3-butyl-3-methyl-1H-imidazolium chloride, one or more complexing agents, one or more reducing agents, water, one or more pH adjusting agents, one or more stabilizers, optionally, one or more grain refiners, optionally, one or more surfactants, and, optionally, one or more secondary accelerators, wherein a pH of the electroless copper plating composition is 12-13.

**[0039]** The electroless copper compositions and methods of the present invention can be used to electroless plate copper on various substrates such as semiconductors, metal-clad and unclad substrates such as printed circuit boards. Such metal-clad and unclad printed circuit boards can include thermosetting resins, thermoplastic resins and combinations thereof, including fibers, such as fiberglass, and impregnated embodiments of the foregoing. Preferably the substrate is a metal-clad printed circuit or wiring board with a plurality of through-holes. The electroless copper plating compositions and methods of the present invention can be used in both horizontal and vertical processes of manufacturing printed circuit boards, preferably, the electroless copper plating compositions methods of the present invention are used in horizontal processes.

**[0040]** Thermoplastic resins include, but are not limited to, acetal resins, acrylics, such as methyl acrylate, cellulosic resins, such as ethyl acetate, cellulose propionate, cellulose acetate butyrate and cellulose nitrate, polyethers, nylon, polyethylene, polystyrene, styrene blends, such as acrylonitrile styrene and copolymers and acrylonitrile-butadiene styrene copolymers, polycarbonates, polychlorotrifluoroethylene, and vinylpolymers and copolymers, such as vinyl acetate, vinyl alcohol, vinyl butyral, vinyl chloride, vinyl chloride-acetate copolymer, vinylidene chloride and vinyl formal.

**[0041]** Thermosetting resins include, but are not limited to allyl phthalate, furane, melamine-formaldehyde, phenol-formaldehyde and phenol-furfural copolymers, alone or compounded with butadiene acrylonitrile copolymers or acrylonitrile-butadiene-styrene copolymers, polyacrylic esters, silicones, urea formaldehydes, epoxy resins, allyl resins, glyceryl phthalates, and polyesters.

**[0042]** The electroless copper plating compositions and methods of the present invention can be used to electroless copper plate substrates with both low and high $T_g$ resins. Low $T_g$ resins have a $T_g$ below 160° C and high $T_g$ resins have a $T_g$ of 160° C and above. Typically, high $T_g$ resins have a $T_g$ of 160° C to 280° C or such as from 170° C to 240° C. High $T_g$ polymer resins include, but are not limited to, polytetrafluoroethylene (PTFE) and polytetrafluoroethylene blends. Such blends include, for example, PTFE with polypheneylene oxides and cyanate esters. Other classes of polymer resins which include resins with a high $T_g$ include, but are not limited to, epoxy resins, such as difunctional and multifunctional epoxy resins, bimaleimide/triazine and epoxy resins (BT epoxy), epoxy/polyphenylene oxide resins, acrylonitrile butadienestyrene, polycarbonates (PC), polyphenylene oxides (PPO), polypheneylene ethers (PPE), polyphenylene sulfides (PPS), polysulfones (PS), polyamides, polyesters such as polyethyleneterephthalate (PET) and polybutyleneterephthalate (PBT), polyetherketones (PEEK), liquid crystal polymers, polyurethanes, polyetherimides, epoxies and composites thereof.

**[0043]** In the method of electroless copper plating with the electroless copper compositions of the present invention, optionally, the substrates are cleaned or degreased, optionally, roughened or micro-roughened, optionally, the substrates are etched or micro-etched, optionally, a solvent swell is applied to the substrates, through-holes are desmeared, and various rinse and anti-tarnish treatments can, optionally, be used.

**[0044]** Preferably, the substrates to be electroless copper plated with the electroless copper plating compositions and methods of the present invention are metal-clad substrates with dielectric material and a plurality of through-holes such as printed circuit boards. Optionally, the boards are rinsed with water and cleaned and degreased followed by desmearing the through-hole walls. Prepping or softening the dielectric or desmearing of the through-holes can begin with application of a solvent swell. Although, it is preferred, that the method of electroless copper plating is for plating through-hole walls, it is envisioned that the method of electroless copper plating can also be used to electroless copper plate walls of vias.

**[0045]** Conventional solvent swells can be used. The specific type can vary depending on the type of dielectric material. Minor experimentation can be done to determine which solvent swell is suitable for a particular dielectric material. The $T_g$ of the dielectric often determines the type of solvent swell to be used. Solvent swells include, but are not limited to, glycol ethers and their associated ether acetates. Conventional amounts of glycol ethers and their associated ether acetates well know those of skill in the art can be used. Examples of commercially available solvent swells are CIRCUPOSIT™ Conditioner 3302A, CIRCUPOSIT™ Hole Prep 3303 and CIRCUPOSIT™ Hole Prep 4120 solutions (available from Dow Advanced Materials).

**[0046]** After the solvent swell, optionally, a promoter can be applied. Conventional promoters can be used. Such promoters include sulfuric acid, chromic acid, alkaline permanganate or plasma etching. Preferably, alkaline permanganate is used as the promoter. Examples of commercially available promoters are CIRCUPOSIT™ Promoter 4130 and CIRCUPOSIT™ MLB Promoter 3308 solutions (available from Dow Advanced Materials). Optionally, the substrate and

through-holes are rinsed with water.

**[0047]** If a promoter is used, a neutralizer is then applied to neutralize any residues left by the promoter. Conventional neutralizers can be used. Preferably, the neutralizer is an aqueous acidic solution containing one or more amines or a solution of 3wt% hydrogen peroxide and 3wt% sulfuric acid. An example of a commercially available neutralizer is CIRCUPOSIT™ MLB Neutralizer 216-5. Optionally, the substrate and through-holes are rinsed with water and then dried.

**[0048]** After neutralizing an acid or alkaline conditioner is applied. Conventional conditioners can be used. Such conditioners can include one or more cationic surfactants, non-ionic surfactants, complexing agents and pH adjusters or buffers. Examples of commercially available acid conditioners are CIRCUPOSIT™ Conditioners 3320A and 3327 solutions (available from Dow Advanced Materials). Suitable alkaline conditioners include, but are not limited to, aqueous alkaline surfactant solutions containing one or more quaternary amines and polyamines. Examples of commercially available alkaline surfactants are CIRCUPOSIT™ Conditioner 231, 3325, 813 and 860 formulations (available from Dow Advanced Materials). Optionally, the substrate and through-holes are rinsed with water.

**[0049]** Optionally, conditioning can be followed by micro-etching. Conventional micro-etching compositions can be used. Micro-etching is designed to clean and provide a micro-roughened metal surface on exposed metal (e.g. innerlayers and surface etch) to enhance subsequent adhesion of plated electroless copper and later electroplate. Micro-etches include, but are not limited to, 60 g/L to 120 g/L sodium persulfate or sodium or potassium oxymonopersulfate and sulfuric acid (2%) mixture, or generic sulfuric acid/hydrogen peroxide. Examples of commercially available micro-etching compositions are CIRCUPOSIT™ Microetch 3330 Etch solution and PREPOSIT™ 748 Etch solution (both available from Dow Advanced Materials). Optionally, the substrate is rinsed with water.

**[0050]** Optionally, a pre-dip can then be applied to the micro-etched substrate and through-holes. Examples of pre-dips include, but are not limited to, organic salts such as sodium potassium tartrate or sodium citrate, 0.5% to 3% sulfuric or nitric acid or an acidic solution of 25 g/L to 75 g/L sodium chloride. An example of a commercially available acidic pre-dip is Pre-Dip CIRCUPOSIT™ 6520 acid solution (available from Dow Electronic Materials).

**[0051]** A catalyst is then applied to the substrate. While it is envisioned that any conventional catalyst suitable for electroless metal plating which includes a catalytic metal can be used, preferably, a palladium catalyst is used in the methods of the present invention. The catalyst can be a non-ionic palladium catalyst, such as a colloidal palladium-tin catalyst, or the catalyst can be an ionic palladium. If the catalyst is a colloidal palladium-tin catalyst, an acceleration step is done to strip tin from the catalyst and to expose the palladium metal for electroless copper plating. If the catalyst is a colloidal palladium-tin catalyst, an acceleration step is done using hydrochloric acid, sulfuric acid or tetrafluoroboric acid as the accelerator at 0.5-10% in water to strip tin from the catalyst and to expose the palladium metal for electroless copper plating. If the catalyst is an ionic catalyst, the acceleration step is excluded from the method and, instead, a reducing agent is applied to the substrate subsequent to application of the ionic catalyst to reduce the metal ions of the ionic catalyst to their metallic state, such as Pd (II) ions to Pd° metal. Examples of suitable commercially available colloidal palladium-tin catalysts are CIRCUPOSIT™ 3340 catalyst and CATAPOSIT™ 44 catalyst (available from Dow Advanced Materials). An example of a commercially available palladium ionic catalyst is CIRCUPOSIT™ 6530 Catalyst. The catalyst can be applied by immersing the substrate in a solution of the catalyst, or by spraying the catalyst solution on the substrate, or by atomization of the catalyst solution on the substrate using conventional apparatus. The catalysts can be applied at temperatures from room temperature to 80° C, preferably, from 30° C to 60° C. The substrate and through-holes are optionally rinsed with water after application of the catalyst.

**[0052]** Conventional reducing agents known to reduce metal ions to metal can be used to reduce the metal ions of the catalysts to their metallic state. Such reducing agents include, but are not limited to, dimethylamine borane (DMAB), sodium borohydride, ascorbic acid, iso-ascorbic acid, sodium hypophosphite, hydrazine hydrate, formic acid and formaldehyde. Reducing agents are included in amounts to reduce substantially all of the metal ions to metal. Such amounts are well known by those of skill in the art. If the catalyst is an ionic catalyst, the reducing agents are applied subsequent to the catalyst being applied to the substrate and prior to metallization.

**[0053]** The substrate and walls of the through-holes are then plated with copper using an electroless copper plating composition of the present invention. Methods of electroless copper plating of the present invention can be done at temperatures of 40 °C or less. Preferably, methods of electroless copper plating of the present invention are done at temperatures from room temperature to 40 °C, more preferably, electroless copper plating is done from room temperature to 35 °C, even more preferably, from 30 °C to 35 °C, most preferably, from 30 °C to 34 °C. The substrate can be immersed in the electroless copper plating composition of the present invention or the electroless copper plating composition can be sprayed on the substrate. Methods of electroless copper plating of the present invention using electroless copper plating compositions of the present invention are done in an alkaline environment of pH greater than 7. Preferably, methods of electroless copper plating of the present invention are done at a pH of greater than 7.5, more preferably, electroless copper plating is done at a pH of 8 to 14, even more preferably, from 10 to 13, further preferably, from 11 to 13, and most preferably, from 12 to 13.

**[0054]** Preferably, the electroless copper plating rates of the present invention are equal to or greater than 0.6 μm/5 min. at temperatures of less than or equal to 40 °C, more preferably, the electroless copper plating rates of the present

invention are equal to or greater than 0.65 μm/5 min., such as from 0.65 μm/5 min. to 0.8 μm/5 min., even more preferably, equal to or greater than 0.7 μm/5 min., such as from 0.7 μm/5 min. to 0.8 μm/5 min., at temperatures of less than or equal to 35 °C, most preferably, electroless plating is done at temperatures from 30 °C to 34 °C.

**[0055]** The methods of electroless copper plating using the electroless copper plating compositions of the present invention enable good average backlight values for electroless copper plating of through-holes of printed circuit boards. Such average backlight values are preferably greater than or equal to 4.5, more preferably from 4.6 to 5, even more preferably from 4.7 to 5, most preferably from 4.8 to 5. Such high average backlight values enable the methods of electroless copper plating of the present invention using the electroless copper plating compositions of the present invention to be used for commercial electroless copper plating, wherein the printed circuit board industry substantially requires backlight values of 4.5 and greater. The electroless copper metal plating compositions and methods of the present invention enable uniform, bright copper deposits over broad concentration ranges of imidazolium compounds or salts thereof, even at high plating rates.

**[0056]** The following examples are not intended to limit the scope of the invention but to further illustrate the invention.

Example 1

Electroless Copper Plating Rates of an Electroless Copper Plating Baths Containing 1-Benzyl-3-Methylimidazolium Chloride

**[0057]** Four (4) electroless copper plating baths are prepared. All four baths include the following components:

Table 1

| Component | Bath 1 | Bath 2 | Bath 3 | Bath 4 (Control) |
|---|---|---|---|---|
| Copper sulfate pentahydrate | 10 g/L | 10 g/L | 10 g/L | 10 g/L |
| Rochelle salts | 40 g/L | 40 g/L | 40 g/L | 40 g/L |
| Sodium hydroxide | 8 g/L | 8 g/L | 8 g/L | 8 g/L |
| Formaldehyde | 4 g/L | 4 g/L | 4 g/L | 4 g/L |
| 2,2'-ditho-disuccinic acid | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm |
| 1-benzyl-3-methylimidazolium chloride | 2.5 ppm | 10 ppm | 20 ppm | ---------- |
| Water | To one liter | To one liter | To one liter | To one liter |

The pH of each bath is 13. Bath 4 is a control. Each bath is used to plate copper on epoxy substrates. Each epoxy substrate is first treated according to the following process prior to electroless copper plating:

(1) Conditioner 231 applied for 1.5 min. at 45 °C;

(2) Rinse with DI water for 2 min. at room temperature;

(3) Nitric acid pre-dip, pH = 2, for 0.5 min. at room temperature;

(4) 100 ppm of CIRCUPOSIT™ 6530 ionic palladium catalyst for 1 min. at 40 °C;

(5) Rinse with DI water for 1 min. at room temperature;

(6) 5 g/L boric acid and 0.6 g/L dimethylamine borane aqueous solution for 1 min. at 30 °C; and,

(7) Rinse with DI water for 1 min. at room temperature.

Electroless copper plating is done at 34 °C for 5 minutes. The plating rate is determined by weighing each substrate using a conventional laboratory analytical balance prior to electroless copper plating and then weighing each substrate subsequent to plating. The difference in the weight of each substrate is then used to calculate the deposit thickness using the laminate surface area, which is 25 $cm^2$ and the density of the copper deposit, 8.92 $g/cm^3$, and the value is converted to plating rate by dividing over the plating time length. The plating rate for each bath is shown in Table 2.

Table 2

| Bath | Plating Rate |
|---|---|
| 1 | 0.69 μm/5 min. |
| 2 | 0.65 μm/5 min. |
| 3 | 0.65 μm/5 min. |
| 4 (Control) | 0.5 μm/5 min. |

Including 1-benzyl-3-methylimidazolium chloride in the copper plating bath increases plating rate, as compared to Bath 4 control. The copper deposits from the baths containing 1-benzyl-3-methylimidazolium chloride appear bright and uniform over substantially all of the epoxy substrates. The copper deposit plated from the control bath shows large areas of irregular and rough, dark deposits with minor regions of bright deposits.

Example 2

Electroless Copper Plating Rates of an Electroless Copper Plating Baths Containing 1-Benzyl-3-Methylimidazolium Chloride and Guanidine Hydrochloride

**[0058]** Six (6) electroless copper plating baths are prepared. The pH of each bath is 13. The baths include the components and amounts as shown in Table 3.

Table 3

| Component | Bath 5 | Bath 6 | Bath 7 | Bath 8 | Bath 9 | Bath 10 (Control) |
|---|---|---|---|---|---|---|
| Copper sulfate pentahydrate | 10 g/L | 10 g/L | 10 g/L | 10 g/L | 10 g/L | 10 g/L |
| Rochelle salts | 40 g/L | 40 g/L | 40 g/L | 40 g/L | 40 g/L | 40 g/L |
| Sodium hydroxide | 8 g/L | 8 g/L | 8 g/L | 8 g/L | 8 g/L | 8 g/L |
| Formaldehyde | 4 g/L | 4 g/L | 4 g/L | 4 g/L | 4 g/L | 4 g/L |
| 2,2'-dithiodisuccinic acid | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm |
| Guanidine hydrochloride | 0.4 ppm | 0.4 ppm | 0.4 ppm | 0.4 ppm | 0.4 ppm | 0.4 ppm |
| 1-benzyl-3-methylimidazolium chloride | 2.5 ppm | 5 ppm | 10 ppm | 15 ppm | 20 ppm | ---------- |
| Water | To one liter | To one liter | To one liter | To one liter | To one liter | To one liter |

Each bath is used to plate copper on epoxy substrates. Each epoxy substrate is treated prior to electroless copper plating as described in Example 1. Electroless copper plating is done at 34 °C for 5 minutes. The plating rate is determined by the same procedure as described in Example 1. The plating rate for each bath is shown in Table 4.

Table 4

| Bath | Plating Rate |
|---|---|
| 5 | 0.74 μm/5 min. |
| 6 | 0.67 μm/5 min. |
| 7 | 0.79 μm/5 min. |
| 8 | 0.63 μm/5 min. |
| 9 | 0.7 μm/5 min. |
| 10 (Control) | 0.5 μm/5 min. |

Including 1-benzyl-3-methylimidazolium chloride in the electro less copper plating baths increases plating rate over the Bath 10 control which included guanidine hydrochloride without the 1-benzyl-3-methylimidazolium chloride. In addition, Bath 10 (control), which included guanidine hydrochloride, has the same plating rate as Bath 4 (control) of Example 1 and is plated under the same conditions as Bath 4 (control) except guanidine hydrochloride is not included in Bath 4 (control). Therefore, the substantial increase in plating rate of the electroless copper plating baths of the invention is due to the 1-benzyl-3-methylimidazolium chloride.

**[0059]** The copper deposits from the baths containing 1-benzyl-3-methylimidazolium chloride appear bright and uniform over substantially all of the epoxy substrates. The copper deposit plated from the control bath shows minor regions of bright deposits intermingled with large areas of irregular and rough deposits.

Example 3

Backlight Experiment with Aqueous Alkaline Electroless Cooper Compositions of the Present Invention Containing 1-Benzyl-3-Methylimidazolium Chloride

**[0060]** The following aqueous alkaline electroless copper compositions of the invention are prepared having the components and amounts disclosed in Table 5. Bath 11 has a pH = 12.5 at room temperature as measured using a conventional pH meter available from Fisher Scientific.

Table 5

| Component | Bath 11 |
|---|---|
| Copper sulfate pentahydrate | 10 g/L |
| Rochelle salts | 40 g/L |
| Sodium hydroxide | 8 g/L |
| Formaldehyde | 4 g/L |
| 2,2'-dithiosuccinic acid | 0.5 ppm |
| Guanidine hydrochloride | 0.4 ppm |
| 1-benzyl-3-methylimidazolium chloride | 10 ppm |
| Water | One liter |

**[0061]** Six (6) different FR/4 glass epoxy panels with a plurality of through-holes are provided: TUC-662, SY-1141, IT-180, 370HR, EM825 and NPGN. The panels are either four-layer or eight-layer copper-clad panels. TUC-662 is obtained from Taiwan Union Technology, and SY-1141 is obtained from Shengyi. IT-180 is obtained from ITEQ Corp., NPGN is obtained from NanYa and 370HR from Isola and EM825 are obtained from Elite Materials Corporation. The $T_g$ values of the panels range from 140° C to 180° C. Each panel is 5cm x 10cm.
The through-holes of each panel are treated as follows:

1. The through-holes of each panel are desmeared with CIRCUPOSIT™ Hole Prep 3303 solution for 6 min. at 80° C;

2. The through-holes of each panel are then rinsed with flowing tap water for 2 minutes;

3. The through-holes are then treated with CIRCUPOSIT™ MLB Promoter 3308 aqueous permanganate solution at 80° C for 8 min.;

4. The through-holes are then rinsed for 2 min. in flowing tap water;

5. The through-holes are then treated with a 3wt% sulfuric acid/3wt% hydrogen peroxide neutralizer at room temperature for 2 min.;

6. The through-holes of each panel are then rinsed with flowing tap water for 2 min.;

7. The through-holes of each panel are then treated with CIRCUPOSIT™ Conditioner 231 alkaline solution for 1.5 min. at 45 °C;

8. The through-holes are then rinsed with flowing tap water for 2 min.;

9. The through-holes are then treated with a sodium persulfate/sulfuric acid etch solution for 1 min. at room temperature;

10. The through-holes of each panel are then rinsed with flowing DI water for 1 min.;

11. The panels are then immersed into acidic Pre-Dip CIRCUPOSIT™ 6520 for 0.5 min. at room temperature and then immersed into CIRCUPOSIT™ 6530 Catalyst which is an ionic aqueous alkaline palladium catalyst concentrate (available from Dow Electronic Materials) for 1 min. at 40 °C, wherein the catalyst is buffered with sufficient amounts of sodium carbonate, sodium hydroxide or nitric acid to achieve a catalyst pH of 9-9.5, then the panels are rinsed with DI water for 1 min. at room temperature;

12. The panels are then immersed into a 0.6 g/L dimethylamine borane and 5 g/L boric acid solution at 30° C for 1 min. to reduce the palladium ions to palladium metal, then the panels are rinsed with DI water for 1 min.;

13. The panels are then immersed in the electroless copper plating composition of Table 5 and copper is plated at 34 °C, at a pH of 12.5 and copper is deposited on the walls of the through-holes for 5 min.;

14. The copper plated panels are then rinsed with flowing tap water for 4 min.;

15. Each copper plated panel is then dried with compressed air; and

16. The walls of the through-holes of the panels are examined for copper plating coverage using the backlight process described below.

**[0062]** Each panel is cross-sectioned nearest to the centers of the through-holes as possible to expose the copper plated walls. The cross-sections, no more than 3 mm thick from the center of the through-holes, are taken from each panel to determine the through-hole wall coverage. The European Backlight Grading Scale is used. The cross-sections from each panel are placed under a conventional optical microscope of 50X magnification with a light source behind the samples. The quality of the copper deposits are determined by the amount of light visible under the microscope that is transmitted through the sample. Transmitted light is only visible in areas of the plated through-holes where there is incomplete electroless coverage. If no light is transmitted and the section appears completely black, it is rated a 5 on the backlight scale indicating complete copper coverage of the through-hole wall. If light passes through the entire section without any dark areas, this indicates that there is very little to no copper metal deposition on the walls and the section was rated 0. If sections have some dark regions as well as light regions, they are rated between 0 and 5. A minimum of ten through-holes are inspected and rated for each board. Backlight values of 4.5 and greater are indicative of commercially acceptable catalysts in the plating industry.

**[0063]** The average backlight value for each type of FR/4 glass epoxy panel is disclosed in the table below.

Table 6

| Panel | Bath 11 |
|---|---|
| 370HR | 4.8 |
| EM825 | 4.7 |
| IT-180 | 4.6 |
| NPGN | 4.6 |
| SY-1141 | 4.4 |
| TU-662 | 4.7 |

Except for the SY-1141 epoxy panel all of the average backlight values exceed 4.5.

Example 4

Electroless Copper Plating Rates of Electro less Copper Plating Baths Containing Methylimidazolium Compounds

**[0064]** The following aqueous alkaline electroless copper compositions of the invention are prepared having the components and amounts disclosed in Table 7. The baths have a pH ranging from 10-13 at room temperature as measured using a conventional pH meter available from Fisher Scientific.

Table 7

| Component | Bath 12 | Bath 13 | Bath 14 | Bath 15 | Bath 16 | Bath 17 |
|---|---|---|---|---|---|---|
| Copper sulfate pentahydrate | 10 g/L | 10 g/L | 10 g/L | 10 g/L | 10 g/L | 10 g/L |
| Rochelle salts | 40 g/L | 40 g/L | 40 g/L | 40 g/L | 40 g/L | 40 g/L |
| Sodium hydroxide | 8 g/L | 8 g/L | 8 g/L | 8 g/L | 8 g/L | 8 g/L |
| Formaldehyde | 4 g/L | 4 g/L | 4 g/L | 4 g/L | 4 g/L | 4 g/L |
| 2,2'-dithiodisuccinic acid | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm | 0.5 ppm |
| 1-ethyl-3-methylimidazolium chloride | 2 ppm | ---------- | ---------- | ---------- | ---------- | ---------- |
| 1-(2-methoxyethyl)-3-methylimidazolium chloride | ---------- | 5 ppm | ---------- | ---------- | ---------- | ---------- |
| 1-butyl-3-methylimidazolium methane sulfonate | ---------- | ---------- | 10 ppm | ---------- | ---------- | ---------- |
| 1-butyl-3-methylimidazolium hydroxide | ---------- | ---------- | ---------- | 20 ppm | ---------- | ---------- |
| 1-ethyl-3-methylimidazolium acetate | ---------- | ---------- | ---------- | ---------- | 30 ppm | ---------- |
| 1-allyl-3-mehtylimidazolium chloride | ---------- | ---------- | ---------- | ---------- | ---------- | 35 ppm |
| Water | To one liter | To one liter | To one liter | To one liter | To one liter | To one liter |

Each bath is used to plate copper on epoxy substrates. Each epoxy substrate is treated prior to electroless copper plating as described in Example 1. Electroless copper plating is done at 34 °C for 5 minutes. The plating rate is determined by the same procedure as described in Example 1.

**[0065]** The electroless copper plating rate for each bath exceeds 0.6 μm/5 min. The copper deposits from the baths appear bright and uniform over substantially all of the epoxy substrates.

Example 5

Backlight Experiment with Aqueous Alkaline Electroless Cooper Compositions of the Present Invention Containing Imidazolium Compounds

**[0066]** Six aqueous alkaline electroless copper plating baths (Baths 18-23) are prepared having the same components and amounts as in Example 4, Table 7 with the exception that each bath includes 15 ppm of the methylimidazolium salts and the pH of the baths ranged from 11-13 at room temperature.

**[0067]** Six (6) each of six (6) different FR/4 glass epoxy panels with a plurality of through-holes are provided: TUC-662, SY-1141, IT-180, 370HR, EM825 and NPGN, as described in Example 3 above. The panels are treated as described in Example 3 and electroless copper plated as described in Example 3 except the temperature of the baths are 34 °C and the pH during plating is 12.5.

**[0068]** After plating, each panel is cross-sectioned nearest to the centers of the through-holes as possible to expose

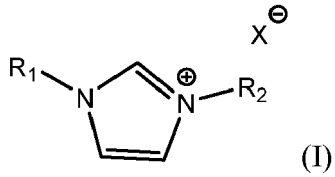
the copper plated walls. The cross-sections, no more than 3 mm thick from the center of the through-holes, are taken from each panel to determine the through-hole wall coverage. The European Backlight Grading Scale is used to determine the plating performance of the baths as described in Example 3. The backlight average values range from 4.5 to 4.7.

## Claims

1. An electroless copper plating composition comprising one or more sources of copper ions, one or more imidazolium compounds, one or more complexing agents, one or more reducing agents, and, optionally, one or more pH adjusting agents, wherein a pH of the electroless copper plating composition is greater than 7.

2. The electroless copper plating composition of claim 1, wherein the one or more imidazolium compounds are in amounts of at least 0.5 ppm.

3. The electroless copper plating composition of claim 1, wherein the one or more imidazolium compounds have a formula:




(I)

wherein $R_1$ is selected from the group consisting of linear or branched, unsubstituted ($C_1$-$C_{10}$)alkyl, linear or branched ($C_1$-$C_{10}$)alkoxy, linear or branched hydroxy($C_1$-$C_{10}$)alkyl, amino($C_1$-$C_{10}$)alkyl, benzyl, phenyl, carbobenzoxy, carbomethoxy, ($C_6$-$C_{10}$) heterocyclic nitrogen group and allyl; and $R_2$ is selected from the group consisting of linear or branched, unsubstituted ($C_1$-$C_{10}$)alkyl, linear or branched ($C_1$-$C_{10}$)alkoxy, linear or branched hydroxy($C_1$-$C_{10}$)alkyl, amino($C_1$-$C_{10}$)alkyl, benzyl, phenyl, carbobenzoxy, carbomethoxy and ($C_6$-$C_{10}$) heterocyclic nitrogen group; and $X^-$ is a counter anion.

4. The electroless copper plating composition of claim 1, wherein the one or more complexing agents are chosen from sodium potassium tartrate, sodium tartrate, sodium salicylate, sodium salts of ethylenediamine tetraacetic acid, nitriloacetic acid and its alkali metal salts, gluconic acid, gluconates, triethanolamine, modified ethylene diamine tetraacetic acids, s,s-ethylene diamine disuccinic acid, hydantoin and hydantoin derivatives.

5. The electroless copper plating composition of claim 1, wherein the one or more reducing agents are chosen from formaldehyde, formaldehyde precursors, formaldehyde derivatives, borohydrides, substituted borohydrides, boranes, saccharides, and hypophosphite.

6. The electroless copper plating composition of claim 1, further comprising one or more compounds chosen from secondary accelerators, surfactants, grain refiners and stabilizers.

7. A method of electroless copper plating comprising:

   a) providing a substrate comprising a dielectric;
   b) applying a catalyst to the substrate comprising the dielectric;
   c) applying an electroless copper plating composition to the substrate comprising the dielectric, wherein the electroless copper plating composition comprises one or more sources of copper ions, one or more imidazolium compounds, one or more complexing agents, one or more reducing agents, and, optionally, one or more pH adjusting agents, wherein a pH of the electroless copper plating composition is greater than 7; and
   d) electroless plating copper on the substrate comprising the dielectric with the electroless copper plating composition.

8. The method of claim 7, wherein the one or more imidazolium compounds are in amounts of at least 0.5 ppm.

9. The method of claim 7, wherein the electroless copper plating composition further comprises one or more compounds chosen from stabilizers, surfactants, grain refiners and secondary accelerators.

**10.** The method of claim 7, wherein the electroless copper plating composition is at 40 °C or less.

**11.** The method of claim 7, wherein the catalyst is a palladium catalyst.

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# EUROPEAN SEARCH REPORT

Application Number
EP 19 17 9174

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C23C

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 30 September 2019 | Le Hervet, Morgan |

CATEGORY OF CITED DOCUMENTS

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## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 19 17 9174

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30-09-2019

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