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(54) **ACIDIC AQUEOUS BINARY SILVER-BISMUTH ALLOY ELECTROPLATING COMPOSITIONS AND METHODS**

(57) Aqueous acid binary silver-bismuth alloy electroplating compositions and methods enable electroplating silver rich binary silver-bismuth deposits. The aqueous acid binary silver-bismuth alloy electroplating compositions include 5-membered heterocyclic nitrogen compounds with a thiol functionality which enable deposition of the silver rich binary silver-bismuth alloys. The silver rich silver-bismuth deposits are matte to semi-bright, uniform and have a low coefficient of friction.

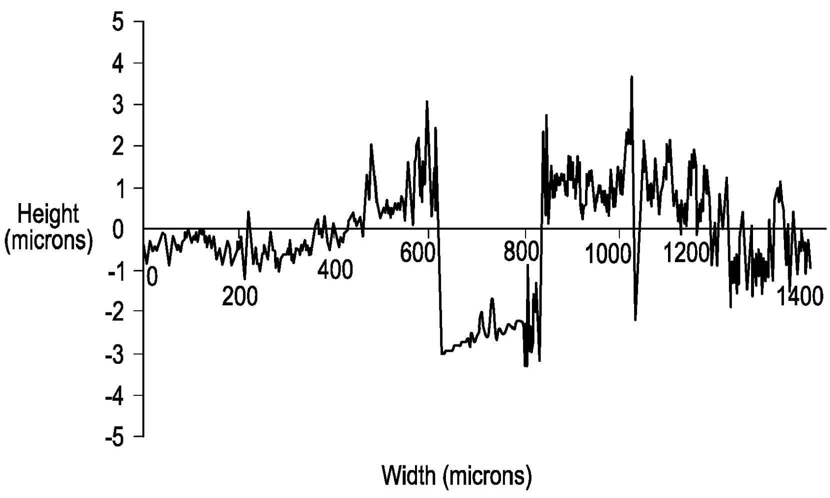

FIG. 2

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Description

Field of the Invention

[0001] The present invention is directed to acidic aqueous binary silver-bismuth alloy electroplating compositions and methods. More specifically, the present invention is directed to acidic aqueous binary silver-bismuth alloy electroplating compositions and methods, wherein the acidic aqueous binary silver-bismuth alloy electroplating compositions include 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality which enable electrodeposition of silver rich binary silver-bismuth alloys having low electrical contact resistance and good wear resistance.

Background of the Invention

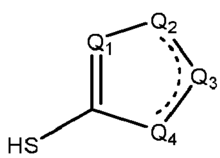
[0002] Silver and silver alloy plating baths are highly desirable for depositing silver and silver alloys on substrates in applications directed to the manufacture of electronic components and jewelry. Substantially pure silver is used as a contact finish because of its excellent electrical properties, specifically, low electrical contact resistance. However, its use as a contact finish for, example, electrical connectors are limited because of their poor resistance to mechanical wear and high silver-on-silver coefficient of friction. The poor resistance to mechanical wear results in the connector becoming physically damaged after a relatively low number of insertion-deinsertion cycles of the connector. A high coefficient of friction contributes to this wear problem. When connectors have a high coefficient of friction, the force required to insert and deinsert the connector is very high and this can damage the connector or limit the connector design options. Silver alloy deposits, such as silver-antimony and silver-tin, result in improved wear properties but have unacceptably poor contact resistance, especially after exposure to high temperatures for prolonged periods of time.

[0003] Since many silver salts are substantially water-insoluble and silver salts which are water-soluble often form insoluble salts with various compounds commonly present in plating baths, the plating industry is faced with numerous challenges to formulate a silver or silver alloy plating bath which is stable long enough for practical plating applications and addresses at least the foregoing problems. Many silver and silver alloy plating baths include cyanide compounds to enable practical applications. However, cyanide compounds are extremely poisonous. Therefore, special waste water treatment is required. This results in a rise in treatment costs. Further, since these baths can only be used in the alkaline range, the types of alloying metals are limited because most metals are not soluble in alkaline environments. Further, exposure of substrates to alkaline baths can cause passivation of the surfaces of the substrates, thus making the surfaces difficult to plate.

[0004] Therefore, there is a need for a silver alloy plating bath which is stable, acidic, produces a deposit that has low electrical contact resistance and low coefficient of friction to provide improved wear resistance.

Summary of the Invention

[0005] The present invention is directed to binary silver-bismuth alloy electroplating compositions comprising a source of silver ions, a source of bismuth ions, and a 5-membered aromatic heterocyclic nitrogen compound having the general formula:

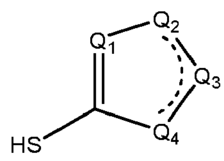


(I)

wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, hydrogen, $(C_1$-$C_4)$alkyl, amino group, aminoalkyl group, carboxyl, carboxy$(C_1$-$C_4)$alkyl, or alkylsulfonate, and a pH of less than 7.

[0006] The present invention is also directed to a method of electroplating binary silver-bismuth alloys on a substrate including:

a) providing the substrate;
b) contacting the substrate with a binary silver-bismuth alloy electroplating composition comprising a source of silver ions, a source of bismuth ions, and a 5-membered aromatic heterocyclic nitrogen compound having the general formula:



(I)

wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, hydrogen, $(C_1$-$C_4)$alkyl, amino group, aminoalkyl group, carboxyl, carboxy$(C_1$-$C_4)$alkyl, or alkylsulfonate, and a pH of less than 7; and

c) applying an electric current to the binary silver-bismuth alloy electroplating composition and the substrate to electroplate a silver-bismuth alloy deposit on the substrate.

[0007] The present invention is further directed to an article comprising a binary silver-bismuth alloy layer adjacent a surface of a substrate, wherein the binary silver-bismuth alloy layer comprises 90% to 99% silver and 1% to 10% bismuth, and has a coefficient of friction of 1 or less.

[0008] Including 5-membered aromatic heterocyclic nitrogen compounds having formula (I) above in aqueous binary silver-bismuth electroplating compositions in an acidic environment enables deposition of silver rich binary silver-bismuth alloys on a substrate such that the silver rich binary silver-bismuth alloys have substantially the good electrical properties of a silver deposit, specifically, low electrical contact resistance. In addition, the silver rich binary silver-bismuth alloy deposits good mechanical wear resistance. The silver rich binary silver-bismuth deposits are uniform and matte to semi-bright in appearance. The binary silver-bismuth alloy electroplating compositions of the present invention are stable.

Brief Description of the Drawings

[0009]

Figure 1 is a scanning electron microscope image at 10,000X of a binary silver-bismuth alloy showing discrete sectors of bismuth in a silver matrix.

Figure 2 is a 2D profilometry graphic of a surface of a silver metal deposit wherein the x-axis and y-axis are calibrated in microns (μm).

Figure 3 is a 3D profilometry graphic of a surface of a silver metal deposit wherein the x-axis, y-axis and z-axis are calibrated in microns (μm).

Figure 4 is a 2D profilometry graphic of a surface of a silver-bismuth alloy deposit of the invention wherein the alloy is composed of 95% silver and 5% bismuth, and the x-axis, y-axis and z-axis are calibrated in microns (μm).

Figure 5 is a 3D profilometry graphic of a surface of a silver-bismuth alloy deposit of the invention wherein the alloy is composed of 95% silver and 5% bismuth, and the x-axis, y-axis and z-axis are calibrated in microns (μm).

Figure 6 is a 2D profilometry graphic of a surface of a silver-bismuth alloy deposit of the invention wherein the alloy is composed of 97% silver and 3% bismuth, and the x-axis, y-axis and z-axis are calibrated in microns (μm).

Figure 7 is a 3D profilometry graphic of a surface of a silver-bismuth alloy deposit of the invention wherein the alloy is composed of 97% silver and 3% bismuth, and the x-axis, y-axis and z-axis are calibrated in microns (μm).

Figure 8 is a 2D profilometry graphic of a surface of a silver-bismuth alloy deposit of the invention wherein the alloy is composed of 97% silver and 3% bismuth, and the x-axis, y-axis and z-axis are calibrated in microns (μm).

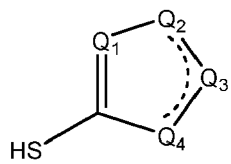
Figure 9 is a 3D profilometry graphic of a surface of a silver-bismuth alloy deposit of the invention wherein the alloy is composed of 97% silver and 3% bismuth, and the x-axis, y-axis and z-axis are calibrated in microns (μm).

Detailed Description of the Invention

[0010] As used throughout the specification the abbreviations have the following meanings, unless the context clearly indicates otherwise: °C = degrees Centigrade; ppm = parts per million; one ppm = one mg/L; g = gram; mg = milligram; L = liter; mL = milliliter; mm = millimeters; cm = centimeter; μm = microns; DI = deionized; A = amperes; ASD = amperes/dm^2 = plating speed; DC = direct current; v = volts, which is the SI unit of electromotive force; mΩ = milliohms = contact resistance; cN = centiNewtons = a unit of force; N = newtons; COF = coefficient of friction; rpm = revolutions per minute; s = seconds; 2D = two-dimensional; 3D = three-dimensional; Ag = silver; Bi = bismuth; Au = gold; Cu = copper; Ag^+ molecular weight = 107.868 g/mole; and 3,6-dithia-1,8-octanediol molecular weight = 182.3 g/mole.

[0011] The term "alky" means an organic functional group having the general formula C_nH_{2n+1} where C is carbon, H is hydrogen and n is an integer. The term "aliphatic" means relating to or denoting organic compounds in which carbon atoms form open chains (as in alkanes), not aromatic rings. The term "binary" in reference of an alloy means a metallic solid composed of a homogenous mixture of two metals. The "----" dashed line in chemical structures means an optional covalent bond. The term "adjacent" means directly in contact with such that two metal layers have a common interface. The term "contact resistance" means electrical resistance as a function of applied force. The term "newtons" is the SI unit of force and it is equal to the force that would give a mass of one kilogram an acceleration of one meter per second per second, and is equivalent to 100,000 dynes. The term "coefficient of friction" is a value that shows the relationship between the force of friction between two objects and the normal reaction between the objects that are involved; and is shown by F_f = (μF_n, wherein F_f is the frictional force, μ is the coefficient of friction and F_n is the normal force. The term "normal force" means a force applied perpendicular to the plane of contact between two objects. The term "discrete" means individually separate and distinct. The term "sector" means an area or portion that is distinct from other areas. The term "matrix" means a surrounding metal or majority metal, i.e., greater than 50%, of a metal alloy. The term "proviso" means a condition or restriction. The term "tribology" means the science and engineering of interacting surfaces in relative motion and includes the study and application of the principles of lubrication, friction and wear. The term "cold welding" means a solid-state welding process in which joining takes place without fusion or heating at the interface of the two parts to be welded and no molten liquid or molten phase is present in the joint. The term "aqueous" means water or water-based. The terms "composition" and "bath" are used interchangeably throughout the specification. The terms "deposit" and "layer" are used interchangeably throughout the specification. The terms "electroplating", "plating" and "depositing" are used interchangeably throughout the specification. The term "matte" means dull or without luster. The terms "a" and "an" can refer to both the singular and the plural throughout the specification. All percent (%) values and ranges indicate weight percent unless otherwise specified. 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%.

[0012] The present invention is directed to an aqueous acidic binary silver-bismuth electroplating composition, wherein the aqueous acidic binary silver-bismuth electroplating composition includes a source of silver ions, a source of bismuth ions and a 5-membered aromatic heterocyclic nitrogen compound having the general formula:

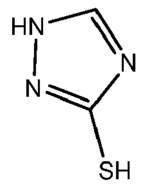


(I)

wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least three of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, hydrogen, (C_1-C_4)alkyl, an amino group, an aminoalkyl group, carboxyl group, carboxy(C_1-C_4)alkyl, or alkylsulfonate, and a pH of less than 7. Preferably, the substituent groups are hydrogen, (C_1-C_2)alkyl, a primary amino group such as NH_2, a secondary amino group such as NH-NH_2, or an amino(C_1-C_4)alkyl, further preferably, the substituent groups are hydrogen, methyl or NH_2, more preferably, a nitrogen of the ring is substituted with hydrogen or methyl group or a nitrogen of the ring is substituted with the NH_2, or a carbon of the ring is substituted with the NH_2, most preferably, a nitrogen of the ring is substituted with hydrogen or methyl.

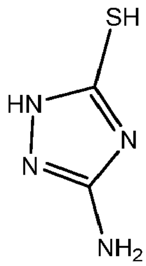
[0013] The matte to semi-bright and uniform silver rich binary silver-bismuth alloy deposits have substantially good electrical properties, such as low electrical contact resistance. The silver rich binary silver-bismuth alloy deposit has a low coefficient of friction such that the silver rich binary silver-bismuth alloy layers have good mechanical wear resistance. The acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention are stable. The aqueous binary silver-bismuth alloy electroplating compositions are free of any additional alloying metals, such as, but not limited to, antimony, tin, copper, nickel, cobalt, cadmium, gold, lead, indium, iron, palladium, platinum, rhodium, ruthenium, tellurium, thallium, selenium and zinc. Preferably, the acidic aqueous silver-bismuth electroplating compositions are cyanide-free.

[0014] Examples of preferred 5-membered aromatic heterocyclic nitrogen compounds of the present invention are the following:



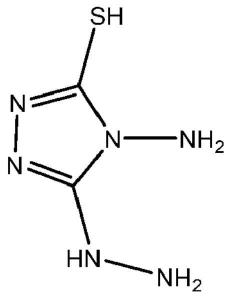
(II)

3-mercapto-1,2,4-triazole;



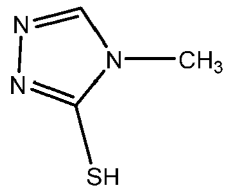
(III)

3-amino-1,2,4-triazole-5-thiol;



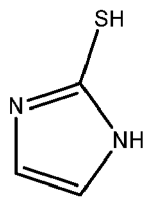
(IV)

4-amino-3-hydrazino-5-mercapto-1,2,4-triazole;



(V)

3-mercapto-4-methyl-4H-1,2,4-trizole;



(VI)

1*H*-imidazole-2-thiol; and

salts of the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality. More preferably, the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention are chosen from one or more of 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole-5-thiol, 3-amino-5-mercapto-1,2,4-triazole, 3-mercapoto-4-methyl-4H-1,2,4-triazole, and salts of the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality; even more preferably, the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention are chosen from one or more of 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole-5-thiol, 3-amino-5-mercapto-1,2,4-triazole, 3-mercapoto-4-methyl-4H-1,2,4-triazole, and salts of the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention; further preferably, the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention are chosen from one or more of 3-mercapto-1,2,4-triazole, 3-mercapoto-4-methyl-4H-1,2,4-triazole, and salts of the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention. Salts of the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention of the present invention include, but are not limited to, alkali metal salts, such as sodium, potassium and lithium salts, ammonium salts, tetraalkyl ammonium salts, magnesium salts, silver salts and bismuth salts.

[0015] The 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality and salts thereof of the present invention are included in sufficient amounts to enable electroplating of a silver rich binary silver-bismuth alloy in an aqueous acid environment. Preferably, the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality of the present invention are included in amounts of 50 ppm or greater, more preferably, in amounts of 100 ppm to 100 g/L, further preferably, from 100 ppm to 20 g/L, even more preferably, from 100 ppm to 10 g/L, most preferably, from 100 ppm to 5 g/L.

[0016] The aqueous acid silver-bismuth alloy electroplating compositions of the present invention include a source of silver ions. Sources of silver ions can be provided by silver salts such as, but not limited to, silver halides, silver gluconate, silver citrate, silver lactate, silver nitrate, silver sulfates, silver alkane sulfonates, silver alkanol sulfonates or mixtures thereof. When a silver halide is used, preferably the halide is chloride. Preferably, the silver salts are silver sulfate, a silver alkane sulfonate, silver nitrate, or mixtures thereof, more preferably, the silver salt is silver sulfate, silver methanesulfonate, or mixtures thereof. Mixtures of silver salts can also be included in the compositions. The silver salts are generally commercially available or can be prepared by methods described in the literature. Preferably, the silver salts are readily water-soluble.

[0017] The amount of silver salts included in the aqueous acid binary silver-bismuth electroplating compositions are in amounts sufficient to provide a desired matte to semi-bright and uniform silver rich binary silver-bismuth alloy deposit, preferably, where the silver content of the silver rich binary silver-bismuth alloy deposit contains 90% to 99.8% silver, further preferably, from 90% to 99.7% silver, most preferably, from 95% to 99.7%, with bismuth the remainder of the alloying metal, excluding unavoidable impurities. Preferably, silver salts are included in the compositions to provide silver ions at a concentration of at least 10 g/L, more preferably, silver salts are included in the compositions in amounts to provide silver ion concentrations in amounts of 10 g/L to 100 g/L, further preferably, silver salts are included in amounts to provide silver ion concentrations of 20 g/L to 80 g/L, most preferably, silver salts are included in amounts to provide silver ions at concentrations of 20 g/L to 60 g/L.

[0018] The aqueous acid silver-bismuth alloy electroplating compositions include a source of bismuth ions which provide the electroplating bath with Bi^{3+} ions in solution. Sources of bismuth ions include, but are not limited to, bismuth salts of alkane sulfonic acids such as bismuth methanesulfonate, bismuth ethanesulfonate, bismuth propanesulfonate, 2-bismuth propane sulfonate and bismuth p-phenolsulfonate, bismuth salts of alkanolsulfonic acids such as bismuth hydroxymethanesulfonate, bismuth 2-hydoxyethane-1-sulfonate and bismuth 2-hydroxybutane-1-sulfonate, and bismuth salts such as bismuth nitrate, bismuth sulfate and bismuth chloride. Mixtures of bismuth salts can also be included in the compositions. Preferably, the bismuth salts are water soluble.

[0019] The amount of bismuth salts included in the aqueous acid binary silver-bismuth electroplating compositions are in amounts sufficient to provide a desired matte to semi-bright and uniform silver rich binary silver-bismuth alloy deposit, preferably, where the bismuth content of the silver rich binary silver-bismuth alloy deposit contains 0.2% to 10% bismuth, further preferably, from 0.3% to 10% bismuth, most preferably, from 0.3% to 5% bismuth. Preferably, bismuth salts are included in the silver-bismuth compositions to provide bismuth (III) ions in amounts of 50 ppm to 10 g/L, further preferably, from 100 ppm to 5 g/L, most preferably, from 200 ppm to 5 g/L. Such bismuth salts are commercially available or can be made according to disclosures in the chemical literature. They are generally commercially available from a variety of sources, such as Aldrich Chemical Company, Milwaukee, Wisconsin.

[0020] Preferably, in the aqueous acid silver-bismuth alloy electroplating compositions of the present invention, the water included as a solvent is at least one of deionized and distilled to limit incidental impurities.

[0021] Optionally, an acid can be included in the binary silver-bismuth alloy electroplating compositions to assist in providing conductivity to the compositions. Acids include, but are not limited to, organic acids such as acetic acid, citric acid, arylsulfonic acids, alkanesulfonic acids, such as methanesulfonic acid, ethanesulfonic acid or propanesulfonic acid, aryl sulfonic acids such as phenylsulfonic acid or tolylsulfonic acid, and inorganic acids such as sulfuric acid, sulfamic acid, hydrochloric acid, hydrobromic acid or fluoroboric acid. Water-soluble salts of the foregoing acids also can be included in the binary silver-bismuth alloy electroplating compositions of the present invention. Preferably, the acids are acetic acid, citric acid, alkane sulfonic acids, aryl sulfonic acids, or salts thereof, more preferably the acids are acetic acid, citric acid, methanesulfonic acid, or salts thereof. Such salts include, but are not limited to, sodium, potassium, silver, bismuth, magnesium, tetraalkylammonium and ammonium salts. Although a mixture of acids can be used, preferably, when used, a single acid is used. The acids are generally commercially available or can be prepared by methods known in the literature. Such acids can be included in amounts to provide a desired conductivity. Preferably, the acids or salts thereof are included in amounts of at least 5 g/L, more preferably, from 10 g/L to 250 g/L, even more preferably, from 30 g/L to 150 g/L, most preferably from 30 g/l to 125 g/L.

[0022] The pH of the aqueous acidic binary silver-bismuth alloy electroplating composition is less than 7. Preferably, the pH is 0 to 6, more preferably, the pH is from 0 to 5, further preferably, the pH is from 0 to 3, even more preferably, the pH is from 0 to 2.5, most preferably, the pH is from 0 to 2.

[0023] Optionally, a pH adjusting agent can be included in the aqueous acid binary silver-bismuth alloy compositions of the present invention. Such pH adjusting agents include inorganic acids, organic acids, inorganic bases or organic bases and salts thereof. Such acids include, but are not limited to, inorganic acids such as sulfuric acid, hydrochloric acid, sulfamic acid, boric acid, phosphoric acid or salts thereof. Organic acids include, but are not limited to, acetic acid, citric acid, amino acetic acid and ascorbic acid or salts thereof. Such salts include, but are not limited to, trisodium citrate. Inorganic bases such as sodium hydroxide and potassium hydroxide and organic bases such as various types of amines can be used. Preferably, the pH adjusting agents are chosen from acetic acid, citric acid, amino acetic acid or salts thereof, most preferably, acetic acid, citric acid or salts thereof. The pH adjusting agents can be added in amounts as needed to maintain a desired pH range.

[0024] Optionally, but preferably, a thioether is included in the aqueous acid binary silver-bismuth alloy electroplating compositions of the present invention. Such thioethers include, but are not limited to, 2,2'-thiodiethanol, 4,4'-thiodiphenol and 4,4'-thiobis(2-methyl-6-tertbutylphenol), dihydroxy bis-sulfide compounds or mixtures thereof. Such dihydroxy bis-sulfide compounds include, but are not limited to, 2,4-dithia-1,5-pentanediol, 2,5-dithia-1,6-hexanediol, 2,6-dithia-1,7-heptanediol, 2,7-dithia-1,8-octanediol, 2,8-dithia-1,9-nonanediol, 2,9-dithia-1,10-decanediol, 2,11-dithia-1,12-dodecanediol, 5,8-dithia-1,12-dodecanediol, 2,15-dithia-1,16-hexadecanediol, 2,21-dithia-1,22-doeicasanediol, 3,5-dithia-1,7-heptanediol, 3,6-dithia-1,8-octanediol, 3,8-dithia-1,10-decanediol, 3,10-dithia-1,8-dodecanediol, 3,13-dithia-1,15-pentadecanediol, 3,18-dithia-1,20-eicosanediol, 4,6-dithia-1,9-nonanediol, 4,7-dithia-1,10-decanediol, 4,1 1-dithia-1,14-tetradecanediol, 4,15-dithia-1,18-octadecanediol, 4,19-dithia-1,22-dodeicosanediol, 5,7-dithia-1,11-undecanediol, 5,9-dithia-1,13-tridecanediol, 5,13-dithia-1,17-heptadecanediol, 5,17-dithia-1,21-uneicosanediol and 1,8-dimethyl-3,6-dithia-1,8-octanediol. Preferably, the dihydroxy bis-sulfide compounds are chosen from 3,6-dithia-1,8-octanediol, 3,8-dithia-1,10-decanediol, 2,4-dithia-1,5-pentanediol, 2,5-dithia-1,6-hexanediol, 2,6-dithia-1,7-heptanediol, 2,7-dithia-1,8-octanediol, more preferably, 3,6-dithia-1,8-octanediol, 2,4-dithia-1,5-pentanediol, 2,5-dithia-1,6-hexanediol, 2,6-dithia-1,7-heptanediol, or 2,7-dithia-1,8-octanediol, even more preferably, 3,6-dithia-1,8-octanediol, 2,6-dithia-1,7-heptanediol, or 2,7-dithia-1,8-octanediol, most preferably, 3,6-dithia-1,8-octanediol.

[0025] Preferably, thioether compounds can be included in the aqueous acid binary silver-bismuth alloy electroplating compositions in a molar ratio with silver of at least 1 mole of thioether to 1 mole of silver, more preferably, from 1 to 5 moles of thioether to 1 mole of silver, even more preferably, from 2 to 4 moles of thioether to 1 mole of silver, and most preferably, from 2.5 to 4 moles of thioether to 1 mole of silver.

[0026] Optionally, but preferably, the aqueous acid binary silver-bismuth electroplating compositions of the present can include an aliphatic thiol terminal compound. Such aliphatic thiol terminal compounds include, but are not limited to, thioglycolic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, cysteine, mercaptosuccinic acid, 3-mercapto-1-propanesulfonic acid, 2-mercaptoethanesulfonic acid, and salts thereof. Salts of the thiol terminal compounds of the present invention include, but are not limited to, alkali metal salts such as sodium and potassium salts, or ammonium salts.

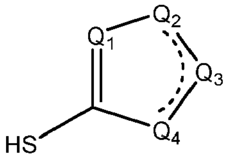
[0027] Preferably, the aliphatic thiol terminal aliphatic compounds of the present invention are included in amounts of 1 g/L or greater, more preferably, the aliphatic thiol terminal compounds are included in amounts of 1 g/L to 100 g/L, most preferably, from 1 g/L to 60 g/L.

[0028] Optionally, one or more surfactants can be included in the aqueous acid silver-bismuth alloy electroplating compositions of the present invention. Such surfactants include, but are not limited to, ionic surfactants such as cationic and anionic surfactants, non-ionic surfactants and amphoteric surfactants. Surfactants can be included in conventional amounts such as 0.05 g/L to 30 g/L.

[0029] Examples of anionic surfactants are sodium di(1,3-dimethylbutyl) sulfosuccinate, sodium-2-ethylhexylsulfate, sodium diamyl sulfosuccinate, sodium lauryl sulfate, sodium lauryl ether-sulfate, sodium di-alkylsulfosuccinates and sodium dodecylbenzene sulfonate. Examples of cationic surfactants are quaternary ammonium salts such as perfluorinated quaternary amines.

[0030] Further optional additives can be included in the silver-bismuth electroplating compositions of the present invention, such as biocides. Conventional biocides well known in the art can be included in the silver-bismuth electroplating compositions of the present invention. Biocides are included in conventional amounts well known to those of ordinary skill in the art. Preferably, compounds which function as levelers are excluded from the silver-bismuth electroplating compositions of the present invention.

[0031] Preferably, the acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention are composed of water, silver ions and counter anions, bismuth (III) ions and counter anions, a 5-membered aromatic heterocyclic nitrogen compound having the general formula:



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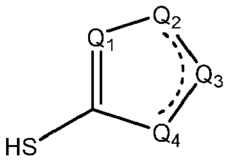
wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, hydrogen, (C_1-C_4)alkyl, an amino group, an aminoalkyl group, carboxyl, carboxy(C_1-C_4)alkyl or alkylsulfonate, optionally a thioether, optionally an aliphatic thiol terminal compound or salt thereof, optionally an acid or salt thereof, optionally a pH adjusting agent, optionally a biocide, and optionally a surfactant, wherein a pH is less than 7.

[0032] Further preferably, the acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention are composed of water, silver ions and counter anions, bismuth (III) ions and counter anions, a 5-membered aromatic heterocyclic nitrogen compound having the general formula:



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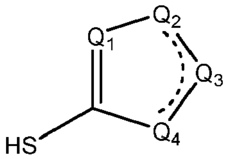
wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, hydrogen, (C_1-C_4)alkyl, an amino group, an aminoalkyl group, carboxyl, carboxy(C_1-C_4)alkyl or an alkylsulfonate, a thioether, optionally an aliphatic thiol terminal compound or salt thereof, optionally an acid or salt thereof, optionally a pH adjusting agent, optionally a biocide, and optionally a surfactant, wherein a pH is 0-6.

[0033] More preferably, the acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention are composed of water, silver ions and counter anions, bismuth (III) ions and counter anions, 5-membered aromatic heterocyclic nitrogen compound having the general formula:



(I)

wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, hydrogen, (C_1-C_4)alkyl, an amino group, an aminoalkyl group, carboxyl, carboxy(C_1-C_4)alkyl or an alkylsulfonate, a dihydroxy bis-sulfide compound, an aliphatic thiol terminal compound or salt thereof, an acid or salt thereof, optionally a pH adjusting agent, optionally a biocide, and optionally a surfactant, wherein a pH is 0-6.

[0034] Even more preferably, the acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention are composed of water, silver ions and counter anions, bismuth (III) ions and counter anions, a compound selected from the group consisting of 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole-5-thiol, 3-amino-5-mercapto-1,2,4-triazole, 3-mercapto-4-methyl-4H-1,2,4-triazole, 1H-imidazole-2-thiol, salts of the 5-membered aromatic heterocyclic nitrogen compounds having a thiol functionality, and mixtures thereof, a dihydroxy bis-sulfide compound, an aliphatic thiol terminal compound selected from the group consisting of thioglycolic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, cysteine, mercaptosuccinic acid, 3-mercapto-1-propanesulfonic acid, 2-mercaptoethanesulfonic acid, and salts thereof, an acid or salt thereof, optionally a pH adjusting agent, optionally a biocide and optionally a surfactant, wherein a pH is 0-3.

[0035] The acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention can be used to deposit binary silver-bismuth alloy layers on various substrates, both conductive and semiconductor substrates. Preferably, the substrates on which silver-bismuth alloy layers are deposited are nickel, nickel alloys, copper and copper alloy substrates. Such nickel alloy substrates include, but are not limited to, nickel phosphorus and nickel boron. Such copper alloy substrates include, but are not limited to, brass and bronze.

[0036] The electroplating composition temperatures during plating can range from room temperature to 70 °C, preferably, from 30 °C to 60 °C, more preferably, from 40 °C to 60 °C. The binary silver-bismuth alloy electroplating compositions are preferably under continuous agitation during electroplating.

[0037] The acidic aqueous binary silver-bismuth alloy electroplating method of the present invention includes providing a substrate, providing the acidic aqueous binary silver-bismuth alloy electroplating composition of the present invention and contacting the substrate with the acidic aqueous binary silver-bismuth alloy electroplating composition such as by immersing the substrate in the composition or spraying the substrate with the composition. Applying a current with a conventional rectifier where the substrate functions as a cathode and there is present a counter electrode or anode. The anode can be any conventional soluble or insoluble anode used for electroplating binary silver-bismuth alloys. The binary silver-bismuth alloys are deposited adjacent a surface of the substrate, wherein the surface of the substrate is nickel, nickel alloy, copper or copper alloy.

[0038] The acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention enable deposition of matte to semi-bright and uniform silver rich silver-bismuth alloy layers over broad current density ranges. The silver rich binary silver-bismuth alloy includes 90% to 99.8% silver and 0.2% to 10% bismuth, preferably, 90% to 99.7% silver and 0.3% to 10% bismuth, most preferably, from 95% to 99.7% silver and from 0.3% to 5% bismuth, excluding unavoidable impurities in the alloy.

[0039] Current densities for electroplating the matte to semi-bright and uniform silver rich silver-bismuth alloy of the present invention can range from 0.1 ASD or higher. Preferably, the current densities range from 0.5 ASD to 70 ASD, further preferably, from 1 ASD to 40 ASD, more preferably, from 1 ASD to 30 ASD, even more preferably from 1 ASD to 15 ASD.

[0040] The thickness of the binary silver-bismuth alloy layers of the present invention can vary depending on the function of the silver-bismuth alloy layer and the type of substrate on which it is plated. Preferably, the binary silver-bismuth alloy layer ranges from 1 μm or greater. Further preferably, the binary silver-bismuth layers have thickness ranges of 1 μm to 100 μm, more preferably, from 1 μm to 50 μm, even more preferably, from 1 μm to 10 μm, most preferably from 1 μm to 5 μm.

[0041] While it is envisioned that the acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention can be used to plate various substrates which can include silver-bismuth alloy layers, preferably, the acidic aqueous binary silver-bismuth alloy electroplating compositions of the present invention are used to electroplate top layers or coatings on electrical connectors where substantial contact forces and wear are expected to prevail. The silver rich binary silver-bismuth alloy deposit is a highly desirable substitute for conventional silver coatings found on conventional connectors. The silver-bismuth alloy deposit has low electrical contact resistance. In addition, the silver-bismuth alloy deposit of the present invention has a low COF, preferably, a COF of 1 or less, more preferably, 0.6 or less. The COF of the silver-bismuth alloy deposit of the present invention has a COF of, preferably, 40% or less than the COF of substantially pure silver deposits, thus the binary silver-bismuth alloy of the present invention has substantial improvement in wear resistance over substantially pure silver. Surface wear can be determined for a metal deposit according to conventional tribological and profilometry measurements well known in the art.

[0042] The following examples are included to further illustrate the invention but are not intended to limit its scope.

Binary Silver-Bismuth Alloy Electroplating Examples 1-22:

Electroplating Process

[0043] Unless otherwise noted, in all cases, the electroplating substrate was a 5cm x 5cm brass (70% copper, 30% zinc) coupon. Prior to electroplating, the coupons were electrocleaned in RONACLEAN™ GP-300 LF Electrolytic Cleaner an alkaline degreaser (available from DuPont) at 80° C for 30 seconds with DC at a current density of 5 ASD. After electrocleaning, the coupons were rinsed with DI water, activated in 10% sulfuric acid for 30 seconds, rinsed with DI water again, then placed in the electroplating bath. Electroplating was performed with DC at a current density of 1 ASD (actual current applied is 0.56 A) for 6 minutes. Electroplating was performed in a square, glass beaker using a platinized titanium anode. Agitation was provided by a 5cm long, TEFLON™-coated stir-bar at a rotation rate of 400 rpm. Electroplating was performed at a temperature of 55 °C. The binary silver-bismuth alloy deposits were about 6 μm thick. All the binary silver-bismuth electroplating baths were aqueous based. Water was added to each bath to bring it to a desired volume. The pH of the electroplating baths was adjusted with potassium hydroxide or methanesulfonic acid.

[0044] The thickness and elemental composition of the electroplated binary silver-bismuth alloy was measured using a Bowman Series P X-Ray Fluorimeter (XRF) available from Bowman, Schaumburg, IL. The XRF was calibrated using pure element thickness standards for silver and bismuth, available from Hitachi (Chiyoda, Tokyo, Japan), Fischer GmbH (Sindelfingen, Germany) and Veeco (Plainview, New York, USA), and calculated alloy composition and thickness by combining the pure element standards with Fundamental Parameter (FP) calculations using the software package accompanying the Bowman Series P X-Ray Fluorimeter.

Contact Resistance Measurements

[0045] Contact resistance was evaluated using a custom designed apparatus containing a Starrett MTH-550 manual force tester stand equipped with a Starrett DFC-20 digital force gauge (Athol, MA, USA). The digital force gauge was equipped with a gold-plated copper probe with a hemispherical tip 2.5 mm in diameter. The electrical resistance of the contact between the gold-plated probe and the flat coupon plated with the silver alloy of interest was measured using a 4-wire resistance measurement as the contact force was varied. The current source was a Keithley 6220 DC Current Source operating at 10 mA and the voltmeter was a Keithley 2182A Nanovoltmeter (Cleveland, OH, USA). These instruments were operated in thermoelectric compensation mode for maximum accuracy.

Wear Resistance Measurements

[0046] Tribological measurements were performed using an Anton Paar TRB3 Pin-on-Disk tribometer equipped with a linear reciprocating stage (available from Anton Paar GmbH, Graz, Austria). All tests were performed using 1 N loading, a stroke length of 10 mm, and a sliding speed of 5 mm/s. All tests were performed "like-on-like", meaning that the flat coupon and the spherical ball were each plated with the same silver (SILVER GLO™ 3K Bright Silver plating bath, a cyanide-based product available from DuPont) or silver-bismuth alloy metal deposit. The ball used was made of C260 brass (70% copper, 30% zinc) and was 5.55 mm in diameter and was electroplated with about 5 μm of silver. The flat coupon was also made of C260 brass and electroplated with about 2 μm of silver or silver-bismuth alloy. During the test, coefficient of friction was monitored using the tribometer. Wear track depth was measured using laser profilometry. The measurements were done for either 100 or 500 cycles, as specified in each case.

[0047] A cycle was one round trip of the tribometer. The sample was moved in one direction, then the direction was reversed and the tribometer was moved back to its original location, all the while under the 1 N load and in contact with the spherical ball. This was one cycle.

[0048] The profilometry measurements were performed using a Keyence VK-X Laser Scanning Confocal Microscope (available from Keyence Corporation of America, Elmwood Park, NJ). The wear tracks were measured using laser profilometry at a magnification of 200X. The 3D and 2D profilometry graphics were created from these measurements using VK-X Multianalyzer software from Keyence.

Example 1 (invention)

[0049] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 0.8 g/L of bismuth ions
cysteine: 1.4 g/L
3-mercapto-1,2,4-triazole: 1.5 g/L
pH adjusted to 1.6

[0050] After plating, the electrodeposited coating appeared semi-bright, with a composition of 98.9% silver and 1.1% bismuth.

Example 2 (invention)

[0051] An aqueous acid binary silver-bismuth alloy electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 5 g/L of bismuth ions
cysteine: 9 g/L
2-mercapto-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0052] After plating, the electrodeposited coating appeared metallic and semi-bright, with a composition of 95% silver and 5% bismuth. **Figure 1** is a scanning electron microscope image at 10,000X magnification of the binary silver-bismuth alloy showing discrete zones of bismuth, indicated by the bright spots, in a silver matrix.

Example 3 (invention)

[0053] An aqueous acid binary silver-bismuth alloy electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 5 g/L of bismuth ions
3-mercapto-1-propanesulfonate, sodium salt: 13.2 g/L
3-mercapto-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0054] After plating, the electrodeposited coating appeared metallic and semi-bright, with a composition of 96% silver and 4% bismuth.

Example 4 (invention)

[0055] An aqueous acid binary silver-bismuth alloy electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 5 g/L of bismuth ions
3-mercapto-1-ethanesulfonate, sodium salt: 12.2 g/L
3-mercapto-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0056] After the plating procedure, the electrodeposited coating appeared metallic and semi-bright, with a composition of 96% silver and 4% bismuth.

Example 5 (invention)

[0057] An aqueous acid binary silver-bismuth alloy electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
Bismuth methanesulfonate to supply 5 g/L of bismuth ions
mercaptosuccinic acid: 11.1 g/L
3-mercapto-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0058] After plating, the electrodeposited coating appeared metallic and matte, with a composition of 98% silver and 2% bismuth.

Example 6 (invention)

[0059] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 5 g/L of bismuth ions
cysteine: 9 g/L
3-mercapto-4-methyl-4H-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0060] After plating, the electrodeposited coating appeared metallic and semi-bright, with a composition of 95% silver and 5% bismuth.

Example 7 (invention)

[0061] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 34 g/L
Mercaptosuccinic acid: 35 g/L
bismuth methanesulfonate to supply 2 g/L of bismuth ions
3-mercapto-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0062] After plating, the electrodeposited coating appeared metallic and semi-bright, with a composition of 97% silver and 3% bismuth.

Example 8 (invention)

[0063] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 34 g/L
Mercaptosuccinic acid: 35 g/L
bismuth methanesulfonate to supply 2 g/L of bismuth ions
3-mercapto-4-methyl-4H-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0064] After plating, the electrodeposited coating appeared metallic and semi-bright, with a composition of 97% silver and 3% bismuth.

Example 9 (invention)

[0065] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 34 g/L
Mercaptosuccinic acid: 35 g/L
bismuth methanesulfonate to supply 2 g/L of bismuth ions
1H-imidazole-2-thiol: 400 ppm
pH adjusted to 2

[0066] After plating, the electrodeposited coating appeared metallic and semi-bright, with a composition of 97% silver and 3% bismuth.

Example 10 (comparative)

[0067] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
bismuth methanesulfonate to supply 10 g/L of bismuth ions
methanesulfonic acid: 150 g/L
PLURONIC™ L-44 surfactant (purchased from BASF): 10 g/L
O-chlorobenzaldehyde: 100 ppm
3,6-dithia-1,8-octanediol: 80 g/L
pH < 1

[0068] After the plating procedure, the electrodeposited coating is metallic and semi-bright, with a composition of 46% silver and 54% bismuth.

Example 11 (comparative)

[0069] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 5 g/L of bismuth ions
cysteine: 9 g/L
4-amino-1,2,4-triazole: 400 ppm
pH adjusted to 2

[0070] After plating, the electrodeposited coating appeared metallic and matte, with a composition of 97% silver and 3% bismuth.

Example 12 (comparative)

[0071] An aqueous acid binary silver-bismuth electroplating bath of the following composition was prepared:

silver methanesulfonate to supply 20 g/L silver ions
3,6-dithia-1,8-octanediol: 102 g/L
bismuth methanesulfonate to supply 5 g/L of bismuth ions
cysteine: 9 g/L
1,2,4-triazole: 400 ppm
pH adjusted to 2

[0072] After plating, the electrodeposited coating appeared metallic and matte, with a composition of 97% silver and 3% bismuth

Example 13 (comparative)

[0073] An aqueous, alkaline, cyanide-based, silver electroplating bath of the following composition was prepared:

potassium silver cyanide to supply 40 g/L silver ions
potassium cyanide: 120 g/L
potassium carbonate: 15 g/L
potassium selenocyanate: 7 mg/L

[0074] After plating, the electrodeposited coating appeared metallic and bright, with a composition of 100% silver.

Example 14 (comparative)

[0075] An aqueous, alkaline, cyanide-based, binary silver-antimony electroplating bath of the following composition was prepared:

potassium silver cyanide to supply 40 g/L silver ions
potassium cyanide: 120 g/L
potassium carbonate: 15 g/L
potassium selenocyanate: 6 mg/L
potassium sodium tartrate: 10 g/L
tripotassium citrate: 19 g/L
potassium antimony tartrate: 7.8 g/L

[0076] After plating, the electrodeposited coating appeared metallic and bright, with a composition of 98% silver and 2% antimony.

Example 15

Contact Resistance Measurements

[0077] Tests were performed using flat, nickel coupons electroplated with about 3 μm of silver from comparative Example 13, silver-antimony alloy (98% silver, 2% antimony) from comparative example 14, and with binary silver-bismuth alloys from the aqueous acid binary silver-bismuth alloy electroplating baths disclosed in Examples 2, 8, and 9 (invention) above. Prior to measurement, the coupons were heated in an oven at 150° C for 100 hours. The contact resistance for the coupons is in Table 1 below.

Table 1

Force (cN)	**Example 2 (invention) (mΩ)**	**Example 8 (invention) (mΩ)**	**Example 9 (invention) (mΩ)**	**Example 13 (comparative) (mΩ)**	**Example 14 (comparative) (mΩ)**
1	18.4	10.4	16.1	8.1	>1000
5	7.6	7.4	8.9	4.5	560
10	4.4	3.6	4.6	2.2	164
20	2.4	2.1	2.7	1.7	118
30	1.6	1.4	2.0	1.4	89
40	1.2	1.2	1.6	1.3	58
50	1.1	1.0	1.2	1.1	28
60	0.9	0.8	1.0	0.8	24
70	0.8	0.7	0.9	0.6	22
80	0.8	0.7	0.8	0.5	21
90	0.7	0.7	0.8	0.5	20
100	0.6	0.6	0.8	0.5	18

Example 16 (comparative)

[0078] Wear resistance measurements were performed on silver metal deposits electroplated using the bath described in Example 13 (comparative). The test was performed for 100 cycles. **Figure** 2 is the 2D profilometry graph of the silver deposit which shows major surface wear of the silver from 600 μm to 800 μm along the x-axis and from +2 μm to -5 μm along the y-axis. **Figure** 3 is the 3D profilometry graph of the silver deposit which further exemplifies the significant surface wear of the silver deposit after 100 cycles. Examination of the ball indicated accumulation of material and significant prow formation was observed at the ends of the wear track indicating cold welding during the wear process. The coefficient of friction was determined to be approximately 1.6 throughout the experiment. The coefficient of friction was measured by a sensor on the tribometer which measured the frictional force and then divides the frictional force by the reported downward force to give the coefficient of friction.

Example 17 (comparative)

[0079] Wear resistance measurements were performed on silver-bismuth alloy deposits electroplated using the bath described in Example 10 (comparative). The test was performed for 500 cycles. The coefficient of friction was determined to be approximately 0.3 throughout the experiment. However, the wear track observed was substantially the same as that observed for Example 16 above showing significant wear.

Example 18 (comparative)

[0080] Wear resistance measurements were performed on silver-bismuth alloy deposits electroplated using the bath described in Example 11 (comparative). The test was performed for 500 cycles. The coefficient of friction was determined to be approximately 0.7 throughout the experiment. However, the wear track observed was substantially the same as that observed for Example 16 above for silver metal showing significant wear.

Example 19 (comparative)

[0081] Wear resistance measurements were performed on silver-bismuth alloy deposits electroplated using the bath described in Example 12 (comparative). The test was performed for 500 cycles. The coefficient of friction was determined to be approximately 0.7 throughout the experiment. However, the wear track observed was substantially the same as that observed for Example 16 above showing serious wear.

Example 20 (invention)

[0082] Wear resistance measurements were performed on silver-bismuth alloy deposits electroplated using the bath described in Example 2 (invention). The test was performed for 500 cycles. **Figure 4** is the 2D profilometry graph of the silver-bismuth alloy deposit which shows no observable wear of the silver-bismuth alloy along the width of the sample. **Figure 5** is the 3D profilometry graph of the silver-bismuth alloy deposit which further shows no observable surface wear of the silver-bismuth alloy deposit after 500 cycles. Examination of the spherical ball showed no accumulation of material and no observable prow formation at the ends of the wear track indicating no cold welding took place during the wear process. The coefficient of friction was determined to be approximately 0.6 throughout the experiment. These results represented a significant improvement over the comparative examples.

Example 21 (invention)

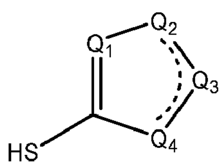
[0083] Wear resistance measurements were performed on silver-bismuth alloy deposits electroplated using the bath described in Example 8 (invention). The test was performed for 500 cycles. **Figure 6** is the 2D profilometry graph of the silver deposit which shows minor wear of the silver-bismuth alloy along the width of the sample, though significantly less than the comparative examples. **Figure 7** is the 3D profilometry graph of the silver-bismuth alloy deposit which further shows minor wear of the silver-bismuth deposit after 500 cycles. Examination of the spherical ball indicated no accumulation of material and no prow formation was observed at the ends of the wear track indicating no cold welding took place during the wear process. The coefficient of friction was determined to be approximately 0.9 throughout the experiment. These results represented a significant improvement over the comparative examples.

Example 22 (invention)

[0084] Wear resistance measurements were performed on silver-bismuth alloy deposits electroplated using the bath described in Example 10 (invention). The test was performed for 500 cycles. **Figure 8** is the 2D profilometry graph of the silver deposit which shows minimal wear of the silver-bismuth alloy along the width of the sample. **Figure 9** is the 3D profilometry graph of the silver-bismuth alloy deposit which further shows the minimal surface wear of the silver-bismuth deposit after 500 cycles. Examination of the spherical ball indicated no accumulation of material and no prow formation was observed at the ends of the wear track indicating no cold welding took place during the wear process. The coefficient of friction was determined to be approximately 0.5 throughout the experiment. These results represented a significant improvement over the comparative examples.

Claims

1. A binary silver-bismuth alloy electroplating composition comprising a source of silver ions, a source of bismuth ions, and a 5-membered aromatic heterocyclic nitrogen compound having a general formula:



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wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, $(C_1$-$C_4)$alkyl, amino group, aminoalkyl group, carboxyl, carboxy$(C_1$-$C_4)$alkyl or alkylsulfonate, and a pH of less than 7.

2. The binary silver-bismuth alloy electroplating composition of claim 1, wherein the 5-membered aromatic heterocyclic nitrogen compound is selected from the group consisting of 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole-5-thiol, 3-amino-5-mercapto-1,2,4-triazole, 3-mercapto-4-methyl-4H-1,2,4-triazole, 1H-imidazole-2-thiol, salts of the 5-membered aromatic heterocyclic nitrogen compounds, and mixtures thereof.

3. The binary silver-bismuth alloy electroplating composition of claim 1, further, comprising a thioether or mixtures thereof.

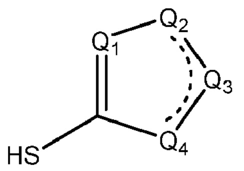
4. The binary silver-bismuth alloy electroplating composition of claim 3, wherein the thioether is a hydroxy bis-sulfide compound.

5. The binary silver-bismuth alloy electroplating composition of claim 1, further comprising an aliphatic thiol terminal compound or mixtures thereof.

6. The binary silver-bismuth alloy electroplating composition of claim 5, wherein the aliphatic thiol terminal compound is selected from the group consisting of thioglycolic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, cysteine, mercaptosuccinic acid, 3-mercapto-1-propanesulfonic acid, 2-mercaptoethanesulfonic acid, salts of the thiol terminal compounds, and mixtures thereof.

7. A method of electroplating a binary silver-bismuth alloy on a substrate comprising:

a) providing the substrate;
b) contacting the substrate with a binary silver-bismuth alloy electroplating composition comprising a source of silver ions, a source of bismuth ions, and a 5-membered aromatic heterocyclic nitrogen compounds having general formula:



(I)

wherein Q_1-Q_4 can be a substituted or unsubstituted nitrogen or a substituted or unsubstituted carbon with the proviso that at least two of Q_1-Q_4 are nitrogen, wherein substituent groups include, but are not limited to, $(C_1$-$C_4)$alkyl, amino group, aminoalkyl group, carboxyl, carboxy$(C_1$-$C_4)$alkyl or alkysulfonate, and a pH of less than 7; and
c) applying an electric current to the binary silver-bismuth alloy electroplating composition and substrate to electroplate a binary silver-bismuth deposit on the substrate.

8. The method of claim 7, wherein the 5-membered aromatic heterocyclic nitrogen compound is selected from the group consisting of 3-mercapto-1,2,4-triazole, 3-amino-1,2,4-triazole-5-thiol, 3-amino-5-mercapto-1,2,4-triazole, 3-mercapto-4-methyl-4H-1,2,4-triazole, 1H-imidazole-2-thiol, salts of the 5-membered aromatic heterocyclic nitrogen compounds, and mixtures thereof.

9. The method of claim 7, wherein the binary silver-bismuth alloy electroplating composition further comprises a thioether or mixtures thereof.

10. The method of claim 7, wherein the binary silver-bismuth electroplating composition further comprises an aliphatic thiol terminal compound or mixtures thereof.

11. An article comprising a binary silver-bismuth alloy layer adjacent a surface of a substrate, wherein the binary silver-bismuth alloy layer comprises 90% to 99.8% silver and 0.2% to 10% bismuth, and has a coefficient of friction of 1 or less.

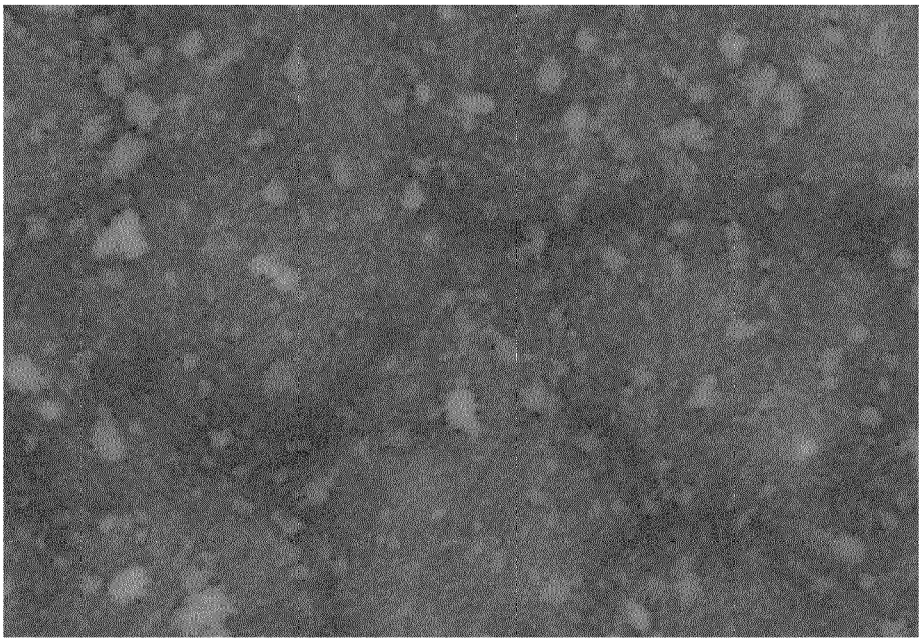


FIG. 1

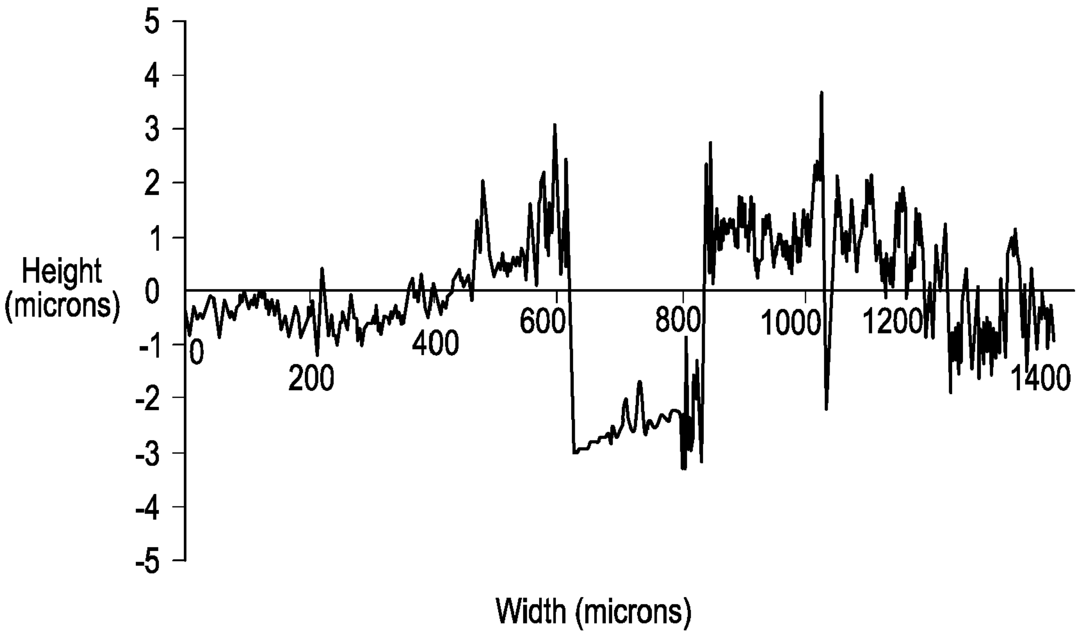

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FIG. 2

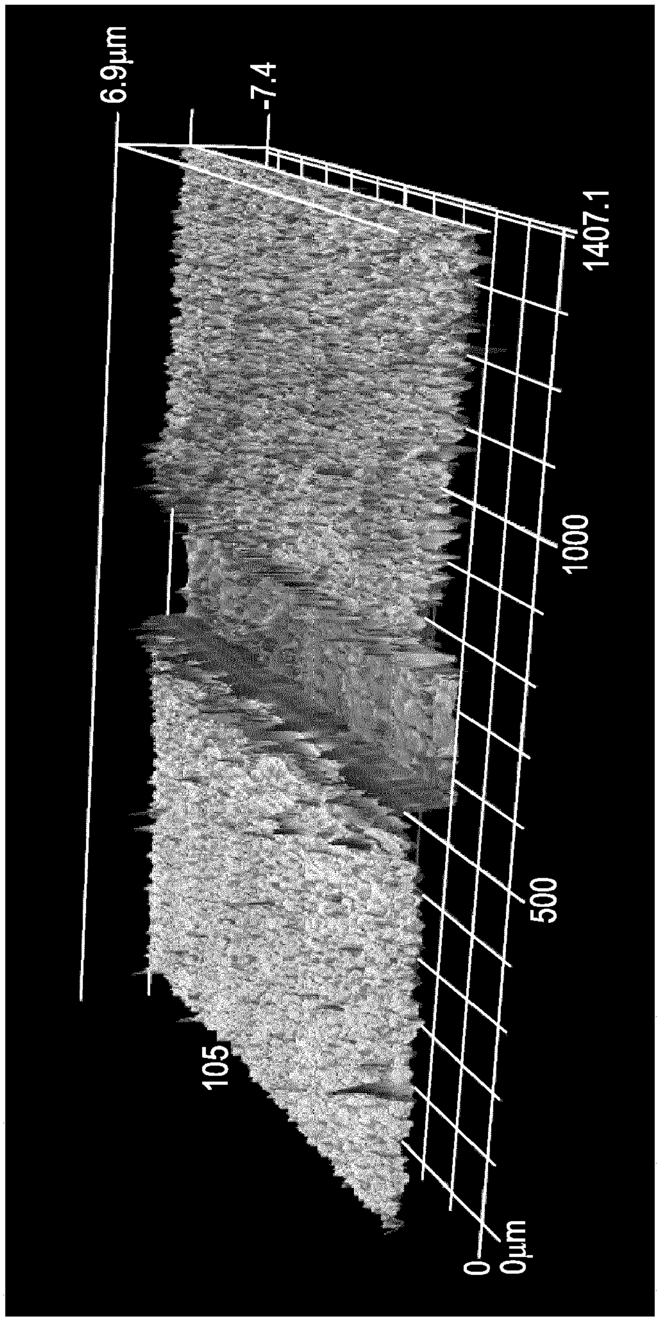

FIG. 3

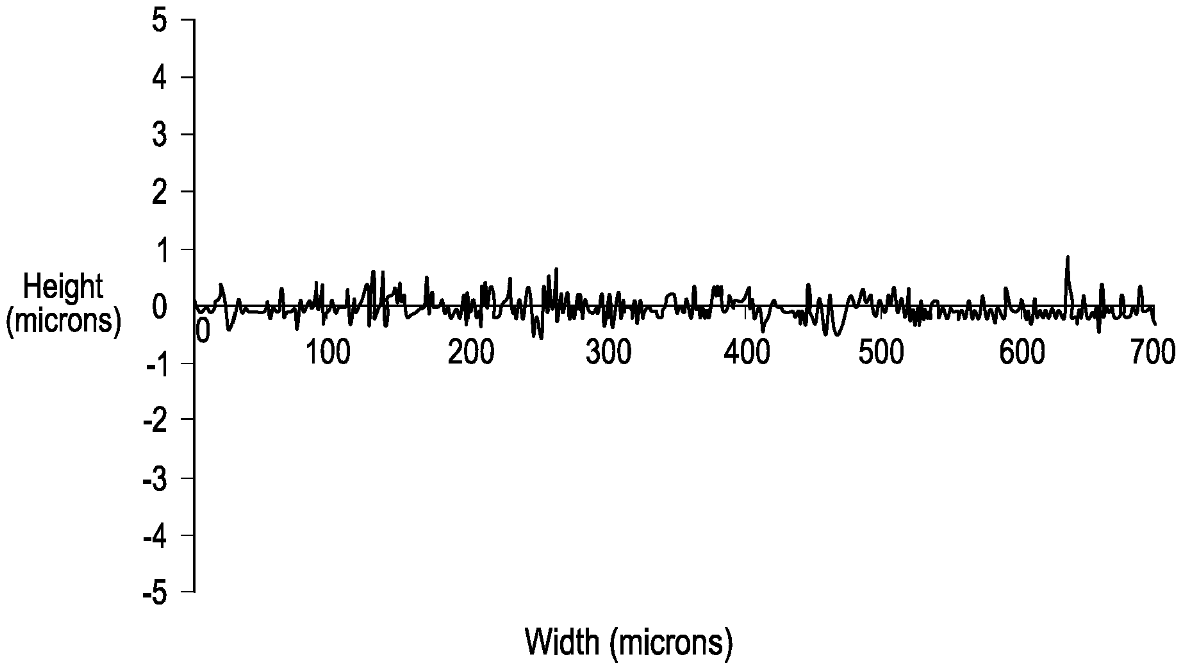
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FIG. 4

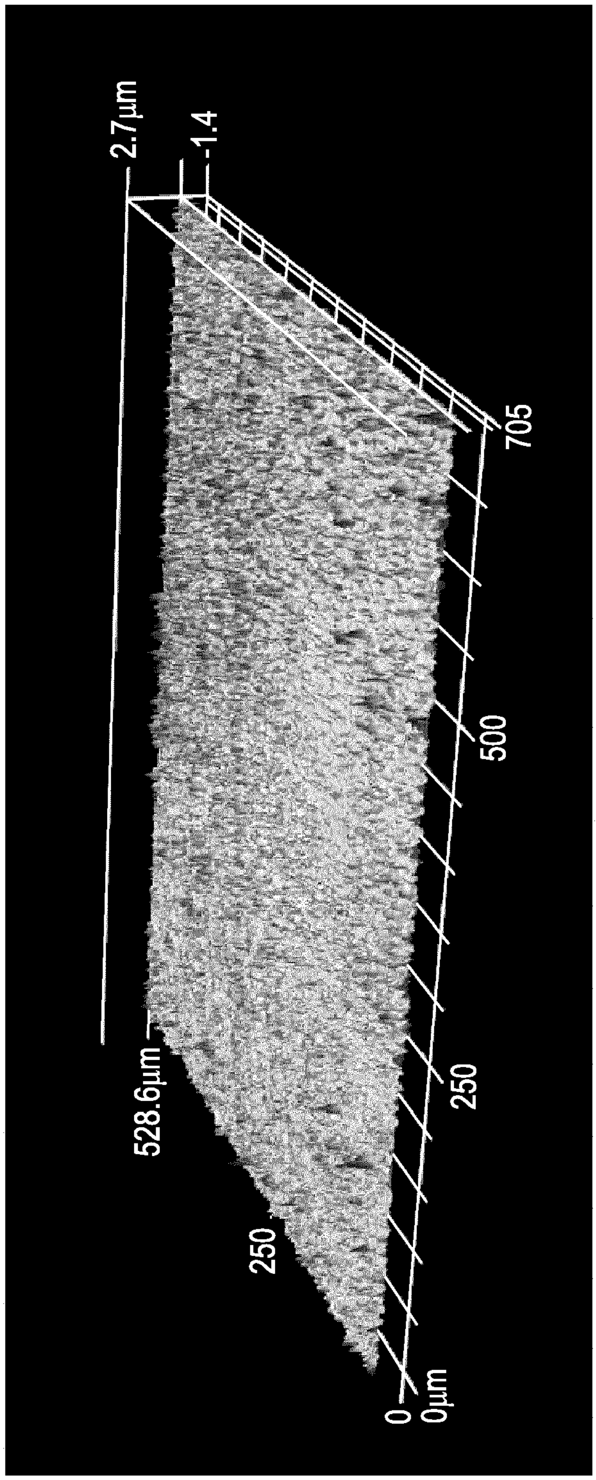

FIG. 5

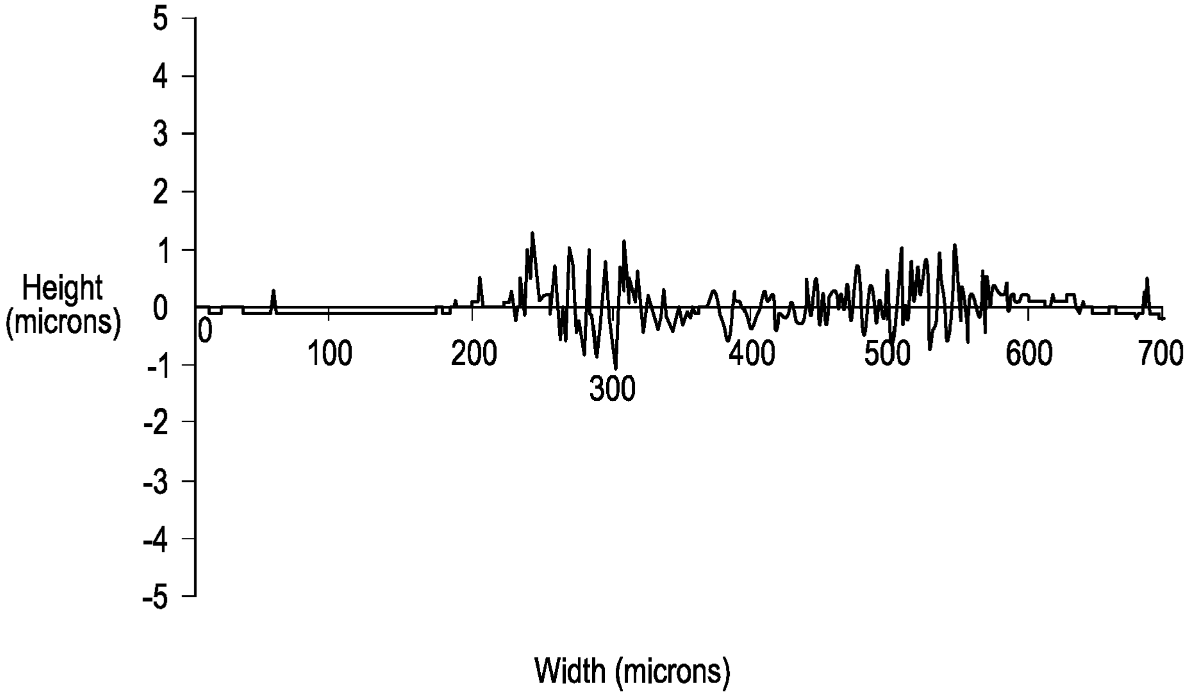
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FIG. 6

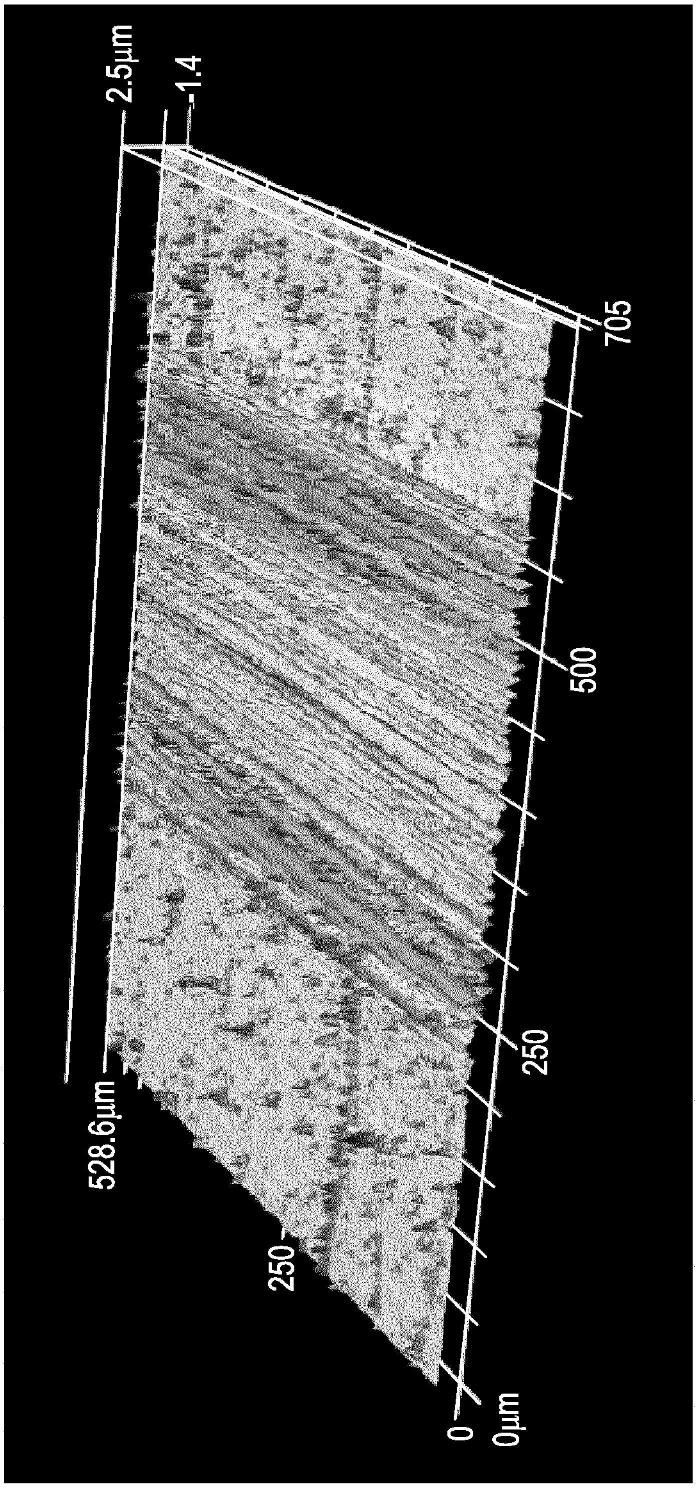

FIG. 7

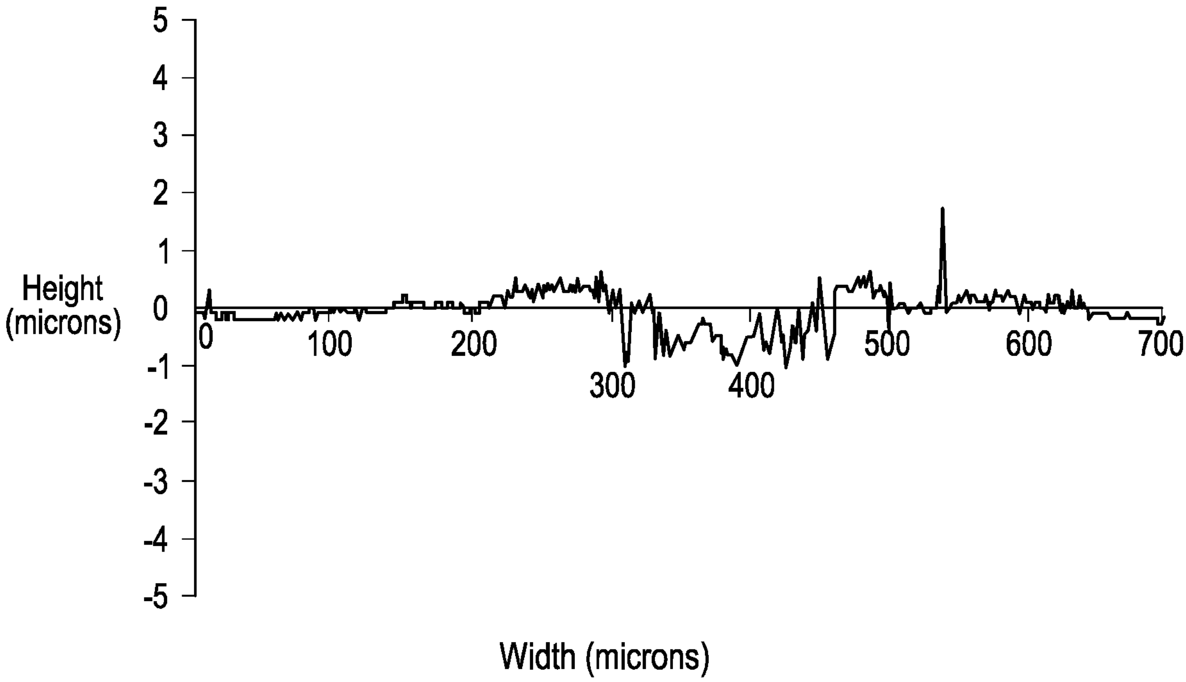
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FIG. 8

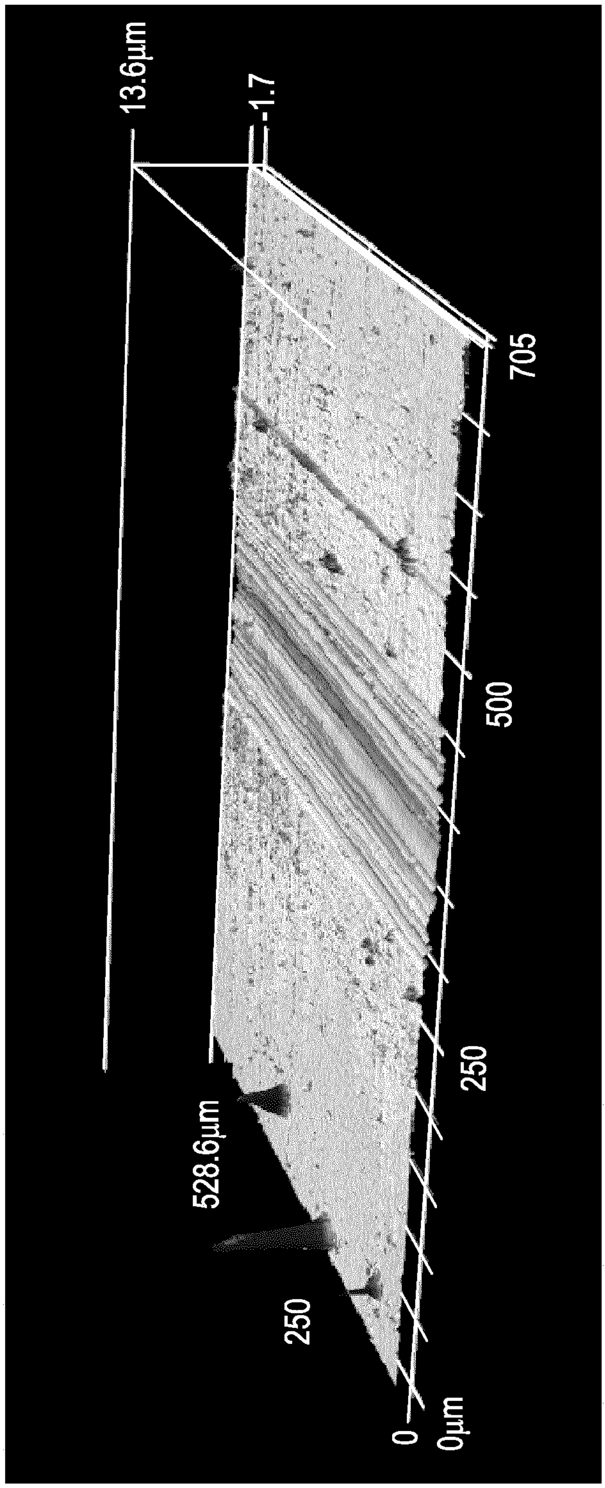

FIG. 9

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EUROPEAN SEARCH REPORT

Application Number
EP 20 20 9654

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	29 April 2021	Crottaz, Olivier

CATEGORY OF CITED DOCUMENTS

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