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(54) Reverse pulse plating composition and method

(57) A composition and method for electroplating a metal on a substrate. The composition has a chloride to brightener concentration ratio of from 20:1 to 125:1. The method of electroplating, which employs the composition, employs pulse patterns that improve physical properties of metal surfaces.

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Description

BACKGROUND OF THE INVENTION

[0001] The present invention is directed to a reverse pulse plating composition and method. More specifically, the present invention is directed to a reverse pulse plating composition and method that reduces brightener decomposition and reduces defects of an electroplated metal layer.

[0002] Numerous compositions and methods for electroplating articles with metal layers or coatings arc employed in many industries. Such methods may involve passing a current between two electrodes in a plating composition or solution where one of the electrodes is an article to be metal plated. Using an acid copper plating solution for purposes of illustration, a plating solution may contain (1) dissolved copper (cupric ions), usually copper sulfate, (2) an acid electrolyte such as sulfuric acid in an amount sufficient to impart conductivity to the solution, and (3) additives to improve efficiency of the plating reaction and the quality of the metal deposit. Such additives include, for example, surfactants, brighteners, levelers, suppressants, and corrosion inhibitors.

[0003] Metals that may be electroplated include, for example, copper, copper alloys, nickel, tin, lead, gold, silver, platinum, palladium, cobalt, chromium, and zinc. Electrolytic metal plating solutions are used for many industrial applications. For example, they may be used in the automotive industry as base layers for subsequently applied decorative and corrosion protective coatings. They also may be used in the electronics industry, such as in the fabrication of printed circuit or wiring boards, and for semiconductor devices. For circuit fabrication in a printed circuit board, a metal such as copper is electroplated over selected portions of the surface of a printed circuit board and onto the walls of through-holes passing between the surfaces of the circuit board base material. The walls of the through-holes are metallized to provide conductivity between circuit layers on each surface of the board.

[0004] Early efforts to make printed circuit boards use electrolytic metal plating solution developed for decorative plating. However, as printed circuit boards became more complex and as industry standards became more rigorous, solutions used for decorative plating were found to be inadequate for printed circuit board fabrication. One serious problem encountered using electrolytic metal plating solutions involved coatings of uneven thickness on the walls of the through-holes with metal deposits thicker at the tope and bottom of the through-holes and thinner at the center, a condition known in the art as "dog boning". The thinner deposit at the center of the through-hole may lead to circuit defects and board rejection.

[0005] Dog boning is believed to be caused by a voltage drop between the top surface of the through-hole and the center of the through-hole. The potential drop is a function of current density, a ratio of the length of the through-hole to the through-hole diameter (aspect ratio) and board thickness. As the aspect ratio and the thickness of the board increase, dog boning becomes more severe due to a voltage drop between the surface of the board and the center of the through-hole. This voltage drop is believed to be caused by a combination of factors including solution resistance, a difference in surface to through-hole over potential due to mass transfer, i,e., a difference in the flow of solution through the through-hole compared to the movement of the solution over the surface of the board, and a charge transfer difference as a consequence of the concentration of solution additives in the through-hole compared to the surface.

[0006] The printed circuit board industry continuously seeks greater circuit densification. To increase density, the industry has resorted to multi-layer circuits with through-holes or interconnections passing through multiple layers, Multi-layer circuit fabrication results in an overall increase in the thickness of the board and a concomitant increase in the length of an interconnection passing through the board. This means that increased circuit densification results in increased aspect ratios and through-hole length and an increase in the severity of the dog boning problem. For high density boards, aspect ratios may exceed ten to one.

[0007] Another problem encountered in metal electroplating are defects such as intermittent surface roughness and non-uniform surface appearance of the plated metal. Intermittent surface roughness and non-uniform surface appearance are believed to be caused by non-uniform current distribution across the surface of the printed wiring board that is being plated. The non-uniform current distribution results in an unequal or uneven deposit of metal on the board surface resulting in the surface roughness and non-uniformity of plated metal layers.

[0008] Another defect, which is often observed, is the formation of dendrites or "whiskers", Whiskers are believed to be crystals of the metal being plated and grow out of the plated surface. Whiskers may range in diameter of from less than 1 micron to as large as several millimeters. Although the cause of whisker growth has been the subject of some debate, there is no question that whiskers are undesirable for a variety of electrical, mechanical, and cosmetic reason. For example, whiskers are readily detached and carried by cooling air flows into electronic assemblies, both within and external to electronic article housings, where they may cause short-circuit failure.

[0009] Plating metal is a complex process that involves multiple ingredients in a plating bath. In addition to metal salts that provide a source of metal, pH adjusters and surfactants or wetting agents, many plating baths contain chemical compounds that improve various aspects of the plating process. Such chemical compounds or additives are auxiliary bath components that are used to improve the brightness of the metal plating, the physical properties of the plated metal especially with respect to ductility and throwing power of an electroplating solution or bath, Throwing power of the solution defined as the ratio of current density flowing at the center of the through-hole to the current density flowing at the surface of the through-hole. Optimum throwing power is achieved when the current density at the center of the through-hole is the same as the current density flowing at the through-hole surface. However, such a current density is difficult to achieve.

[0010] A main concern is additives that have an effect on the bright finish, leveling and uniformity of metal deposition on surfaces. Maintaining bath concentrations of such additives within close tolerances is important to obtain high quality metal deposits. The additives do breakdown during metal plating, The additives breakdown duc to oxidation at the anode, by reduction at the cathode, and by chemical degradation.

[0011] When additives breakdown during plating, the breakdown products may result in metal layer deposit characteristics that are less than satisfactory for industry standards. Regular additions of additives based upon empirical rules established by workers in the industry to try and maintain optimum concentrations of the additives have been employed. However, monitoring the concentrations of the additives that improve metal plating is still difficult because additives are present in plating baths in small concentrations, i.e., parts per million of solution. Accordingly, the level of the additives in the bath eventually changes such that the additive concentrations are out of the acceptable range of tolerance, If the additive concentration goes too far out of range of tolerance, the quality of the metal deposit suffers and the deposit may be dull in appearance and/or brittle or powdery in structure. Other consequences include low throwing power and/or plating folds with bad leveling. Electroplating of through-hole interconnections in the manufacture of multilayer printed circuit boards is an example of where quality plating is required.

[0012] Many of the foregoing problems are found in reverse pulse plating baths and methods, Reverse pulse plating is an electroplating process where the electrical current is alternated between a cathodic current (forward pulse) and an anodic current (reverse pulse) during the electroplating process. Typical pulses or waveforms are a reverse to forward voltage ratio of 3 to 1 and times of 10 to 20 milliseconds for the forward waveform and 0.5 to 1 millisecond for the reverse. However, such waveforms often result in undesirable intermittent surface roughness and non-uniform surface appearance on plated metal layers, especially at current densities of 100 amps/cm^2.

[0013] Another problem with reverse pulse plating baths is their short bath life, which may be in terms of a few days, i.e., two to three days, of optimum performance. Preferably optimum bath performance is continuous (from 6 months to at least a year). The longer the duration of the optimum performance of a bath the more economically efficient is the electroplating process. The short life of a reverse pulse plating bath is due to additive breakdown, especially due to the build-up of brightener by product. The rate at which byproducts form is primarily governed by the brightener concentration and secondarily by the idle time at which the by product is formed on an anode surface. Reverse pulse plating often uses high brightener concentrations, i.e., in excess of 1 ppm (part per million), to help prevent or reduce poor performance in leveling, throwing power and corner cracking. Poor throwing power results in rough metal surfaces and non-uniform metal layers. Corner cracking is a condition where the plated metal layer begins to separate from the plated substrate. However, high brightener concentrations may result in high concentrations of byproducts, which may shorten the electroplating bath life. Accordingly, there is a need for an improved reverse pulse plating composition or bath and an improved reverse pulse plating method to address the foregoing problems.

SUMMARY OF THE INVENTION

[0014] The present invention is directed to a composition including chloride and a brightener having a concentration ratio of the chloride to the brightener ranges from 20:1 to 125:1, and a brightener concentration of 0.001 ppm to 1.0 ppm. The composition may be employed as a metal plating solution or bath for electrolytic deposition of metals on a substrate. In addition to the chloride and brightener, the composition includes a source of metal ions. The source of metal ions may be a salt of the metal that is to be electroplated on the substrate.

[0015] The composition of the present invention also may include other additives such as levelers, suppressors, carriers, surfactants, buffers as well as other components that may be used in electroplating baths. The compositions of the present invention may have an aqueous or organic solvent.

[0016] Another embodiment of the present invention is directed to a method which includes (a) generating an electromotive force through a cathode, anode and a composition in electrical communication to provide an electric field around the cathode, the anode and the composition, the composition comprises metal ions, brighteners and chloride ions, the chloride ions to brighteners are at a concentration ratio of from 20:1 1 to 125: 1; (b) modifying the electric field around the cathode, the anode and the composition to provide a pulse pattern or a combination of pulse patterns comprising (i) cathodic current followed by anodic current; (ii) cathodic current followed by anodic current followed by cathodic DC current; (iii) cathodic current followed by anodic current followed by equilibration; or (iv) cathodic current followed by anodic current followed by cathodic DC current then followed by equilibration to electroplate a metal on the cathode.

[0017] Advantageously, the compositions and methods prevent or at least reduce dendrite or whisker formation on metal plated substrates, reduce dog boning as well as intermittent surface roughness, and provide a uniform metal layer on the substrates. Other advantages include improved leveling performance, improved throwing power and reduced corner cracking. Also additive decomposition is reduced to provide electroplating baths having a longer operating life.

[0018] A primary objective of the present invention is to provide a composition with reduced additive breakdown.

[0019] Another objective is to provide a composition that has an improved electroplating life.

[0020] A further objective of the present invention is to provide a method of metal plating a substrate that reduces metal plating defects.

[0021] Still yet another objective is to provide a method of plating a metal that has an improved throwing power.

[0022] Other objectives and advantages of the methods and compositions may be ascertained by a person of skill in the art after reading the disclosure of the invention and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

[0023] Compositions include chloride ion and brighteners in concentration ratios of from 20:1 to 125: 1, and a brightener concentration of 0.001 ppm to 1.0 ppm. The compositions also may include other additives depending on the particular function of the composition. The compositions may be employed as electroplating solutions for plating a metal on a substrate, When the compositions are employed as electroplating baths, metal ions of the metal to be plated are included in the composition as well as other additives to assist in optimizing performance of the electroplating bath.

[0024] The compositions are suitable for electroplating by reverse pulse plating, Accordingly, another embodiment of the present invention is a reverse pulse plating method to electroplate a metal on a substrate, An electromotive force (emf) is generated from a suitable electrical source to provide an electric field around an electroplating apparatus including an anode, cathode and a composition including chloride ions and brighteners in a concentration ratio of from 20:1 to 125:1 and metal ions. The anode, cathode and composition are in electrical communication with each other to provide a complete electrical circuit with the source of the electromotive force. Typically the cathode is the substrate on which the metal is plated.

[0025] During electroplating of a metal, the electric field around the electroplating apparatus may be modified to provide (i) a cathodic current (forward pulse or waveform) followed by an anodic current (reverse pulse or waveform); (ii) a cathodic current followed by an anodic current (reverse pulse or waveform) followed by cathodic DC current (direct current), (iii) a cathodic current followed by an anodic current (reverse pulse or waveform) followed by equilibration (open circuit); (iv) a cathodic current followed by an anodic circuit (reverse pulse or waveform) followed by cathodic DC current (direct current) then followed by equilibration (open circuit); or combinations of pulse patterns (i), (ii), (iii), or (iv) provided that the net result of the pulse electroplating process results in a metal layer formed on the substrate to be metal plated. Net current for each pattern or combination of patterns is in the cathodic or plating direction. During cathodic current (AC or alternating current) a metal is being plated on the cathode, while during anodic current metal is being removed or stripped from the cathode. During cathodic DC current metal is again being plated on the cathode, and during equilibration there is no metal being deposited on the cathode or stripped from the cathode. There is no plating or stripping during equilibration because the electrical circuit is open and there is no emf to plate or strip. In other words, workers choose a particular pulse pattern or combination of pulse patterns such that the net result provides a metal layer or coat on the substrate, which typically is the cathode of the plating apparatus. The particular order of each pulse pattern and the time duration during an electroplating process of each pulse pattern and their respective waveforms, DC currents and equilibrations may vary depending on the dimensions of the substrate and the desired thickness of the metal layer(s), Reverse to forward voltage ratios range from 1.5 to 5.5, preferably from 2.5 to 3.5. The pulse patterns provide for reduced intermittent surface roughness and improved uniform metal layer(s) in contrast to many conventional pulse plating patterns. The pulse plating patterns also have improved throwing power in contrast to many conventional pulse plating patterns.

[0026] Examples of pulse patterns that may be used to electroplate a substrate include pulse pattern (i) by itself during the entire electroplating process; a combination of pulse patterns (i) and (ii); a combination of pulse patterns (i), (ii) and (iii); a combination of pulse patterns (i), (ii), (iii), and (iv); or a combination of pulse patterns (i), (iii) and (iv). The particular order of each pulse pattern and the time duration of each including their respective waveforms, DC currents and equilibrations may vary depending on the dimensions of the substrate and the desired thickness of the metal layer (s), Some minor experimentation may be employed to determine which combination of pulse patterns and duration of the pulse patterns optimize the electroplating process for a given substrate. Such minor experimentation is common in the electroplating art to optimize electroplating processes. A preferred pulse pattern is (i) a cathodic current (forward pulse or waveform) followed by an anodic current (reverse pulse or waveform).

[0027] Current densities may range from 5 milliamps(mA)/cm^2 to 200 mA/cm^2, preferably from 5 mA/cm^2 to 125 mA/cm^2, more preferably from 5 mA/cm^2 to 50 mA/cm^2. Forward pulses range in time from 40 milliseconds (ms) to 1 second, preferably from 40 ms to 800 ms, and reverse pulses may range from 0.25 ms to 15 ms, preferably from 1 ms to 3 ms for pulse pattern (i). Forward pulses range from 40 ms to 1 second, preferably from 40 ms to 800 ms and reverse pulses range from 0.25 ms to 15 ms, preferably from 1 minute to 10 ms, and the DC current ranges from 5 seconds to 90 seconds, preferably from 10 seconds to 60 seconds for pulse pattern (ii). Forward pulses range from 40 ms to 1 second, preferably from 40 ms to 800 ms and reverse pulses range from 0.25 ms to 15 ms, preferably from 1 minute to 10 ms, and the equilibration ranges from 5 seconds to 90 seconds, preferably from 10 seconds to 60 seconds in pulse pattern (iii), Forward pulses range from 40 ms to 1 second, preferably from 40 ms to 800 ms, reverse pulses range from 0.25 ms to 15 ms, preferably from 1 minute to 10 ms, DC current ranges from 5 seconds to 90 seconds, preferably from 10 seconds to 60 seconds, and equilibration ranges from 5 seconds to 90 seconds, preferably from 10 seconds to 60 seconds for pulse pattern (iv).

[0028] Pulse times, pulse patterns and applied voltages of the cathodic and anodic waveforms may be adjusted to provide that the overall process is cathodic, i.e., there is a net deposition of metal on a substrate. Workers may adapt the pulse time waveforms and their frequencies to a particular application based on the teachings of the process of the invention.

[0029] The electroplating compositions may be employed to plate any metal that may be electroplated on a substrate, Examples of such metals include copper, tin, nickel, cobalt, chromium, cadmium, lead, silver, gold, platinum, palladium, bismuth, indium, rhodium, ruthenium, iridium, zinc, or alloys thereof, The electroplating compositions are especially suitable for electroplating copper and copper alloy to a substrate. Metals are included in the compositions as soluble salts. Any suitable metal salt may be employed to practice the present invention provided that the metal salt is soluble in the composition solvent. Examples of suitable copper compounds include copper halides, copper sulfates, copper alkane sulfonate, copper alkanol sulfonate, or mixtures thereof. Such copper compounds are water-soluble.

[0030] A sufficient amount of a metal salt is included in the electroplating composition such that the concentration of the respective metal ion is from 0.010 grams/liter to 200 grams/liter, preferably from 0.5 grams/liter to 100 grams/liter. When copper is the metal, a sufficient amount of copper salt is employed such that the copper ion concentration preferably ranges from 0.01 to 100 grams/liter, more preferably from 0.10 grams/liter to 50 grams/liter. Solvents of the electroplating composition may be water or an organic solvent such as alcohol or other suitable organic solvent employed in electroplating. Mixtures of solvents also may be employed.

[0031] Sources of chloride ion include any suitable chloride salt or other source of chloride that is soluble in the electroplating compositions solvent. Examples of such chloride ion sources are sodium chloride, potassium chloride, hydrogen chloride (HCl), or mixtures thereof. A sufficient amount of chloride ion source is included in a composition such that the chloride ion concentration ranges from 0,02 ppm to 125 ppm, preferably from 0.25 ppm to 60 ppm, more preferably from 5 ppm to 35 ppm.

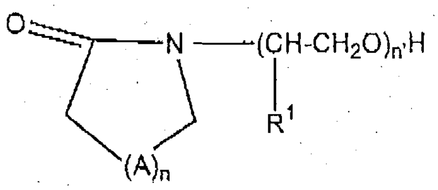
[0032] Brighteners that may be employed in the compositions and methods of the present invention include any brightener that is suitable for the metal that is to be electroplated, Brighteners may be specific for the metal that is plated, Workers in the art are familiar with the particular brightener that may be employed with a particular metal. Brighteners are included in the electroplating compositions at a range of from 0,001 ppm to 1.0 ppm, preferably from 0.01 ppm to 0.5 ppm, more preferably from 0.1 ppm to 0.5 ppm. Thus, chloride to brightener concentrations of the compositions range from 20:1 to 125:1, preferably 25:1 to 120:1, more preferably from 50:1 to 70:1. Such ranges of chloride ion to brightener are suitable for reducing or preventing whisker formation, corner cracking and brightener byproduct formation during electroplating, especially for electroplating copper or copper alloys. Such chloride to brightener ratios also improves leveling, and throwing power of an electroplating bath, especially in copper or copper alloy electroplating.

[0033] Examples of suitable brighteners include sulfur containing compounds that have a general formula $S\text{-}R\text{-}SO_3$, where R is substituted or unsubstituted alkyl or substituted or unsubstituted aryl group. More specifically, examples of suitable brighteners include compounds having structural formulas $HS\text{-}R\text{-}SO_3X$, $XO_3\text{-}S\text{-}R\text{-}S\text{-}S\text{-}R\text{-}SO_3X$ or $XO_3\text{-}S\text{-}Ar\text{-}S\text{-}S\text{-}Ar\text{-}SO_3X$ where R is a substituted or unsubstituted alkyl group, and preferably is an alkyl group having from 1 to 6 carbon atoms, more preferably is an alkyl group having from 1 to 4 carbon atoms; Ar is an aryl group such as phenyl or naphthyl; and X is a suitable counter ion such as sodium or potassium. Specific examples of such compounds include n,n-dimethyl-dithiocarbamic acid-(3-sulfopropyl)ester, carbonic acid-dithio-o-ethylester-s-ester with 3-mercapto-1-propane sulfonic acid (potassium salt), bissulfopropyl disulfide (BSDS), 3-(benzthiazolyl-s-thio)propyl sulfonic acid (sodium salt), pyridinium propyl sulfonic sulfobetaine, or mixtures thereof. Other suitable brighteners are described in U.S. Pat. Nos. 3,770,598, 4,374,709, 4,376,685, 4,555,315, and 4,673,469. Also aromatic and aliphatic quaternary amines may be added to the compositions to improve metal brightness.

[0034] Examples of other suitable brighteners include 3-(benzthiazoyl-2-thio)-propylsulfonic acid sodium salt, 3-mercaptopropane-1-sulfonic acid sodium salt, ethylenedithiodipropylsulfonic acid sodium salt, bis-(p-sulfophenyl)-disulfide disodium salt, bis(ω-sulfobutyl)-disulfide disodium salt, bis-(ω-sulfohydroxypropyl)-disulfide disodium salt, bis-(ω-sulfopropyl)-disulfide disodium salt, bis-(ω-sulfopropyl)-sulfide disodium salt, methyl-(ω-sulfopropyl)-disulfide sodium salt, methyl-(ω-sulfopropyl)-trisulfide disodium salt, o-ethyl-dithiocarbonic acid-S-(ω-sulfopropyl)-ester potassium salt, thioglycolic acid, thiosphosphoric acid-o-ethyl-bis-(ω-sulfopropyl)-ester disodium salt, thiophosphoric acid-tris(ω-sulfopropyl)-ester trisodium salt, N,N-dimethyldithiocarbamic acid (3-sulfopropyl) ester sodium salt (DPS), (o-ethyldithiocarbonato)-S-(3-sulfopropyl)-ester potassium salt (OPX), 3-[(amino-iminomethyl)-thio]-1-propanesulfonic acid (UPS), 3-(2-benthiazolylthio)-1-propanesulfonic acid sodium salt (ZPS), thiol of bissulfopropyl disulfide (MPS), or mixtures thereof,

[0035] In addition to soluble metal compounds, chloride ions and brighteners, the compositions of the present invention also may include levelers, suppressors (carriers), surfactants) buffering agents and other compounds used in conventional electroplating baths.

[0036] Examples of suitable levelers include lactam alkoxylates having a formula:



where A represents a hydrocarbon radical such as $-CH_2-$, R^1 is hydrogen or methyl, n is an integer from 2 to 10, preferably from 2 to 5, and n' is an integer from 1 to 50. Examples of such compounds include β-propiolactam ethoxylate, γ-butyrolactam-hexa-ethoxylate, δ-valerolactam-octa-ethoxylate, δ-valerolactam-penta-propoxylate, ε-caprolactam-hexa-ethoxylate, or ε-caprolactam-dodeca-ethoxylate. Such leveling agents are included in electroplating compositions in amounts of from 0.002 to 3 grams/liter, preferably from 0.005 to 0,2 grams/liter.

[0037] Another example of suitable levelers include polyalkylene glycol ethers of formula:

$$[R^2O(CH_2CH_2O)_m(CH(CH_3)-CH_2O)_p-R^3]_a$$

where m is an integer of from 8 to 800, preferably from 14 to 90, p is an integer of from 0 to 50, preferably from 0 to 20, R^2 is a (C_1-C_4) alky), R^3 is an aliphatic chain or an aromatic group and a is either 1 or 2.

[0038] Amounts of polyalkylene glycol ether that may be included in the compositions ranges from 0.005 to 30 grams/liter, preferably from 0.02 to 8.0 grams/liter. Relative molecular mass may be from 500 to 3500 grams/mole, preferably from 800 to 4000 grams/mole.

[0039] Such polyalkylene glycol ethers are known in the art or may be produced according to processes which are known in the art by converting polyalkylene glycols with an alkylating agent such as dimethyl sulfate or tertiary butene.

[0040] Examples of such polyalkylene glycol ethers include dimethyl polyethylene glycol ether, dimethyl polypropylene glycol ether, di-tertiary butyl polyethylene glycol ether, stearyl monomethyl polyethylene glycol ether, nonylphenol monomethyl polyethylene glycol ether, polyethylene polypropylene dimethyl ether (mixed or block polymer), octyl monomethyl polyalkylene ether (mixed or block polymer), dimethyl-bis(polyalkylene glycol)octylene ether (mixed or block polymer), and β-naphthol monomehtyl polyethylene glycol.

[0041] Additional levelers that may be employed to practice the present invention include nitrogen and sulfur containing levelers with a formula $N-R^4-S$, where R^4 is a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group. The alkyl groups may have from 1 to 6 carbons, typically from 1 to 4 carbons. Suitable aryl groups may include substituted or unsubstituted phenyl or naphthyl. Substituents of the alkyl and aryl groups may be, for example, alkyl, halo, or alkoxy. Examples of specific levelers include 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine, 2-mercaptothiazoline, ethylene thiourea, thiourea, and alkylated polyalkyleneimine. Such levelers are included in amounts of 500 ppb (parts per billion) or less, preferably from 100 to 500 ppb, Other suitable leveling agents are described in U.S. Pat, Nos. 3,770,598, 4,374,709, 4,376,685, 455,315 and 4,673,459.

[0042] Any suppressor (carrier) that is employed in metal plating may be employed in the practice of the present invention. While the concentrations of suppressors may vary from one electroplating bath to another, suppressors typically range from 100 ppm or greater, Examples of such suppressors are polyhydroxy compounds such as polyglycols, e.g., poly (ethylene glycol), poly(propylene glycol) and copolymers thereof, An example of a preferred suppressor is poly(ethylene glycol). A suitable concentration range for poly(ethylene glycol) is from 200 ppm to 2000 ppm. The poly(ethylene glycol) may range in molecular weight from 1000 to 12000, preferably from 2500 to 5000.

[0043] Any suitable buffer or pH adjuster may be employed in the present invention. Such pH adjusters may include, for example, inorganic acids such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, or mixtures thereof. Sufficient acid is added to the compositions such that the pH ranges from 0 to 14, preferably from 0 to 8.

[0044] During electroplating the compositions or electroplating baths may range in temperature of from 20° C to 110°

C, Temperature ranges for specific metals may vary and such temperature ranges are well known in the art. Copper electroplating baths may be maintained at a temperature range of from 20° C to 80° C with acid copper baths (pH from 0 to 4) at temperatures of from 20° C to 50° C, Metal plating is continued for a time sufficient to form a deposit of desired thickness. Plating time for a printed wiring board may range from 45 minutes to 8 hours. For circuit board manufacture, a desired thickness may range from 62 mils to 400 mils (0.001 mils/inch and 2,54 cm/inch).

[0045] The composition and method of the present invention is suitable for metal plating through-holes of multi-layer circuit boards with aspect ratios of at least 10:1 and through-hole interconnections of at least 0.16 cm, and blind vias of 0,063 cm. The composition and method or the present invention, in addition to the other advantages, reduces or eliminates dog-boning in contrast to many conventional electroplating methods.

[0046] Both vertical and horizontal plating processes may be employed. In vertical processes the substrate, such as a printed wiring board, is sunk in a vertical position into a container containing a plating bath composition of the present invention. The substrate, which functions as a cathode, is situated in the vertical position opposite to at least one soluble or insoluble anode. The substrate and the anode are connected to a current source and an electrical current or electric field is generated the substrate, anode and plating composition. Any suitable source for emf may be employed. Various apparatus for generating an emf are well known in the art. Plating composition is directed continuously through a container with the cathode, anode and plating composition by means of transporting equipment such as a pump. Any suitable pump employed in electroplating processes may be employed to practice the present invention. Such pumps are well known in the electroplating industry and are readily available.

[0047] In the horizontal plating process, the substrate or cathode is transported through a conveyorized unit in a horizontal position with a horizontal direction of movement. Electroplating composition is injected continuously from below and/or above and onto the substrate by means of splash nozzles or flood pipes. Anodes arc arranged at a spacing relative to the substrate and are brought into contact with the electroplating composition by means of a suitable device. The substrate is transported by means of rollers or plates. Such horizontal apparatus are well known in the art.

[0048] The compositions and method of the present invention eliminate or reduce dog-boning, increase throwing power, reduce or prevent corner cracking as well as whisker formation, and provide an improved metal layer surface and leveling performance. Additionally, the compositions of the present invention are more stable than many conventional plating compositions. Accordingly, the present invention is an improvement in the metal plating art.

[0049] While the present invention is described with an emphasis on electroplating in the printed wiring board industry, the present invention may be employed in any suitable plating process. The composition and method may be employed in metal plating in the manufacture of electrical devices such as printed circuit and wiring boards, integrated circuit, electrical contact surfaces and connectors, electrolytic foil, silicon wafers for microchip applications, semi-conductors and semi-conductor packaging, lead frames, optoelectronics, and optoelectronic packaging, and solder bumps, such as on wafers.

[0050] All numerical ranges in the present application are inclusive and combinable.

[0051] The following example is provided to better describe the present invention, and is not intended to limit the scope of thc invention.

Example 1

Compositions to Reduce or Eliminate Whiskers

[0052] Eight copper metal electroplating baths were prepared to verify the ability of chloride to prevent or reduce whisker (dendrite) formation on copper metal surfaces during electroplating of copper on a substrate. Each electroplating composition or bath was an aqueous bath that contained 80 grams/liter of copper sulfate pentahydrate as the metal ion source, 225 grams/liter of sulfuric acid to maintain the pH of the baths at 4.0. Chloride ion concentration in each of the baths was 25 ppm. The chloride ion source was HCl. In addition to the foregoing components, each bath also contained a carrier component at a concentration of either 0.25 ppm or 1 ppm, and a brightener (BSDS) in an amount of either 0.1 ppm or 0.2 ppm to provide a chloride to brightener ratio of either 125:1 1 or 250:1. Carriers that were employed in each solution are disclosed in the table below. All of the carriers listed in the table below are block copolymers.

[0053] Each bath was placed in a separate standard 1.5 liter Gornell cell and a 9.5 cm x 8.25 cm copper clad panel (cathode) was placed in each cell with air circulation and mechanical agitation during the electroplating process. A copper anode was employed as the auxiliary electrode. Current density during the electroplating process was maintained at 32 mAmps/cm^2. Each panel was electroplated for 60 minutes using a forward to reverse waveform of 10 ms to 0.2 ms. The source of the emf was a Technu pulse rectifier.

Table

Sample Number	Carrier	Carrier Level in parts per million	Chloride/Brightener Ratio	Whisker Count
1	Ingepal CA877	1	250	6
2	Ingepal CA877	1	125	1
3	Pluronic®F68	1	250	>5
4	Pluronic® F68	1	125	1
5	Nape 14-90	0.25	250	>5
6	Nape 14-90	0.25	125	1
7	Tetronic® 304	1	250	2
8	Tetronic® 304	1	125	0

[0054] After each panel was plated with a copper layer, the panels were removed from the Gornell cell and examined for whiskers. Examination was done with the naked eye and by touching the surfaces of each panel and counting the whiskers.

[0055] Panels that were plated in baths with a chloride to brightener ratio of 125 had whisker counts of 1 or 0 (samples 2, 4, 6, and 8). Panels that had a chloride to brightener ratio of 250 had whisker counts of 6, >5 or 2 (samples 1, 3, 5, and 7). Accordingly, the compositions that had a chloride to brightener ratio of 125 eliminated or reduced whisker count.

Example 2

Whisker Reduction

[0056] Four electroplating baths were prepared to verify the function of the pulse waveform with respect to the formation for whiskers (dendrites). All four baths contained the same concentration of chemical components, and all substrates were plated using the same anodes, and tank assembly. The anodes were freshly etched prior to each plating experiment. The concentration of inorganic components in each bath was 82 g/L $CuSO_4•5H_2O$, 216.5 g/L H_2SO_4, and the Cl-/brightener ratio was 44. The concentration of suppressor in each bath was 15 ml/l. In a 1.5 liter Haring plating cell, a 15 cm X 6,3 cm copper clad panel was electroplated at 10.7 mA/cm2 in each plating bath using a different pulse waveform as shown in the Table. After plating, the boards were physically scanned for whiskers, sec Table. As shown in the Table, as the forward wave was made longer, the number of whiskers was reduced significantly. This effect was particularly marked as the forward wave reaches 50 ms and above,

Table

Forward time, ms	Reverse time, ms	Number of Whiskers
10	0.5	69
20	1	37
50	2.6	27
100	5	21

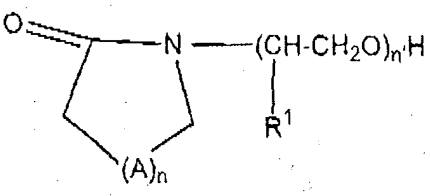
Claims

1. A composition comprising chloride ion and a brightener having a concentration ratio of chloride ion to brightener of from 20:1 to 125:1 at a brightener concentration of from 0.001 ppm to 1.0 ppm.

2. The composition of claim 1, wherein the chloride ion to brightener concentration ratio is from 25:1 to 120:1.

3. The composition of claim 1, further comprising metal ions such as copper ions, nickel ions, tin ions, lead ions, chromium ions, palladium ions, gold ions, silver ions, platinum ions, indium ions, cadmium ions, bismuth ions, cobalt ions, rhodium ions, ruthenium ions, or zinc ions.

4. The composition of claim 5, further comprising levelers such as lactam alkoxylates having a formula:



where A is a hydrocarbon radical, R^1 is hydrogen or methyl, n is an integer of from 2 to 10, and n' is an integer from 1 to 50.

5. The composition of claim 1, further comprising levelers such as polyalkylene glycol ether of formula $[R^2\text{-O}(CH_2CH_2O)_{m'}(CH(CH_3)\text{-}CH_2O_p\text{-}R^3]_a$ where m is an integer of from 8 to 800, p is an integer of from 0 to 50, R^2 is a (C_1-C_4) alkyl, R^3 is an aliphatic chain or an aromatic group, and a is 1 or 2.

6. The composition of claim 1, further comprising compounds having a formula N-R^4-S where R^4 is a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group.

7. A method comprising:

(a) generating an electromotive force through a cathode, anode and a composition in electrical communication to provide an electric field around the cathode, the anode and the composition, the composition comprises metal ions, brighteners and chloride ions, the chloride ions to brighteners concentration ratio is from 20:1 to 125:1;
(b) modifying the electric field around the cathode, the anode and the composition to provide a pulse pattern or a combination of pulse patterns comprising (i) cathodic current followed by anodic current; (ii) cathodic current followed by anodic current followed by cathodic DC current; (iii) cathodic current followed by anodic current followed by equilibration; or (iv) cathodic current followed by anodic current followed by cathodic DC current then followed by equilibration to electroplate a metal on the cathode.

8. The method of claim 7, wherein the cathodic current is from 40 ms to 1 second and the anodic current is from 0.25 ms to 5 ms for pulse pattern (i).

9. The method of claim 7, wherein the cathodic current is from 40 ms to 1 second and the anodic current is from 0.25 minutes to 15 minutes and the cathodic DC current is from 5 seconds to 90 seconds of pulse pattern (ii),

10. The method of claim 7, wherein the cathodic current is from 40 ms to 1 second and the anodic current is from 0.25 minutes to 15 minutes and the cathodic DC current is from 5 seconds to 90 seconds and equilibration is from 5 seconds to 90 seconds,