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(54) **ELECTROLYTIC COPPER PLATING SOLUTIONS**

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Related U.S. Application Data

(63) Continuation-in-part of application No. 09/667,268, filed on Sep. 22, 2000, now Pat. No. 6,605,204.

(60) Provisional application No. 60/403,954, filed on Aug. 16, 2002. Provisional application No. 60/159,381, filed on Oct. 14, 1999. Provisional application No. 60/187,108, filed on Mar. 6, 2000.

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(57) **ABSTRACT**

Disclosed are copper electroplating solutions, methods for using the solutions and products formed by using such methods and solutions in which the solutions contain copper alkanesulfonate salts and free alkanesulfonic acids, wherein the free acid has a concentration from about 0.05 to about 2.50 M, and which are intended for the metallization of micron-sized dimensioned trenches or vias, through-holes and microvias.

ELECTROLYTIC COPPER PLATING SOLUTIONS

REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 60/403,954, filed Aug. 16, 2002.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates to copper electroplating solutions, methods for using the solutions and products formed by using such methods and solutions. More particularly, the invention provides electrolytic copper plating solutions that have sulfonic acid anions and use of same for effective plating of electronic features such as trenches and vias with aspect ratios of about 1:1 and diameters of 1 to 500 microns.

[0004] 2. Description of the Prior Art

[0005] Electroplating articles with copper coatings is well known in the industry. Electroplating methods involve passing a current between two electrodes in a plating solution where one electrode, the cathode, is the article to be plated. A common plating solution would be an acid copper plating solution containing (1) a dissolved copper salt such as cupric sulfate, (2) an acid typically of the same anion used with the copper salt such as sulfuric acid in an amount sufficient to impart conductivity to the electrolyte and (3) additives such as surfactants, brighteners, levelers and suppressants to enhance the effectiveness and quality of plating. See generally U.S. Pat. Nos. 5,068,013; 5,174,886; 5,051,154 and 5,068,013 for a discussion of copper plating baths.

[0006] Commercial copper solutions include copper sulfate, copper pyrophosphate, copper fluoroborate and copper cyanide. Copper sulfate and fluoroborate solutions are typically used at medium and high current densities whereas copper pyrophosphate and copper cyanide are used to deposit copper at low to medium current densities. Because of health concerns associated with handling cyanide and fluoroboric acid and waste-treatment concerns with pyrophosphate, the most widely used commercial copper plating solution is copper sulfate. Copper sulfate solutions are used to deposit a copper coating on substrates such as printed circuit boards, automobile parts and household fixtures. The copper ion concentration varies from about 10 grams per liter to about 75 grams per liter. The sulfuric acid concentration may vary from about 10 grams per liter to about 300 grams per liter. Copper plating for electronic components usually use low copper metal concentrations and high free acid concentrations.

[0007] The use of sulfonic acids in electroplating has been described previously.

[0008] Proell, W. A. in U.S. Pat. No. 2,525,942 claims the use of alkanesulfonic acid electrolytes in electroplating. However, only mixed alkanesulfonic acids were used and only specific claims were made for lead, nickel, cadmium, silver and zinc.

[0009] Proell, W. A. in U.S. Pat. No. 2,525,943 specifically claims the use of alkanesulfonic acid electrolytes in copper electroplating. However, only mixed alkanesulfonic acids were used and the exact composition of the mixture was not disclosed.

[0010] Proell, W. A.; Faust, C. L.; Agruss, B.; Combs, E. L. in *The Monthly Review of the American Electroplaters Society* 1947, 34, 541-9 describes preferred formulations for copper plating from mixed alkanesulfonic acid based electrolytes. Again, however, only mixed alkanesulfonic acids were used.

[0011] Dahms, W. and Wunderlich, C. in a German Patent #4,338,148 discloses a methanesulfonate-based copper plating system which incorporates organic sulfur compounds as additives.

[0012] Jiqing, Cai, Diandu Yu Huanbao 1995, 15(2), 20-2 disclosed some benefits of using methanesulfonate-based acid copper plating formulations. The greatest benefit was stated to be superior surface cleaning and etching prior to the actual plating step.

[0013] Bernards, R. F.; Fisher, G.; Sonnenberg, W.; Cerwonka, E. J.; Fisher S., U.S. Pat. No. 5,051,154, describes surface active additives for copper plating with only minor mention of MSA as one of a number of possible electrolytes. However, no examples employing MSA are included.

[0014] Andricacos, P. C., Chang, I. C., Hariklia, D. and Horkans, J. in U.S. Pat. No. 5,385,661 discuss a process which allows for the electrodeposition of Cu alloys containing small amounts of tin and lead via under-potential deposition. The patent discloses MSA is exceptionally well suited for allowing this type of process to occur properly, owing mostly to the weakly complexing nature of methanesulfonic acid/methanesulfonate. A paper on this subject (J. Electrochem. Soc.; 1995; 142(7); 2244-2249) was also published.

[0015] Recently, copper plating has been used in semiconductor chip manufacture to provide chip interconnections. Semiconductors have been interconnected through aluminum conductors. However, industrial advances calls for enhanced performance, including ultra large-scale integration (ULSI) and faster circuits with interconnects as small as 200 nm and less. At these small feature sizes, the resistivity of aluminum is too high to allow the electronic signal to pass at required speeds. Copper has an inherently small resistivity and as such is a more suitable metal to meet the demand for next generation of semiconductor devices.

[0016] Typical processes for aluminum interconnects in semiconductor chips may involve ion etching of metal layers, e.g. a process that includes metal deposition, photolithographic patterning, line definition through reactive ion etching and dielectric deposition. Use of copper in advanced interconnects precludes the use of reactive ion etching due to the paucity of copper compounds with vapor pressures sufficient to enable removal of the copper as may be desired.

[0017] The damascene process has evolved in the semiconductor industry as a method to pattern and deposit metal in-laid structures into electronic features such as trenches and vias. The damascene process starts with deposition of dielectric usually by chemical vapor deposition of silicon materials or organic dielectrics followed by curing, or spin coating silicon materials or other inorganic or organic dielectrics. Patterning is next done using photolithographic processes and then reactive ion etching defines the vias and trenches (interconnects) in the dielectric. Barrier layers made from refractory-type materials are deposited into the features using a chemical vapor deposition method. A thin copper seed layer is deposited on the barrier layer to impart

conductivity to the features. This is followed by copper electroplating to fill the small features. Excess copper and barrier layer materials may be removed by chemical or mechanical polishing processes.

[0018] Several improvements in electroplating solutions and techniques have been made as the small electronic features to be plated evolved in degree of difficulty and standards for plating increased. Even with the improvements in electroplating processes, circumstances may exist that can lead to plating defects due to inadequate copper fill in the vias or trenches or through-holes. These defects are incomplete fill in the via or through-hole (e.g., dimples), overplating (e.g., mounds above the features), inclusion of non-metals and voids (e.g., holes in the copper coating).

[0019] Although conventional copper plating systems can be suitable for plating vias and trenches as large as 1 micron and even larger such as 1 to 500 microns with aspect ratios varying from less than 1:1 to about 5:1, defects such as dimples, overplates, seams, voids and inclusions can occur with conventional copper electrolytes and methods when attempting to plate features that are relatively small or low to moderate aspect ratios. These defects can occur as a result of conformal copper plating, i.e., where all surfaces that must be plated with copper at the same rate. Defects may also arise due to non-conformal fill as a result of inadequate wetting of the electronic features by the copper plating solution, adsorption of gas bubbles on the side walls of the features, too rapid of plating rates of the features leading to over-plate structures due to non-uniform adsorption of the sulfur-containing accelerating agent or dimples in the copper fill deposit because of preferential adsorption of the suppressor additive in the vias or through-holes.

[0020] It thus would be desirable to have new electroplating compositions. It would be particularly desirable to have new copper electroplating compositions that can plate copper effectively (e.g., absence of dimples, overplates, voids, inclusions and seams) in low (<3:1) aspect ratio apertures, including trenches and vias or through-holes.

SUMMARY OF THE INVENTION

[0021] Copper electroplating compositions have been found that effectively plate a wide variety of articles, including integrated circuits such as those with damascene structures, printed circuit boards and other electronic packaging devices.

[0022] Compositions of the invention contain a copper alkanesulfonate salt and free alkanesulfonic acid, wherein the free acid has a concentration from about 0.05 to about 2.50 M. The compositions additionally may contain an halide ion, and, optionally, one or more additives such as a suppressor agent, a brightener agent, a leveler agent or a surfactant. The compositions are intended for the metallization of micron-sized dimensioned trenches or vias, through-holes and microvias.

DETAILED DESCRIPTION OF THE INVENTION

[0023] The compositions and methods of the invention are particularly useful for filling vias, microvias and trenches and through-holes required by today's and future semiconductor and printed circuit board fabrication requirements

(including vias having aspect ratios of at least 0.5:1 and up to 4:1 and diameters of 0.5 microns to about 500 microns or more) by reliably plating copper deposits from electrolytes containing sulfonate anions (and other acid anions such as sulfate) that are essentially or completely free of dimples, overplates, voids, inclusions or other plating imperfections.

[0024] The present invention has found that it is better to use a pure alkanesulfonate solution rather than the mixed sulfonate solutions of the prior art since the shorter chain alkanesulfonates have been found to deposit better at higher free acid concentration and the longer carbon chain sulfonates work better at lower free acid.

[0025] The alkanesulfonic acids are distinguished from sulfuric acid by their unique balance of physical properties. For instance, the surface tension lowering capability of the alkanesulfonic acids increases up with chain length. However, so also does a general decrease in the aqueous solubility of metal alkanesulfonates go up with chain length.

[0026] The most preferred embodiment of the invention focuses on the unexpected superiority of C₁ to C₃ alkanesulfonic acids and derivatives thereof as electrolytes for copper electroplating. These acids have the best balance of metal alkanesulfonate solubility and surface tension lowering capability. The lower surface tension of the alkanesulfonates increases the surface activity which is important for plating into micron-dimensioned holes, while the metal salt solubility is important for plating generally. The solution conductivity of the sulfonic acids are generally lower than those based on sulfuric acid at an equivalent free acid concentration. This lower conductivity results in a shift in the primary current density distribution to low current density areas on the article to be plated with copper resulting in a more uniform copper deposit. Based on theory, the invention can be altered by the use of C₁ to C₃ alkanesulfonic acid derivatives.

[0027] Electroplating baths of the invention are characterized in significant part by comprising a high concentration of a sulfonate anion (RSO₃⁻). Without being bound by any theory, it is believed that the high sulfonate anion concentrations can modulate the plating rate in recesses such as vias, trenches and through-holes. This is counterintuitive to conventional thought and completely unexpected since the sulfonate anion is chemically similar to the accelerator type-additives used in many commercial acid copper electrolytes. Such accelerator anions usually have a sulfur moiety and a sulfonic acid moiety on the same molecule similar to the sulfonate anion. However, instead of accelerating copper deposition into the small features on electronic components leading to defects such as dimples or overplate structures like the sulfur-containing accelerator additive, the sulfonate molecule modulates copper deposition leading to a more uniform, defect-free copper deposit.

[0028] In particular, preferred electroplating compositions of the invention have a sulfonate concentration of at least about 0.05 mol/liter, more preferably a sulfonate concentration of at least about 0.2 mol/liter, still more preferably at least about 0.4 mol to about 1.0 mol/liter of plating solution. Adequate results have been achieved with even higher sulfonate concentrations, e.g. copper plating baths having a sulfonate concentration of at least about 2.25 mol/liter.

[0029] Preferably, the sulfonate anion concentration is maintained at such high concentrations throughout the entire

or at least a substantial portion of a plating cycle. A portion of the acid anion may be another acid anion molecule such as sulfate, fluoroborate, sulfamate, acetate, phenylsulfonate, phenolsulfonate, tolylsulfonate, phosphonate and pyrophosphate.

[0030] In addition to a sulfonate anion, the plating bath may also contain other additives commonly used in acid copper electrolytes such as suppressor additives, brighteners, accelerators, levelers and a surfactant-type agent. It has been surprisingly found that use of such a sulfonate acid anion combination with suppressors, accelerators, brighteners and levelers can result in effective "bottom-up fill" copper plating of a via or trench or other electronic features such as through holes in printed circuit boards without defects such as dimples, overplate, inclusions, seams or voids.

[0031] In particular, the sulfonate acid anion enables modulated plating rates at the bottom of a electronic feature, permitting copper to plate the entire aperture in a substantially "bottom-fill" fashion, without 1) resulting in low copper deposition in the middle of the aperture (e.g., dimples), 2) premature sealing of the aperture top that can result in inclusions or voids and 3) overplating the aperture resulting in overplate structures that must be subsequently mechanically and chemically removed.

[0032] The invention also includes articles of manufacture, including electronic packaging devices such as printed circuit boards, multichip modules, semiconductor integrated circuits, mechanical-electronic machine devices (i.e., MEMS devices) and the like that contain a copper deposit produced from a plating solution of the invention. Other aspects of the invention are discussed infra.

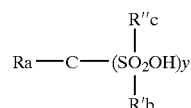
[0033] As discussed above, electroplating solutions of the invention are particularly effective in plating various electronic articles having vias, microvias, trenches or through-holes with low (0.5:1 to 3:1) aspect ratios.

[0034] In particular, solutions of the invention are useful in plating electronic devices such as printed circuit boards, microchip module packaging and blind 3-dimensional structures, particularly semiconductor integrated circuits and other circuit systems. The electroplating solutions of the invention are particularly useful to copper fill vias and microvias and through-holes of such electronic devices without defects commonly found with the use of prior chemistries based on non-sulfonate chemistries.

[0035] Preferred electroplating solutions of the invention generally comprise at least one soluble copper salt, an acid electrolyte, a halogen ion and additives.

[0036] More particularly, electroplating compositions of the invention preferably contain a copper salt of an alkyl or aryl sulfonic acid; an electrolyte, preferably an acidic aqueous solution such as a sulfonic acid solution with a chloride or other halide ion source; and one or more additives such as a brightener agent, a suppressor agent and a leveler agent and the like.

[0037] A variety of copper alkane salts may be employed in the subject electroplating solutions wherein the alkane-sulfonic acid of the anionic portion of the copper salt and any free acid are introduced as an alkyl or aryl sulfonic acid of formula:



[0038] wherein a+b+c+y equals 4;

[0039] R, R' and R'' are the same or different and each independently may be hydrogen, phenyl, Cl, F, Br, I, CF₃ or a lower alkyl group such as (CH₂)_n where n is from 1 to 7, preferably 1 to 3, and that is unsubstituted or substituted by oxygen, Cl, F, Br, I, CF₃, —SO₂OH. Preferred alkyl sulfonic acid are methanesulfonic, ethanesulfonic and propanesulfonic acids and the alkyl polysulfonic acids are methanedisulfonic acid, monochloromethanedisulfonic acid, dichloromethanedisulfonic acid, 1,1-ethanedisulfonic acid, 2-chloro-1,1-ethanedisulfonic acid, 1,2-dichloro-1,1-ethanedisulfonic acid, 1,1-propanedisulfonic acid, 3-chloro-1,1-propanedisulfonic acid, 1,2-ethylene disulfonic acid, 1,3-propylene disulfonic acid, trifluoromethanesulfonic acid, butanesulfonic acid, perfluorobutanesulfonic acid, pentanesulfonic, and the aryl sulfonic acids are phenylsulfonic, phenolsulfonic and tolylsulfonic acids.

[0040] Other copper salts may also be in the copper electrolyte such as copper sulfate, copper acetate, copper fluoroborate, copper sulfamate, cupric nitrates or copper phosphonates. Copper methanesulfonate is a particularly preferred copper salt. A copper salt may be suitably present in a relatively wide concentration range in the electroplating compositions of the invention. Preferably, a copper salt will be employed at a concentration from about 10 to about 300 grams per liter of plating solution, more preferably at a concentration of from about 25 to about 200 grams per liter of plating solution, still more preferably at a concentration of from about 40 to about 175 grams per liter of plating solution.

[0041] Additionally, in the present invention it has been found that a concomitant decrease in free acid with an increase in the carbon chain length produces defect-free deposits. The ethanesulfonic and propanesulfonic acid solutions operate best at lower free acid concentrations, less than 1.50 M free acid. The lower free acid concentrations minimize corrosion of the copper seed-layer leading to less defects in the electroplated copper layer. The sulfonates also deposit a smoother copper coating compared to sulfuric acid. The trifluoromethanesulfonate solutions yields commercially acceptable coatings over a wide free acid concentration range not disclosed by Proell.

[0042] The electrolyte may also contain free acid to increase solution conductivity. The preferred free acid has the same anion as the copper salt anion but mixtures of free acids are also within the scope of this invention. Preferred alkyl sulfonic acid are methanesulfonic, ethanesulfonic and propanesulfonic acids and the alkyl polysulfonic acids are methanedisulfonic acid, monochloromethanedisulfonic acid, dichloromethanedisulfonic acid, 1,1-ethanedisulfonic acid, 2-chloro-1,1-ethanedisulfonic acid, 1,2-dichloro-1,1-

ethanedisulfonic acid, 1,1-propanedisulfonic acid, 3-chloro-1,1-propanedisulfonic acid, 1,2-ethylene disulfonic acid, 1,3-propylene disulfonic acid, trifluoromethanesulfonic acid, butanesulfonic acid, perfluorobutanesulfonic acid, pentanesulfonic acid and the aryl sulfonic acids are phenylsulfonic and tolylsulfonic acids. The free acid concentration ranges from about 1 g/l to about 300 g/l, more preferably at a concentration of from about 25 to about 200 grams per liter of plating solution, still more preferably at a concentration of from about 40 to about 175 grams per liter of plating solution.

[0043] The invention also includes electroplating baths that are substantially or completely free of an added sulfonic acid and may be neutral or essentially neutral (e.g. pH of at least less than about 7 or 7.5). Such plating compositions are suitably prepared in the same manner with the same components as other compositions disclosed herein but without an added sulfonic acid.

[0044] Plating baths of the invention preferably employ an acidic electrolyte, which typically will be an acidic aqueous solution and that preferably contains a halide ion source, particularly a chloride ion source. Examples of other suitable halides include bromide and iodide. A wide range of halide ion concentrations (if a halide ion is employed) may be suitably utilized, e.g. from about 0 (where no halide ion employed) to 200 parts per million (ppm) of halide ion in the plating solution, more preferably from about 10 to about 75 ppm of halide ion source in the plating solution.

[0045] In addition to the copper salts, acid electrolyte and a halogen ion, plating baths of the invention optionally may contain a variety of other components, including organic additives such as suppressors agents, accelerator agents, leveling agents and the like. The use of a suppressor agent in combination with an accelerator or brightener additive is particularly preferred and provides surprisingly enhanced plating performance, particularly in bottom-fill plating of small diameter and/or low to moderate aspect ratio vias or microvias and through-holes.

[0046] Without being bound by any theory, it is believed such enhanced bottom-fill plating may occur due to the concentration of the suppressor agent being comparatively decreased at a bottom of a via or microvia or within the through-holes as a result of diffusional effects through the length of the via, microvia or through-hole. The reduced suppressor additive concentration results in an enhanced copper plating rate at the bottom portions of the via, microvia regions or in the middle of the trough-hole. At the surface of the feature to be plated (at the top of the via or microvia or the surface of the printed circuit board), the suppressor agent concentration remains relatively high and constant relative to the via, microvia bottom regions or in the middle of the through-hole. Therefore, the top area of the feature to be plated has a comparatively suppressed or slowed plating rate because of the enhanced suppressor agent concentration relative to the bottom portion of the article being plated with copper. Preferred suppressor agents for use in the compositions of the invention are polymeric materials, preferably having hetero-atom substitution, particularly oxygen linkages.

[0047] Preferred suppressor agents are high molecular weight polyethers, such as those of the following formula:

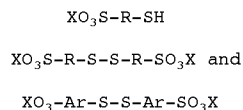


[0048] where R is an aryl or alkyl group containing from about 2 to 20 carbon atoms; each X, Y, X' and Y' is independently hydrogen; alkyl preferably methyl, ethyl or propyl; aryl such as phenyl; aryl such as benzyl, and preferably one or more of X, Y, X' and Y' is hydrogen; and n is an integer between 5 and 100,000. Preferably, R is ethylene and n is greater than 5,000 and less than 75,000.

[0049] As discussed above, it has been discovered that by having a high sulfonate anion concentration, beyond conventional levels of typical accelerator type-additives, uniform plating of particularly low to high aspect ratio vias and microvias and other difficult-to-plate electronic features such as through-holes in printed circuit boards is now possible.

[0050] A wide variety of brighteners, including known brightener agents, may be employed in the copper electroplating compositions of this invention. Typical brighteners contain one or more sulfur atoms, and typically without any nitrogen atoms and a molecular weight of about 1500 or less. Brightener compounds that have sulfide and/or sulfonic acid groups are generally preferred, particularly compounds that comprise a group of the formula $\text{R}'-\text{S}-\text{R}-\text{SO}_3\text{X}$, where R is an optionally substituted alkyl (which include cycloalkyl), optionally substituted heteroalkyl, optionally substituted aryl group, or optionally substituted heteroalicyclic; X is a counter ion such as ammonium, sodium or potassium; and R' is hydrogen or a chemical bond (i.e. $-\text{S}-\text{R}-\text{SO}_3\text{X}$ or substituent of a larger compound). Typically alkyl groups will have from one to about 20 carbons, more typically one to about 6 or 12 carbons. Heteroalkyl groups will have one or more hetero (N, O or S) atoms in the chain, and preferably have from 1 to about 16 carbons, more typically 1 to about 8 or 12 carbons. Carboxycyclic aryl groups are typical aryl groups, such as phenyl and naphthyl. Heteroaromatic groups also will be suitable aryl groups, and typically contain 1 to about 3 N, O or S atoms and 1-3 separate or fused rings and include e.g. coumarinyl, quinolinyl, pyridyl, pyrazinyl, pyrimidyl, furyl, pyrrolyl, thienyl, thiazolyl, oxazolyl, oxidizolyl, triazole, imidazolyl, indolyl, benzofuranyl, benzothiazol, and the like. Heteroalicyclic groups typically will have 1 to 3 N, O or S atoms and from 1 to 3 separate or fused rings and include e.g. tetrahydrofuranly, thienyl, tetrahydro-pyranly, piperdinyl, morpholino, pyrrolindinyl, and the like. Substituents of substituted alkyl, heteroalkyl, aryl or heteroalicyclic groups include e.g. C_{1-8} alkoxy; C_{1-8} alkyl, halogen, particularly F, Cl and Br; cyano, nitro, and the like.

[0051] More specifically, useful brighteners include those of the following formula:



[0052] where in the above formulae R is an optionally substituted 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 optionally substituted aryl group such as optionally substituted phenyl or naphthyl; and X is a suitable counter ion such as ammonium, sodium or potassium.

[0053] Some specific suitable brighteners include e.g. n,n-dimethyl-dithiocarbamic acid-(3-sulfopropyl)ester; 3-mercapto-propylsulfonic acid-(3-sulfopropyl)ester; 3-mercapto-propylsulfonic acid (sodium salt); carbonic acid-dithio-o-ethyl-ester-s-ester with 3-mercapto-1-propane sulfonic acid (potassium salt); bisulfopropyl disulfide; 3-(benzthiazolyl-s-thio)propyl sulfonic acid (sodium salt); pyridinium propyl sulfobetaine; 1-sodium-3-mercapto-propane-1-sulfonate; sulfoalkyl sulfide compounds disclosed in U.S. Pat. No. 3,778,357; the peroxide oxidation product of a dialkyl amino-thiox-methyl-thioalkanesulfonic acid; and combinations of the above. Additional suitable brighteners are also described in U.S. Pat. Nos. 3,770,598, 4,374,709, 4,376,685, 4,555,315, and 4,673,469, all incorporated herein by reference. Particularly preferred brighteners for use in the plating compositions of the invention are n,n-dimethyl-dithiocarbamic acid-(3-sulfopropyl)ester and bis-sodium-sulfonopropyl disulfide.

[0054] Use of one or more leveling agents in plating baths of the invention is generally preferred. In general, useful leveling agents include those that contain a substituted amino group such as compounds having R—N—R', where each R and R' is independently a substituted or unsubstituted alkyl group or a substituted or unsubstituted aryl group. Typically the alkyl groups have from 1 to 8 carbon atoms, more typically from 1 to 4 carbon atoms. Suitable aryl groups include substituted or unsubstituted phenyl or naphthyl. The substituents of the substituted alkyl and aryl groups may be, for example, alkyl, halo and alkoxy. More specifically, suitable leveling agents include e.g. 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine; 2-mercaptothiazoline; ethylene thiourea; thiourea; alkylated polyalkyleneimine; phenazonium compounds disclosed in U.S. Pat. No. 3,956,084; N-heteroaromatic rings containing polymers; quaternized, acrylic, polymeric amines; polyvinyl carbamates; pyrrolidone; and imidazole. A particularly preferred leveler is 1-(2-hydroxyethyl)-2-imidazolidinethione. Typical concentrations of leveling agents range from about 0.05 to 1.5 mg per liter of plating solution. Suitable leveling agents are described and set forth in U.S. Pat. Nos. 3,770,598; 4,374,709; 4,376,685; 4,555,315 and 4,673,459.

[0055] Surfactants useful in the present invention include e.g. amines such as ethoxylated amines, polyoxyalkylene amines and alkanol amines; amides; polyglycol-type wetting agents, such as polyethylene glycols, polyalkylene glycols and polyoxyalkylene glycols; high molecular weight polyethers; polyethylene oxides (mol. wt. 100,000 to 3 million); block copolymers of polyoxy-alkylenes; alkylpolyether sulfonates; complexing surfactants such as alkoxyated diamines; Particularly suitable surfactants for plating compositions of the invention are commercially available polyethylene glycol copolymers, including polyethylene glycol copolymers. Surfactants described in U.S. Ser. No. 2001/0, 047,943A1 are particularly preferred. Surfactants are typically added to copper electro-plating solutions in concentrations ranging from about 1 to 20,000 ppm based on the weight of the bath, more preferably about 5 to 12,000 ppm.

[0056] The invention also includes the use of complexing agents for cupric or cuprous ions which include monocarboxylic, dicarboxylic and tricarboxylic acid such as citric acid, tartaric acid, potassium sodium tartrate, oxalic acid and phosphonic acids in the copper sulfonate electrolyte.

[0057] The term "copper plating" as used in this specification includes the plating of copper and copper alloys. Copper alloys include metals from Group 1B, 2B, 3A, 3B, 4A, 4B, 5B, 6B, 7B, and 8 of the periodic table.

[0058] Plating baths of the invention are preferably employed at or above room temperature, e.g. up to and somewhat above 65° C. The plating composition is preferably agitated during use such as by using an air sparger, physical movement of the work piece, impingement of the solution or other suitable method. Plating is preferably conducted at a current ranging from 0.1 to 400 ASF depending upon substrate characteristics. Plating time may range from about 5 minutes to 1 hour or more, depending on the difficulty of the work piece. See generally the examples which follow for exemplary preferred procedures.

[0059] The invention described also includes the use of direct, pulse or periodic current waveforms to effectively deposit a defect-free copper layer in the electronic features.

[0060] The invention described may also use a soluble copper anode or an insoluble or inert anode material.

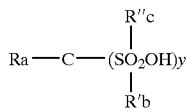
[0061] A wide variety of substrates may be plated with the compositions of the invention, as discussed above. The compositions of the invention are particularly useful to plate difficult work pieces, such as circuit board substrates with small diameter and low aspect vias or through-holes, integrated circuits with low aspect ratio vias, integrated circuits with high aspect ratio microvias and other electronic features. The plating compositions of the invention also will be particularly useful for plating integrated circuit devices, such as formed semiconductor devices and the like.

[0062] As discussed above, low aspect ratios of at least 0.5:1 to about 3:1, having diameters of about 1 to 500 microns or larger have been effectively copper plated with no defects (e.g. no voids or inclusions as detectable by ion beam examination) using plating solutions of the invention. Microvias with diameters below 0.5 microns, or even below about 0.2 microns, and aspect ratios of 4:1, 6:1, 7:1, 10:1 or greater, and even up to about 15:1 or greater can be effectively plated (e.g. no voids or inclusions detectable by ion beam examination) using plating solutions of the invention.

[0063] The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims. This invention provides a novel means of using biocides more effectively. By combining typical biocides with the alkanolamines described herein, one can obtain much better microbial control per unit of biocide than is obtainable without the alkanolamine.

1. A solution for copper electroplating which contains copper alkanesulfonate salts and free alkanesulfonic acids, wherein the free acid has a concentration from about 0.05 to about 2.50 M, and which is intended for the metallization of micron-sized dimensioned trenches or vias, through-holes and microvias.

2. The solution of claim 1 wherein the alkanesulfonic acid of the anionic portion of the copper salt and any free acid are introduced as an alkyl or aryl sulfonic acid of formula:



wherein $a+b+c+y$ equals 4,

R, R' and R'' are the same or different and each independently may be hydrogen, phenyl, Cl, F, Br, I, CF₃ or a lower alkyl group such as (CH₂)_n where n is from 1 to 7 and that is unsubstituted or substituted by oxygen, Cl, F, Br, I, CF₃, —SO₂OH:

3. The solution of claim 1 wherein the alkanesulfonic acid is derived from an alkyl monosulfonic acid, an alkyl polysulfonic acid or an aryl mono or polysulfonic acid.

4. The solution of claim 1 wherein the alkyl sulfonic acid is methanesulfonic, ethanesulfonic and propanesulfonic acids and the alkyl polysulfonic acids are methanedisulfonic acid, monochloromethanedisulfonic acid, dichloromethanedisulfonic acid, 1,1-ethanedisulfonic acid, 2-chloro-1,1-ethanedisulfonic acid, 1,2-dichloro-1,1-ethanedisulfonic acid, 1,1-propanedisulfonic acid, 3-chloro-1,1-propanedisulfonic acid, 1,2-ethylene disulfonic acid, 1,3-propylene disulfonic acid, trifluoromethanesulfonic acid, butanesulfonic acid, perfluorobutanesulfonic acid, and pentanesulfonic acid and the aryl sulfonic acid are phenylsulfonic, phenolsulfonic and tolylsulfonic acids.

5. The solution of claim 1 wherein the alkanesulfonic acid is methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid or trifluoromethanesulfonic acid.

6. The solution of claim 1 wherein the acid is a mixture of an alkanesulfonic acid with other acids.

7. The solution of claim 1 which contains a halogen ion from 0.01 to 200 mg/l.

8. The solution of claim 1 wherein no free acid is used.

9. The composition of claim 1 wherein the pH is between 0.05 to 7.5.

10. The solution of claim 1 wherein the copper salt is supplied as a mixture of a copper alkanesulfonate with other metal salts selected from metals in Group 1B, 2B, 3A, 3B, 4A, 4B, 5B, 6B, 7B, or 8 of the periodic table.

11. The composition of claim 1 wherein the suppressor additive is a high molecular weight polyether containing oxygen linkages.

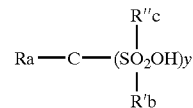
12. The composition of claim 1 wherein a sulfur-containing accelerator or brightener agent is at least about 0.05 to 100 mg per liter of the electroplating composition.

13. The composition of claim 1 wherein brightener agent is bis-sodium-sulfonopropylsulfide.

14. The composition of claim 1 containing a nitrogen-containing leveler additive.

15. A process for the metallization of micron dimensioned trenches or vias or through-holes, wherein the process employs an electroplating solution containing copper alkanesulfonate salts and free alkanesulfonic acids, wherein the free acid has a concentration of from about 0.05 to about 3.50 M, and electric current is passed through the solution to electroplate copper onto a substrate.

16. The process of claim 15 wherein the alkanesulfonic acid of the anionic portion of the copper salt and any free acid are introduced as an alkyl or aryl sulfonic acid of formula:



wherein $a+b+c+y$ equals 4,

R, R' and R'' are the same or different and each independently may be hydrogen, phenyl, Cl, F, Br, I, CF₃ or a lower alkyl group such as (CH₂)_n where n is from 1 to 7 and that is unsubstituted or substituted by oxygen, Cl, F, Br, I, CF₃, —SO₂OH.

17. The process of claim 15 wherein the substrate is a semiconductor device or a printed circuit board with a thin metallized surface containing micron or sub-micron dimensioned trenches, through-holes, or vias, and wherein the plating solution effectively plates copper into said trenches, through-holes or vias.

18. The process of claim 15 wherein direct current, pulsed current or periodic reverse current is used.

19. The process of claim 15 wherein a soluble or an insoluble or inert anode is used.

20. The process of claim 15 wherein the temperature of the copper electrolyte is between 20° C. to 70°.

21. The process of claim 15 wherein the copper is pure copper or a copper alloy with a metal from Group 1B, 2B, 3A, 3B, 4A, 4B, 5B, 6B, 7B, or 8 of the periodic table.

22. The process of claim 15 wherein the substrate is a printed circuit board substrate or semiconductor with one or more vias or microvias or through-holes.

23. The process of claim 15 wherein the via or microvias or through-holes have an aspect ratio of about 1:1 and diameters of about 1 to 500 microns.

24. The process of claim 15 wherein copper is deposited to fill the one or more vias to provide a copper plate in the absence of dimples, overplate, voids or inclusions.

25. An article of manufacture comprising an electronic device substrate containing one or more through-hole, via, microvia or trench, the aperture walls having thereon an electrolytic copper deposit obtained from an electroplating composition from claim 1 that contains copper alkanesulfonate salts and free alkanesulfonic acids, a halogen ion, a suppressor additive, an accelerator additive, optionally a leveling additive and optionally a surfactant.

26. The article of claim 25 wherein the substrate is printed board substrate, a microchip module substrate, or a semiconductor chip substrate.

27. The article of claim 25 wherein the substrate comprises the one or more via, microvia or through-hole that has an aspect ratio of at least about 1:1 and diameters of at least about 1 microns to 500 microns.

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