



(11)

EP 3 023 520 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.05.2016 Bulletin 2016/21

(51) Int Cl.:
C25D 3/48 (2006.01) C25D 3/62 (2006.01)

(21) Application number: **15193859.4**

(22) Date of filing: **10.11.2015**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **21.11.2014 US 201414549571**

(71) Applicant: **Rohm and Haas Electronic Materials
LLC
Marlborough, MA 01752 (US)**

(72) Inventors:
• **FOYET, Adolphe
Luzern 6014 (CH)**
• **CLAUSS, Margit
6010 Kriens (CH)**
• **BUCHS, Reto
NW 6374 Buochs (CH)**

(74) Representative: **Houghton, Mark Phillip
Patent Outsourcing Limited
1 King Street
Bakewell, Derbyshire DE45 1DZ (GB)**

(54) **ENVIRONMENTALLY FRIENDLY GOLD ELECTROPLATING COMPOSITIONS AND METHODS**

(57) Gold electroplating compositions are substantially free of many environmental toxins to provide an environmentally friendly pure gold electroplating composition. The substantially pure gold electroplating compo-

sitions may electroplate gold over a broad current density range to deposit bright to matte gold layers on various types of electronic components and decorative articles.

EP 3 023 520 A1

Description

Field of the Invention

5 **[0001]** The present invention is directed to environmentally friendly gold electroplating compositions and methods. More specifically, the present invention is directed to environmentally friendly gold electroplating compositions and methods where soft gold may be electroplated over broad current density ranges to provide bright soft gold deposits even under jet and pulse current plating conditions.

10 Background of the Invention

[0002] Electrolytic gold is typically used in connectors and electronic finishing because of the exceptional performance of gold for these particular uses. Gold is one of the most reliable materials for electronic components because of its anticorrosion properties, electrical conductivity and thermal stability. Substantially pure gold is generally electroplated from cyanide electrolytic plating baths containing several additives and metallic brighteners. Some of those additives such as hydrazine are toxic and are now restricted by many national and international regulations. Most commercial pure gold baths contain free-cyanide and one or more grain refiner such as arsenic, thallium and lead which are known to be toxic to the environment, thus disposal of waste from such gold plating baths must be discrete and is also time consuming and costly to the industry. In addition, such gold electroplating baths present undue hazards to workers using the baths.

[0003] U.S. 5,277,790 to Morrissey discloses a cyanide-free gold electroplating bath where gold is provided as a soluble sulfite complex. Although the gold electroplating bath is cyanide-free, it undesirably generates sulfur dioxide at elevated temperatures. Sulfur dioxide is a toxic gas with a pungent odor. To address the problem even more sulfites are added to the plating solution. In addition, the gold is plated at relatively low plating rates from near 0 to 30 mA/cm². Accordingly, there is a need for an improved gold electroplating bath which is environmentally friendly and can plate over broad current density ranges.

Summary of the Invention

30 **[0004]** Gold electroplating compositions including one or more sources of gold ions from gold-cyanide salts, one or more sources of phosphate ions, one or more sources of phosphonic acids or salts thereof, sodium potassium tartrate and one or more sources of antimony (III) ions, the gold electroplating compositions are substantially free of free-cyanide.

[0005] Method of electroplating gold include providing a gold electroplating composition including one or more sources of gold ions from gold-cyanide salts, one or more sources of phosphate ions, one or more sources of phosphonic acids or salts thereof, sodium potassium tartrate and one or more sources of antimony (III) ions, the gold electroplating compositions are substantially free of free-cyanide; contacting a substrate with the gold electroplating composition; and electroplating gold on the substrate using direct current or pulse current at a current density of 0.03 ASD or greater.

[0006] The gold electroplating compositions are environmentally friendly and may plate bright soft gold deposits over broad current density ranges including under high speed jet plating conditions. The soft gold deposits also have fine grain structures. The electroplating gold compositions may be used to plate gold strike layers on electronic components and may be used to electroplate soft gold layers in the formation of contacts for connectors and gold layers on switches or printed circuit boards. The gold electroplating compositions may also be used to deposit soft gold layers on decorative articles. The gold deposits also have fine grain structures. Small grain size reduces porosity in thin film. The brightness of the deposits is also a direct consequence of this small grain size. Generally, the roughness of matte or semi bright deposit is high as compared to bright deposits which are smooth.

Brief Description of the Drawings

[0007]

50 Figure 1 is a SEM at 20,000 magnification showing the microstructure of a soft gold deposit electroplated with a gold electroplating composition containing antimony (III) ions.

Figure 2 is a SEM at 20,000 magnification showing the microstructure of a gold deposit electroplated with a conventional gold electroplating bath containing lead as a grain refiner.

Detailed Description of the Invention

[0008] As used throughout this specification, the following abbreviations shall have the following meanings, unless

the context clearly indicates otherwise: °C = degrees Centigrade; g = gram; mg = milligrams; L = liter; mL = milliliters; cm = centimeters; mm = millimeters; μm = microns = micrometers; ppb = parts per billion; ms = milliseconds; DC = direct current; ASD = amperes/decimeter squared = A/dm^2 and ASTM = American Standard Testing Method.

[0009] The terms "electroplating" and "plating" are used interchangeably throughout this specification. The terms "composition", "solution" and "bath" are used interchangeably throughout the specification. The terms "a" and "an" refer to both the singular and the plural.

[0010] All percentages are by weight, unless otherwise noted. All numerical ranges are inclusive and combinable in any order, except where it is logical that such numerical ranges are constrained to add up to 100%.

[0011] Compositions include gold ions from one or more gold-cyanide salts such as alkali gold cyanide compounds such as potassium gold cyanide, sodium gold cyanide and ammonium gold cyanide. Preferably the alkali gold cyanide compound is potassium gold cyanide. Although gold ions are provided by gold-cyanide salts, there is no free-cyanide added in the gold electroplating compositions such as cyanide alkali metal salts or any salt, except gold salts, which may provide free cyanide ligands.

[0012] In addition to the gold-cyanide salts, additional gold ions may be provided by alkali gold thiosulfate compounds such as trisodium gold thiosulfate and tripotassium gold thiosulfate, gold halides such as gold chloride, hydrogen tetrachloroaurate and gold trichloride. Preferably gold ions are provided only from gold-cyanide salts. Such gold compounds are generally commercially available from a variety of suppliers or may be prepared by methods well known in the art.

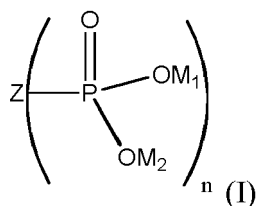
[0013] The amount of gold salts added to the compositions is in amounts which provide gold ions at desired concentrations. In general, gold ions are in amounts of 4 g/L to 20 g/L, preferably from 8 g/L to 20 g/L, more preferably from 15 g/L to 20 g/L. The amount of gold ions in the electroplating compositions depends on the type of plating, such as jet, rack or barrel plating.

[0014] Conducting inorganic acid and salts thereof are included in the gold electroplating compositions. Such conducting acids, include, but are not limited to phosphoric acid, sulfuric acid and hydrochloric acid and salts thereof. Preferably, the conducting inorganic acid and salts thereof are chosen from phosphoric acid and potassium dihydrogen phosphate, sodium dihydrogen phosphate, potassium phosphate, sodium phosphate and mixtures thereof. Preferably, phosphoric acid is added when using potassium phosphate

[0015] Alkaline compounds also may be added to maintain the pH of the compositions at desired levels of 5 to 6.8, preferably 5.8 to 6.7, more preferably from 6 to 6.3. Such alkaline compounds include, but are not limited to, hydroxides, carbonates, and other salts of sodium, potassium and magnesium. For example, NaOH, KOH, K_2CO_3 , Na_2CO_3 , NaHCO_3 and mixtures thereof are suitable alkaline compounds. Typically, the alkaline materials are included in amounts of 1 g/L to 100 g/L.

[0016] Organophosphorus compounds are included as chelating agents for the gold ions in the gold electroplating compositions. They deprotonate and chelate with gold ions in the pH range of the gold electroplating compositions and the chelating capabilities of these compounds is good enough such that free cyanide from potassium cyanide or sodium cyanide is not added to stabilize the gold compositions.

[0017] The organophosphorus compounds include those compounds having the following formulation:



wherein n is an integer from 2 to 3, inclusive, M_1 and M_2 may be the same or different and are chosen from hydrogen, ammonium, lower alkyl amine having 1-9 carbon atoms, preferably 1-5 carbon atoms or an alkali metal cation such as sodium, potassium and lithium, preferably the alkali metal cation is potassium or sodium, and Z is a radical equal in valence to n and is a linear or branched, substituted or unsubstituted (C_1 - C_{12})alkyl or an N-substituted (C_2 - C_3)alkyl where the Z radical has a carbon atom linked to a phosphorus atom of formula (I). Preferably, Z is a linear or branched, substituted or unsubstituted (C_1 - C_4)alkyl where the substituent group is hydroxyl. Such compounds are included in amounts of 5 g/l to 200 g/L, preferably from 20 g/L to 150 g/L, more preferably from 50 g/l to 120 g/L.

[0018] A class of compounds falling within the above general formula includes aminotri (lower alkylidene phosphonic acids). Examples of such compounds include aminotri(methylene phosphonic acid), aminotri(ethylidene phosphonic acid), aminotri(isopropylidene phosphonic acid), aminodi(methylene phosphonic acid) mono (ethylidene phosphonic acid), aminodi(methylene phosphonic acid) mono(isopropylidene phosphonic acid), aminomono(methylene phosphonic acid) di(ethylidene phosphonic acid) and aminomono(methylene phosphonic acid) diisopropylidene phosphonic acid.

[0019] Lower alkylidene diphosphonic acid compounds within the scope of the above formula are methylene diphos-

phonic acid, ethylidene diphosphonic acid, isopropylene diphosphonic acid, isopropylidene diphosphonic acid, 1-hydroxyethylidene diphosphonic acid, 1-hydroxypropylidene diphosphonic acid, butylidene diphosphonic acid.

[0020] Particularly preferred organophosphorus compounds are tetrapotassium 1-hydroxyethylidene diphosphonate, tetrasodium 1-hydroxyethylidene diphosphonate and hydroxyethylene-1,1-diphosphonic acid.

[0021] Antimony (III) ions are included as potassium antimony tartrate in combination with sodium potassium tartrate. Although antimony (III) ions may be added as antimony chloride or antimony sulfate, antimony (III) is preferably added as antimony tartrate. The salts of antimony (III) are added to the gold electroplating compositions in amounts to provide 1 mg/L to 20 mg/L, preferably 5 mg/L to 15 mg/L of antimony (III) ions. Sodium potassium tartrate is added to the gold electroplating compositions in amounts of 10 g/l to 50 g/L, preferably from 15 g/l to 35 g/L. Additional tartrate may be added to the gold electroplating compositions as tartaric acid, potassium tartrate or other water soluble tartrate salts and compounds in the amounts specified for the sodium potassium tartrate; however, the most preferred source of tartrate is sodium potassium tartrate for preventing the antimony (III) ions from oxidizing to antimony (V) ions. While not being bound by theory, the presence of the antimony (III) ions may provide for a bright gold deposit even under jet plating conditions. In addition, antimony may provide for a soft gold deposit.

[0022] Optionally, the gold plating compositions may include one or more organic acids, such as citric acid, malic acid, oxalic acid, formic acid or polyethylene amino acetic acid or inorganic acids such as phosphoric acid. Such acids help maintain the pH of the compositions in the desired range. Typically, the acids are included in amounts of 1 g/L to 200 g/L.

[0023] Optionally, a wide variety of additional gold chelating or complexing agents may be included in the compositions. Suitable gold complexing agents include, but are not limited to thiosulfuric acid, thiosulfate salts such as sodium thiosulfate, potassium thiosulfate, potassium sorbate and ammonium thiosulfate, ethylenediamine tetraacetic acid and its salts, iminodiacetic acid and nitrilotriacetic acid.

[0024] The one or more additional chelating or complexing agents may be added in conventional amounts, or such as in amounts of 1 g/L to 100 g/L, or such as 10 g/L to 50 g/L. The one or more complexing agents are generally commercially available or may be prepared from methods well known in the art.

[0025] The compositions also may include one or more surfactants. Any suitable surfactant may be used in the compositions. Such surfactants include, but are not limited to, alkoxyalkyl sulfates (alkyl ether sulfates) and alkoxyalkyl phosphates (alkyl ether phosphates). The alkyl and alkoxy groups typically contain from 10 to 20 carbon atoms. Examples of such surfactants are sodium lauryl sulfate, sodium capryl sulfate, sodium myristyl sulfate, sodium ether sulfate of a C₁₂-C₁₈ straight chain alcohol, sodium lauryl ether phosphate and corresponding potassium salts.

[0026] Other suitable surfactants which may be used include, but are not limited to, N-oxide surfactants. Such N-oxide surfactants include, but are not limited to, cocodimethylamine N-oxide, lauryldimethylamine N-oxide, oleyldimethylamine N-oxide, dodecyldimethylamine N-oxide, octyldimethylamine N-oxide, bis-(hydroxyethyl)isodecyloxypropylamine N-oxide, decyldimethylamine N-oxide, cocamidopropyl dimethylamine N-oxide, bis(hydroxyethyl) C₁₂-C₁₅ alkoxypropylamine N-oxide, lauramine N-oxide, laurami-dopropyl dimethylamine N-oxide, C₁₄-C₁₆ alkyl dimethylamine N-oxide, N,N-dimethyl (hydrogenated tallow alkyl) amine N-oxide, isostearamidopropyl morpholine N-oxide, and isostearamidopropyl pyridine N-oxide.

[0027] Other suitable surfactants include, but are not limited to, betaines, and alkoxylates such as the ethylene oxide/propylene oxide (EO/PO) compounds. Such surfactants are well known in the art.

[0028] Many of the surfactants may be commercially obtained or made by methods described in the literature. Typically, the surfactants are included in the compositions in amounts of 0.1 g/L to 20 g/L.

[0029] The components of the compositions may be combined by any suitable method known in the art. Typically, the components are mixed in any order and the compositions are brought to a desired volume by adding sufficient water. Some heating may be necessary to solubilize certain composition components. The gold electroplating compositions are substantially free of arsenic, lead, thallium, hydrazine and sulfites. In general, substantially free means that the metals, hydrazine and sulfites are not readily detectable with most conventional analytical apparatus or, if they are detectable, they are at levels of 100 ppb or less.

[0030] In general, current density may range from 0.03 ASD and higher using DC or pulse plating. For barrel plating applications, current densities may be from 0.05 ASD to 2.5 ASD using DC current. Gold ion concentrations preferably range from 4 g/L to 8 g/L. For rack plating applications, current densities may range from 0.05 ASD to 4 ASD using DC current. Gold ion concentrations preferably range from 8 g/L to 12 g/L; however, the applicable current density may be extended to 6 ASD for rack plating when using pulse current with ON: OFF times of 1: 3 ms. When jet plating with jet plating equipment, gold ion concentrations preferably range from 12 g/L to 20 g/L. Bright deposit may be obtained from 2 ASD to 70 ASD pulse peak current and ON:OFF pulse parameter of 1:1 to 1:4 ms. The jet agitation can be varied from 100 L/hour to 1000 L/hour depending on the applied current density. It is preferable to use high agitation at higher pulse peak current. The soft gold electroplating compositions may be used in rack plating, barrel plating and high speed jet plating by adjusting the gold concentration and the plating parameters. Unlike many conventional pure gold electroplating compositions, the gold electroplating compositions can be used with jet plating equipment for high speed gold deposition. Jet plating or plating at higher current densities is fast and provides increased electroplating efficiency on production

lines than plating at lower current densities. Such high speed jet plating methods are highly desirable for mass production.

[0031] In addition to providing a bright deposit at high current densities, the soft gold electroplating compositions deposit substantially uniform soft gold deposits. Gold hardness is typically expressed as knoop hardness values and represents the average of a number of tests using a 25 gram indenting tool. The knoop hardness is from 91 to 129 a gold class B according to ASTM B488-11 as plated. After annealing the knoop hardness is 78 or a gold class A. The purity of the gold deposits is 99.9% and is type III purity.

[0032] Plating times may vary. The amount of time depends on the desired thickness of the gold on the substrate. Typically, the thickness of the gold is from 0.01 microns to 50 microns, or such as from 0.1 microns to 2 microns, or such as from 0.2 microns to 0.5 microns.

[0033] Conventional gold plating apparatus may be used to electroplate gold on substrates. The anodes are insoluble anodes such as stainless steel, platinum, platinum-clad tantalum, platinized titanium and graphite. Preferably, the anode is a platinized titanium anode.

[0034] The soft gold electroplating compositions may be used to electroplate gold layers on metals such as nickel, nickel alloys, copper, copper alloys, tin and tin alloys. Preferably, the gold electroplating compositions are used to electroplate gold on nickel and nickel alloys such as contacts, connectors, switches and printed circuit boards. The gold electroplating compositions may also be used to plate gold layers on decorative articles such as jewelry. The gold electroplating compositions may also be used to plate strike layers on substrates to improve adhesion between metal layers.

[0035] The soft gold electroplating compositions are environmentally friendly and may plate bright gold deposits over the applicable current density ranges using DC or pulse current and under barrel, rack or jet plating conditions. The gold deposits also have fine grain structures. Small grain size reduces porosity in thin film. The brightness of the deposits is also a direct consequence of this small grain size. Generally, the roughness of matte or semi-bright deposit is high as compared to bright deposits which are smooth.

[0036] The following examples are intended to illustrate the invention, but are not intended to limit its scope.

Example 1

[0037] An aqueous soft gold electroplating bath having the following composition was prepared:

Table 1

COMPONENT	AMOUNT
Gold from potassium gold cyanide	8 g/L
Potassium dihydrogenate phosphate	79 g/L
Hydroxyethylene-1,1-diphosphonic acid	113 g/L
Potassium hydroxide	64 g/L
KATHONE™ LXE Biocide ¹	50 mg/L
Sodium potassium tartrate	20 g/L
Antimony (III) from potassium antimony tartrate	8 mg/L (antimony (III))
¹ 5-Chlor-2 methyl-4-isothiazol-3-on, magnesium nitrate, copper nitrate and 2-methyl-2H-isothiazol-3-one available from The Dow Chemical Company, Midland, MI.	

[0038] Five double sided nickel pre-plated copper test panels 15 x 20 mm² were immersed in 500 mL baths of the soft gold electroplating bath for 3 minutes to plate gold on nickel. The anode was a platinized titanium electrode. The baths were agitated using a magnetic stirrer during the entire 3 minutes. The baths had a pH of 6.2 and the temperatures of the baths were 55 °C. DC current was applied with a current density of 1 ASD. After the 3 minute period, the coupons were removed from the baths, rinsed with deionized water and air dried. The gold deposits were bright. The thickness of the gold deposits was measured with a FISHERSCOPE™ X-ray apparatus, model XDV-SD, and was determined to be 1.7 microns. The panels were then analyzed for the microstructure of the gold deposit using a SEM microscope at 20,000 magnification. Figure 1 shows one of the SEMs taken with the microscope. The SEM showed small grain structure.

Example 2 (Comparative)

[0039] An aqueous gold electroplating bath having the following formula was prepared:

Table 2

COMPONENT	AMOUNT
Gold from potassium gold cyanide	8 g/L
Potassium dihydrogenate phosphate	79 g/L
Hydroxyethylene-1,1-diphosphonic acid	113 g/L
Potassium hydroxide	64 g/L
KATHONE™ LXE Biocide	50 mg/L
Acetic acid	5 g/L
Lead acetate trihydrate	6 mg/L as lead

[0040] Five double sided nickel pre-plated copper test panels 15 x 20 mm² were immersed in a 500 mL bath of the gold electroplating baths for 3 minutes to plate gold on nickel. The anode was a platinized titanium electrode. The baths were agitated using a magnetic stirrer during the entire 3 minutes. The baths had a pH of 6.2 and the temperatures of the baths were 55 °C. DC current was applied with a current density of 1 ASD. After the 3 minute period, the coupons were removed from the baths, rinsed with deionized water and air dried. The thickness of the gold deposits was 1.7 microns. The panels were then analyzed for the microstructure of the gold deposit using a SEM microscope at 20,000 magnification. Figure 2 shows one of the SEMs taken with the microscope. The SEM showed coarse grain structure. This microstructure was in agreement with the optical appearance of the deposit which was semi-bright. The grain structure and the optical appearance of gold plated from Table 2 were inferior to that of the gold electroplating composition of Example 1 where the test panels were electroplated with gold from an electroplating bath containing antimony (III) from potassium antimony tartrate with sodium potassium tartrate and free of lead.

Example 3

[0041] Eight double sided nickel pre-plated copper test panels 15 x 20 mm² were immersed separately in 500 mL baths containing gold electroplating baths having the formulation in Table 1 of Example 1. The anode was a platinized titanium electrode. Electroplating gold on nickel was done for 3 minutes for each bath. The baths were agitated using a magnetic stirrer during the entire plating time. The baths had a pH of 6.2 and the temperatures of the baths were 55 °C. DC current was applied with varying current densities from one panel to another. The current densities were 0.5 ASD, 1.2 ASD, 1.5 ASD, 2 ASD, 2.5 ASD, 3 ASD, 3.5 ASD and 4 ASD. After plating, the panels were removed from the baths, rinsed with deionized water and air dried. All of the gold deposits had a bright appearance.

[0042] The electroplating process described above was repeated except that the gold electroplating bath of Table 2 of Example 2 was used. After plating, the gold deposits electroplated from 0.5 ASD to 3 ASD had semi-bright deposits; however, the gold plated at 3.5 ASD and 4 ASD had a dull-matte appearance. The results showed that the gold electroplating bath of Table 1 had an improved plating performance in terms of applicable current density and appearance over the lead containing gold electroplating bath of Table 2.

Example 4

[0043] A soft gold electrolytic plating bath as shown in the table below was prepared:

Table 3

COMPONENT	AMOUNT
Gold from potassium gold cyanide	20 g/L
Potassium dihydrogenate phosphate	79 g/L
Hydroxyethylene-1,1-diphosphonic acid	113 g/L
Potassium hydroxide	64 g/L
KATHONE™ LXE Biocide	50 mg/L
Sodium potassium tartrate	20 g/L

(continued)

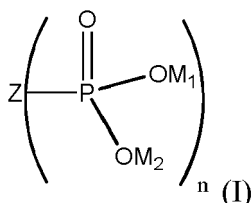
COMPONENT	AMOUNT
Antimony (III) from potassium antimony tartrate	10 mg/L (antimony (III))

[0044] A double sided nickel pre-plated copper test panel 15 x 20mm² was mounted on jet plating equipment containing 1000 mL of the soft gold electroplating bath of Table 3. The anode was a platinized titanium electrode. The baths had a pH of 6.2 and the temperature of the bath was 60 °C. Pulse current was applied with a peak current density of 50 ASD with an ON:OFF time of 1:3 ms. This corresponded to an average current density of 12.5 ASD. The jet agitation or flow rate was set to 800 L/hour. After the 10 second plating period, the panels were removed from the bath, rinsed with deionized water and air dried. All of the panels had a bright gold deposit.

[0045] The process was repeated with the gold electroplating bath of Table 2 except the amount of gold ions was 20 g/L gold. The same jet agitation and plating parameters described above were used. The gold deposits were strongly matte or burned in appearance. The test was repeated except the pulse peak current density was 30 ASD with the same flow rate as above. This corresponded to the average current density of 7.5 ASD. All of the deposits were matte. The electroplating bath of table 2 did not provide a bright or even a semi-bright gold deposit at high current density under jet agitation, thus the gold bath was inferior in performance to the gold plating bath of Table 3.

Claims

1. A gold electroplating composition comprising one or more sources of gold ions from gold-cyanide salts, one or more sources of phosphate ions, one or more sources of phosphonic acids or salts thereof, sodium potassium tartrate and one or more sources of antimony (III) ions, the gold electroplating composition is free of free-cyanide.
2. The gold electroplating composition of claim 1, wherein the gold-cyanide salts are chosen from potassium gold cyanide, sodium gold cyanide, and ammonium gold cyanide.
3. The gold electroplating composition of claim 1, wherein the one or more sources of phosphate ions are chosen from phosphoric acid, sodium dihydrogenate phosphate and potassium dihydrogenate phosphate.
4. The gold electroplating composition of claim 1, wherein the one or more phosphonic acids have a formula:



wherein n is an integer from 2 to 3, M₁ and M₂ may be the same or different and are chosen from hydrogen, ammonium, lower alkyl amine or an alkali metal cation and Z is a radical equal in valence to n and is a linear or branched, substituted or unsubstituted (C₁-C₁₂)alkyl or an N-substituted (C₂-C₃)alkyl wherein the Z radical has a carbon atom linked to a phosphorus atom of formula (I).

5. The gold electroplating composition of claim 1, wherein the one or more sources of antimony (III) ions are chosen from potassium antimony tartrate, sodium antimony tartrate, antimony sulfate and antimony chloride.
6. The gold electroplating composition of claim 1, wherein the gold electroplating composition is substantially free lead, arsenic, thallium, hydrazine and sulfites.
7. A method of electroplating gold comprising:
 - a. providing a gold electroplating composition comprising one or more sources of gold ions from gold-cyanide salts, one or more sources of phosphate ions, one or more sources of phosphonic acids or salts thereof, sodium potassium tartrate and one or more sources of antimony (III) ions, the gold electroplating composition is sub-

stantially free of free-cyanide;

b. contacting a substrate with the gold electroplating composition; and

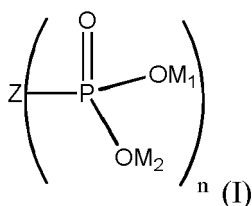
c. electroplating gold on the substrate using direct current or pulse current at a current density of 0.03 ASD or greater.

8. The method of electroplating gold of claim 7, wherein the current density is from 1 ASD to 50 ASD.

9. The method of electroplating gold of claim 7, wherein the gold-cyanide salts are chosen from potassium gold cyanide, sodium gold cyanide, and ammonium gold cyanide.

10. The method of electroplating gold of claim 7, wherein the one or more sources of phosphate ions are chosen from phosphoric acid, sodium dehydrogenate phosphate and potassium dehydrogenate phosphate.

11. The method of electroplating gold of claim 7, wherein the one or more phosphonic acids have a formula:



wherein n is an integer from 2 to 3, M₁ and M₂ may be the same or different and are chosen from hydrogen, ammonium, lower alkyl amine or an alkali metal cation and Z is a radical equal in valence to n and is a linear or branched, substituted or unsubstituted (C₁-C₁₂)alkyl or an N-substituted (C₂-C₃)alkyl wherein the Z radical has a carbon atom linked to a phosphorus atom of formula (I).

12. The method of electroplating gold of claim 7, wherein the one or more sources of antimony (III) ions are chosen from potassium antimony tartrate, sodium antimony tartrate, antimony sulfate and antimony chloride.

13. The method of electroplating gold of claim 7, wherein the gold electroplating composition is substantially free of free-cyanide, lead, arsenic, thallium, hydrazine and sulfites.

14. The method of electroplating gold of claim 7, wherein the substrate is a printed circuit board, a contact for a connector, switch or decorative article.

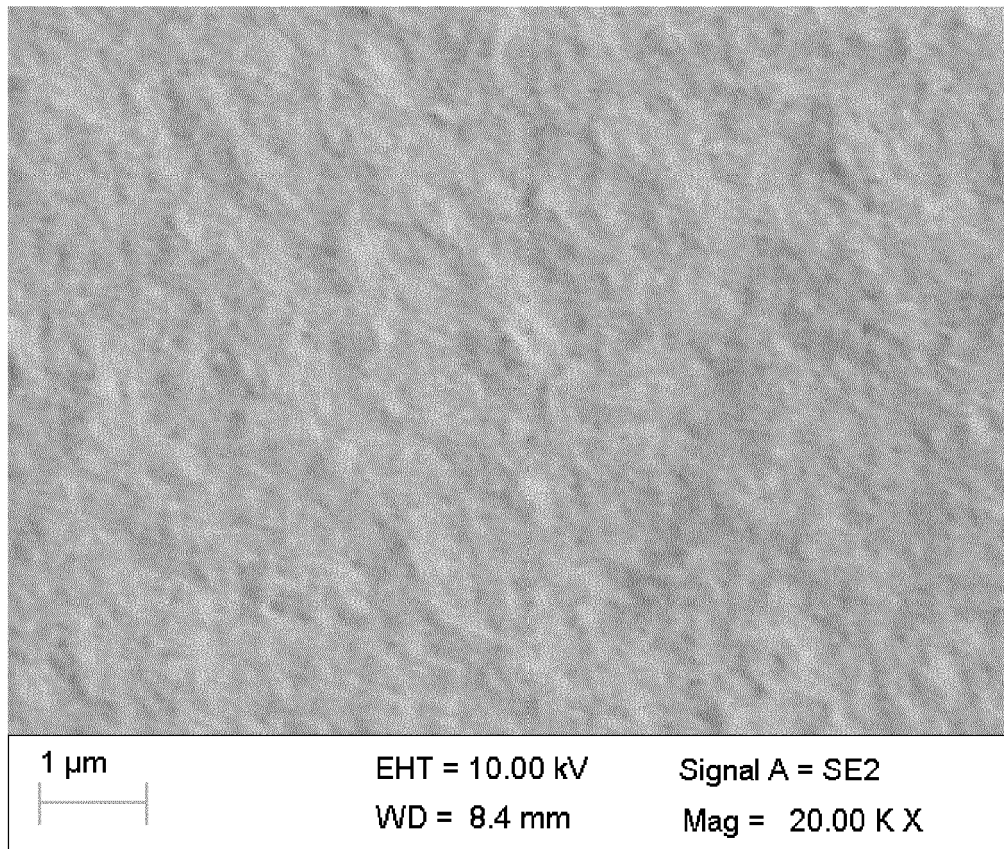
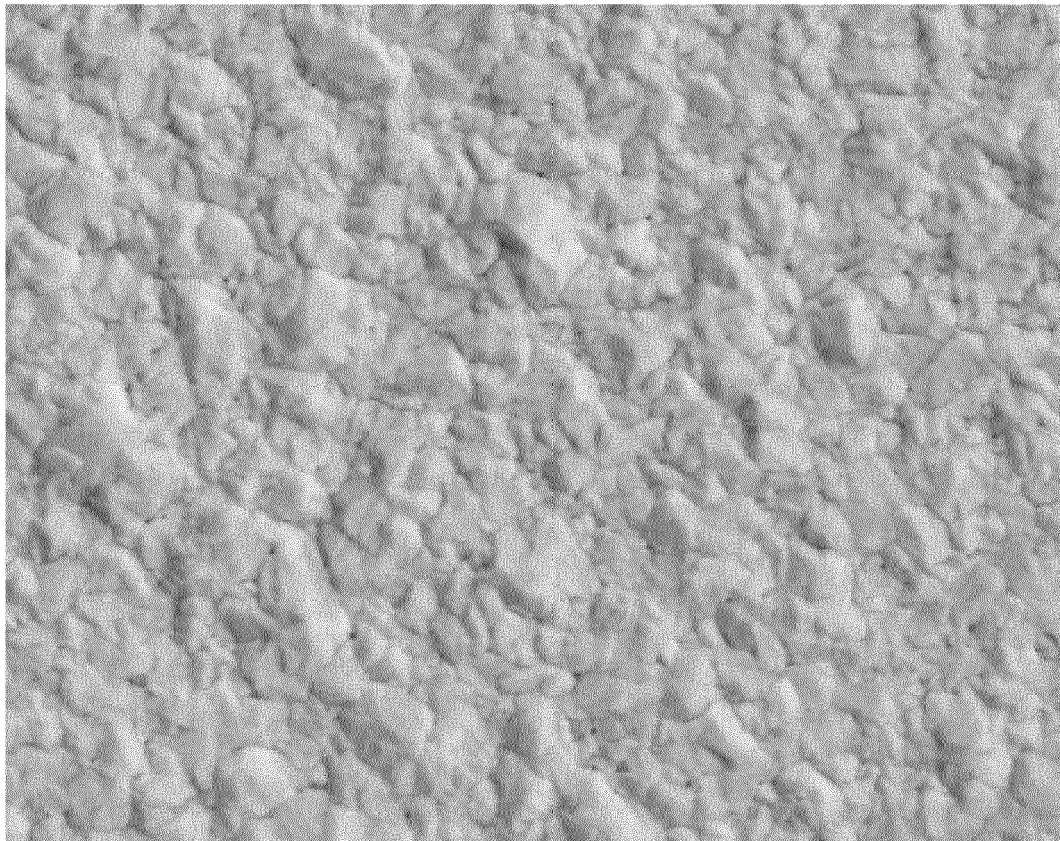


FIGURE 1



1 μm

EHT = 10.00 kV
WD = 8.3 mm

Signal A = SE2
Mag = 20.00 K X

FIGURE 2



EUROPEAN SEARCH REPORT

Application Number
EP 15 19 3859

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 27 23 910 A1 (SYST TRAITEMENT SUR) 15 December 1977 (1977-12-15) * Acidic bath I, mixtures F and H and component e); page 5, lines 1-4; example 1 *	1-14	INV. C25D3/48 C25D3/62
A	GB 2 046 794 A (ENGELHARD MIN & CHEM) 19 November 1980 (1980-11-19) * abstract; example 5 * * page 1, lines 44-49 *	1-14	
A	EP 2 669 407 A1 (BLUCLAD S R L [IT]) 4 December 2013 (2013-12-04) * abstract; claim 1 * * paragraph [0018] *	1-14	
A	US 3 706 635 A (KOWALSKI XAVIER) 19 December 1972 (1972-12-19) * abstract; claim 9 * * column 1, line 44 - column 2, line 8 * * column 2, lines 33-64 *	1-14	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		5 April 2016	Telias, Gabriela
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 15 19 3859

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-04-2016

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 2723910 A1	15-12-1977	CH 615464 A5	31-01-1980
		DE 2723910 A1	15-12-1977
		FR 2353656 A1	30-12-1977

GB 2046794 A	19-11-1980	AR 225759 A1	30-04-1982
		AU 5717880 A	09-10-1980
		BR 8001854 A	18-11-1980
		DE 3013191 A1	23-10-1980
		DK 146980 A	05-10-1980
		FR 2453226 A1	31-10-1980
		GB 2046794 A	19-11-1980
		IT 1127414 B	21-05-1986
		JP S55134191 A	18-10-1980
		NL 8001999 A	07-10-1980

EP 2669407 A1	04-12-2013	NONE	

US 3706635 A	19-12-1972	BE 791401 A1	14-05-1973
		CA 1009177 A	26-04-1977
		DE 2255728 A1	24-05-1973
		FR 2160458 A1	29-06-1973
		GB 1370387 A	16-10-1974
		JP S568113 B2	21-02-1981
		JP S4861337 A	28-08-1973
		US 3706634 A	19-12-1972
		US 3706635 A	19-12-1972

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5277790 A, Morrissey [0003]