(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 686 319 A1**

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.07.2020 Bulletin 2020/31

(51) Int Cl.:
C25D 3/54 *(2006.01)* ***C25D 3/56*** *(2006.01)*
C25D 5/12 *(2006.01)* ***C25D 5/50*** *(2006.01)*

(21) Application number: **20153749.5**

(22) Date of filing: **24.01.2020**

(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:
KH MA MD TN

(30) Priority: **25.01.2019 US 201916257132**

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(54) INDIUM ELECTROPLATING COMPOSITIONS AND METHODS FOR ELECTROPLATING INDIUM ON NICKEL

(57) Indium electroplating compositions electroplate substantially defect-free, whisker-free, uniform indium layers which have a smooth surface morphology on nickel. The indium electroplating compositions are environmentally friendly and include select amino acids to provide for the smooth, uniform and defect-free indium deposits.

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The present invention is directed to indium electroplating compositions and methods for electroplating indium on nickel layers where the indium deposit is uniform, substantially void-free, whisker-free and has a smooth surface morphology. More specifically, the present invention is directed to acid indium electroplating compositions and methods of electroplating indium on nickel layers where the indium deposit is uniform, substantially void-free, whisker-free and has a smooth surface morphology, wherein the indium electroplating compositions are environmentally friendly and include select amino acids to provide the uniform matte, substantially void-free, whisker-free and smooth surface morphology indium deposit.

Background of the Invention

[0002] Electrolytic indium is very attractive in the connectors industry for press-fit applications. Indium can be used as a replacement metal for tin. Tin usually grows whiskers under stress conditions. As electronic components become smaller, it is important to eliminate the risk of whisker formation which can create electrical short circuits. The advantage of indium over tin is that indium is less susceptible to whisker formation even after reflow.

[0003] Connector pins (copper alloy) for press-fit applications are initially coated with nickel followed by indium flash adjacent to the nickel. The thickness of indium layer is generally from 0.2-1 μm. The problem is that many electrolytic indium processes are unable to plate such a thin layer with uniform thickness distribution and with good adhesion on the nickel without using a strike layer (adhesion promotor coating). Such strike layers can have a thickness of 1-100nm.

[0004] The ability to reproducibly plate void-free uniform matte indium of target thickness and smooth surface morphology on nickel layers is challenging. Indium reduction occurs at potentials more negative than that of proton reduction, and significant hydrogen bubbling at the cathode causes increased surface roughness. Indium (1^+) ions, stabilized due to the inert pair effect, formed in the process of indium deposition catalyze proton reduction and participate in disproportionation reactions to regenerate Indium (3^+) ions. In the absence of a complexing agent, indium ions begin to precipitate from solutions above pH > 2. Plating indium on nickel is challenging because nickel is a good catalyst for proton reduction and is more noble than indium, nickel can cause corrosion of indium in a galvanic interaction. Indium may also form undesired intermetallic compounds with nickel. Another problem with indium plating is the generation of hydrogen gas. Such hydrogen gas generation can result in rough and irregular indium deposits unsuitable for electronic components and devices.

[0005] In addition, many conventional indium plating baths include environmentally unfriendly additives required to enable acceptable indium plating performance, such as certain suppressors, many levelers, grain refiners, certain buffers and compounds used to inhibit hydrogen evolution during plating. Many governments around the world are passing stricter environmental laws and regulations with respect to how chemical waste is treated and the types of chemicals industries may use in development and manufacturing processes. For example, in the European Union the regulation Registration, Evaluation, Authorization and Restriction of Chemicals, known as REACh, has banned numerous chemicals or is in the process of banning chemicals used in plating baths from substantial industrial use.

[0006] Accordingly, there is a need for improved indium compositions for electroplating indium metal layers on nickel substrates and which are environmentally friendly.

Summary of the Invention

[0007] The present invention is directed to an indium electroplating composition consisting of water; one or more sources of indium ions; one or more acids selected from the group consisting of inorganic acids, alkane sulfonic acids, and salts of the acids, wherein the inorganic acids are selected from the group consisting of sulfamic acid and sulfuric acid; and one or more amino acids selected from the group consisting alanine, arginine, aspartic acid, asparagine, glutamic acid, glycine, glutamine, histidine, leucine, lysine, threonine, isoleucine, serine, and valine; optionally one or more alloying metal; and optionally one or more pH adjuster.

[0008] The present invention is also directed to a method of electroplating indium on nickel comprising:

a) providing a substrate comprising a nickel layer adjacent to a copper or copper alloy layer;

b) contacting the substrate comprising the nickel layer adjacent to the copper or the copper alloy layer with an indium electroplating composition consisting of water; one or more sources of indium ions one or more acids selected from the group consisting of inorganic acids, alkane sulfonic acids, and salts of the acids, wherein the inorganic acids are selected from the group consisting of sulfamic acid and sulfuric acid; and one or more amino acids selected from the group consisting alanine, arginine, aspartic acid, asparagine, glutamic acid, glycine, glutamine, histidine, leucine, lysine, threonine, isoleucine, serine, and valine; optionally one or more alloying metal; and optionally one or more pH adjuster; and

c) electroplating an indium layer adjacent to the nickel layer of the substrate with the indium electroplating composition.

[0009] The aqueous acid indium electroplating compositions and methods of the present invention can be used to plate indium metal layers having a thickness of > 0.1 μm on nickel without using a strike. The current efficiency for the aqueous acid indium electroplating compositions is high, and the indium deposit is uniform and matte, substantially void-free, whisker-free, has a smooth surface morphology and shows good adhesion on Nickel. Post annealing of the substrates with the indium deposit shows minor to substantially no dewetting. During indium electroplating hydrogen gas evolution is substantially inhibited to enable smooth uniform matte indium deposits. The indium electroplating compositions contain only registered and REACh compliant compounds.

Detailed Description of the Inventions

[0010] As used throughout the specification, the following abbreviations have the following meanings, unless the context clearly indicates otherwise: ° C = degrees Centigrade; g = gram; mg = milligram; L = liter; A = amperes; dm = decimeter; ASD = A/dm^2 = current density; μm = micron = micrometer; indium ion = In^{3+}; nm = nanometers = 10^{-9} meters; μm = micrometers = 10^{-6} meters; M = molar; min. = minute; IC = integrated circuits; XRF = X-ray fluorescence; and e.g. = example.

[0011] The terms "depositing", "plating" and "electroplating" are used interchangeably throughout this specification. The term "aqueous" means water based or the solvent of the composition is water. The term "adjacent' means in direct contact or two separate surfaces or planes having a common interface. The term "interface" means point(s) of contact between two surfaces or planes. The term "plane" means a substantially flat surface such that a straight line joining any two points on it lies wholly in it. The term "surface" means outer area or upper most area of an article or structure. The term "copolymer" is a compound composed of two or more different monomers or oligomers. The term "dewetting" means the retraction of indium plating at some position on the nickel surface after reflow, wherein this position of the nickel is called the non-wettable area and occurs when adhesion is poor. The term "matte" means dull and flat in appearance without shine. Unless otherwise noted all plating baths are aqueous solvent based, i.e. water based, plating baths. All amounts are percent by weight and all ratios are by moles, 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%.

[0012] The aqueous acid indium compositions of the present invention include one or more sources of indium ions which are soluble in an aqueous environment. Such sources include, but are not limited to, indium salts of alkane sulfonic acids, such as methanesulfonic acid, ethanesulfonic acid, and butane sulfonic acid, indium salts of sulfamic acid, sulfate salts of indium, chloride and bromide salts of indium, nitrate salts, hydroxide salts, indium oxides, fluoroborate salts, indium salts of carboxylic acids, such as citric acid, acetoacetic acid, glyoxylic acid, pyruvic acid, glycolic acid, malonic acid, hydroxamic acid, iminodiacetic acid, salicylic acid, glyceric acid, succinic acid, malic acid, tartaric acid, hydroxybutyric acid, indium salts of amino acids, such as arginine, aspartic acid, asparagine, glutamic acid, glycine, glutamine, leucine, lysine, threonine, isoleucine, and valine. Preferably, the source of indium ions is one or more indium salts of sulfuric acid, sulfamic acid, and alkane sulfonic acids. More preferably, the source of indium ions is one or more indium salts of sulfuric acid, sulfamic acid and methane sulfonic acid. Most preferably, the source of indium ions is indium sulfate.

[0013] The indium ions from the water-soluble salts of indium are included in the compositions in sufficient amounts to provide an indium deposit of desired thickness. Preferably, the indium ions from the water-soluble indium salts are included in the compositions in amounts of 5 g/L to 70 g/L, more preferably, from 10 g/L to 50 g/L, most preferably, from 10 g/L to 40 g/L.

[0014] One or more amino acids selected from the group consisting of alanine, arginine, aspartic acid, asparagine, glutamic acid, glycine, glutamine, histidine, leucine, lysine, threonine, isoleucine, serine, and valine are included in the indium plating compositions of the present invention. Preferably, the indium electroplating compositions of the present invention are free of amino acids having sulfur and sulfur functional groups. Preferably, the one or more amino acids are selected from the group consisting of arginine, aspartic acid, asparagine, glycine, glutamine, lysine, serine and histidine, more preferably, the one or more amino acids are selected from the group consisting of arginine, asparagine, glycine, aspartic acid, lysine and serine, even more preferably, the one or more amino acids are selected from the group consisting of glycine, lysine and serine. Most preferably, the amino acid is glycine. Including one or more of the amino acids in the indium electroplating compositions of the present invention inhibits hydrogen gas evolution during indium electroplating and stabilizes indium ions such that no substantial precipitation of the indium ions occurs at a relatively high pH of >1.5.

[0015] One or more of the foregoing amino acids can be included in the indium plating compositions of the present invention in amounts of 5 g/L or greater. Preferably, the one or more amino acids of the present invention can be included in amounts of 10 g/l to 200 g/L, more preferably, the amino acids can be included in amounts of 25 g/L to 150 g/L (e.g.

30 g/L to 120 g/L, 30 g/L to 100 g/L or 25 g/L to 75 g/L), even more preferably, the amino acids can be included in amounts of 25 g/l to 100 g/L (e.g. 30 g/L to 100 g/L or 40 g/L to 100 g/L), most preferably, the amino acids are included in amounts of 50 g/L to 100 g/L (e.g. 50 g/L to 90 g/L).

[0016] One or more acids selected from the group consisting of inorganic acids, alkane sulfonic acids, and salts of the acids, wherein the inorganic acids are selected from the group consisting of sulfamic acid and sulfuric acid. Alkane sulfonic acids include, but are not limited to methanesulfonic acid, ethanesulfonic acid, and butane sulfonic acid. Preferably, the one or more acids are selected from the group consisting of sulfuric acid, sulfamic acid and methane sulfonic acid, more preferably, the one or more acids are selected from the group consisting of sulfuric acid and sulfamic acid, most preferably, the acid is sulfamic acid.

[0017] One or more of the foregoing acids or salts thereof are included in the indium electroplating compositions of the present invention in amounts of 10 g/L or greater. Preferably, the one or more acids are included in the indium plating compositions in amounts of 10 g/L to 300 g/L, more preferably, from 50 g/L to 250 g/L, even more preferably from 50 g/L to 200 g/L, most preferably from 50 g/L to 100 g/L.

[0018] The pH of the aqueous acid indium electroplating compositions of the present invention range from 5 or less, preferably from 1-4, more preferably, from 1-3, even more preferably, from 1.5-3, most preferably, from 1.5-2.5.

[0019] Optionally, one or more pH adjusters can be included in the indium electroplating compositions to provide and maintain a desired acid pH. The pH adjuster can include buffers which include an acid and the salt of its conjugate base. Acids are selected from glyoxylic acid, pyruivic acid, hydroxamic acid, iminodiacetic acid, salicylic acid, succinic acid, hydroxybutyric acid, acetic acid, acetoacetic acid, tartaric acid, phosphoric acid, oxalic acid, carbonic acid, ascorbic acid, butanoic acid, thioacetic acid, glycolic acid, malic acid, formic acid, heptanoic acid, hexanoic acid, hydrofluoric acid, lactic acid, nitrous acid, octanoic acid, pentanoic acid, uric acid, nonanoic acid, decanoic acid, sulfurous acid, sulfuric acid, alkane sulfonic acids and aryl sulfonic acids such as methanesulfonic acid, ethanesulfonic acid, benzenesulfonic acid, toluenesulfonic acid, sulfamic acid. Bases such as potassium hydroxide and sodium hydroxide can also be used as pH adjusters alone or combination with one or more of the foregoing acids. Preferably, the one or more pH adjustors are selected from the group consisting of sulfamic acid, sulfuric acid, potassium hydroxide and sodium hydroxide, more preferably, the one or more pH adjusters are selected from the group consisting of sulfamic acid, sulfuric acid and potassium hydroxide.

[0020] Optionally, the aqueous acid indium electroplating compositions can include one or more alloying metal. Preferably, the one or more alloying metal is selected from the group consisting of tin, copper, bismuth and silver, more preferably, the one or more alloying metal is selected from the group consisting of tin, copper and silver, most preferably, the alloying metal is tin. The alloying metals can be added to the indium compositions as water soluble metal salts. Such water-soluble metal salts are well known to those of skill in the art. Many are commercially available or can be prepared from descriptions in the literature. One or more sources of alloying metal can be added to the indium electroplating compositions in amounts such that the indium alloy has from 1wt% to 3wt% of one or more alloying metals. Preferably, alloying metals are excluded from the indium compositions. It is preferred that only indium metal is plated.

[0021] Optionally, one or more sources of chloride can be added to the indium electroplating compositions of the present invention. Sources of chloride include, but are not limited to, sodium chloride and potassium chloride. Preferably, when one or more sources of chloride is added to the indium electroplating composition, the concentration of chloride can range from 1-50 g/L.

[0022] Conventional hydrogen gas suppressors, such as copolymers of epihalohydrin and nitrogen-containing organic compounds, are excluded from the indium electroplating compositions of the present invention. Preferably, many conventional additives, such as levelers, suppressors, brighteners, grain refiners, alloying metals and surfactants are also excluded of the indium electroplating compositions of the present invention.

[0023] Preferably, in the aqueous acid indium electroplating compositions of the present invention, the water is at least one of deionized and distilled water to limit incidental impurities.

[0024] Preferably, the aqueous acid indium electroplating composition of the present invention consists of water; one or more sources of indium ions, including both indium (In^{3+}) cations and counter anions; one or more acids selected from the group consisting of inorganic acids, wherein the inorganic acids are selected from the group consisting of sulfamic acid and sulfuric acid, and alkane sulfonic acids, including salts of sulfamic acid, sulfuric acid and alkanesulfonic acid; one or more amino acids selected from the group consisting of alanine, arginine, aspartic acid, asparagine, glycine, glutamine, histidine, leucine, lysine, threonine, isoleucine, serine, and valine; optionally one or more sources of chloride; and optionally one or more pH adjusters.

[0025] More preferably, the aqueous acid indium electroplating composition of the present invention consists of water; one or more sources of indium ions, including both indium (In^{3+}) cations and counter anions; one or more acids selected from the group consisting of sulfamic acid, sulfuric acid, methane sulfonic acid and salts of the foregoing acids; one or more amino acids selected from the group consisting of arginine, aspartic acid, asparagine, glycine, glutamine, lysine and serine; one or more sources of chloride; and optionally one or more pH adjusters.

[0026] Most preferably, the aqueous acid indium electroplating composition of the present invention consists of water;

one or more sources of indium ions, including both indium (In^{3+}) cations and counter anions; one or more acids selected from the group consisting of sulfamic acid and sulfuric acid, wherein the most preferred acid is sulfamic acid; one or more amino acids selected from the group consisting of arginine, asparagine, glycine, lysine and serine, wherein glycine, lysine and serine are the more preferred amino acids, and glycine is the most preferred; and optionally one or more pH adjusters.

[0027] Preferably, the aqueous acid indium electroplating composition of the present invention can be used to electroplate indium metal or an indium alloy directly adjacent to a nickel layer, wherein the nickel layer is directly adjacent to copper or a copper alloy. More preferably, the aqueous acid indium electroplating composition of the present invention can be used to electroplate indium metal directly adjacent to a nickel layer, wherein the nickel layer is directly adjacent copper or a copper alloy. Nickel layer thickness preferably ranges from 0.1-5μm. Conventional strike layers of indium or silver having thickness values ranging from 1-100nm, more typically, from 1-40nm are excluded from the nickel surface such that the indium metal or indium alloy can be electroplated directly adjacent the nickel and provide a matte, uniform, void-free and substantially whisker-free indium deposit of > 100nm which has good adhesion to the nickel. Such adhesion can be tested by cross-hatch tests, pin bending tests and reflow test followed by dewetting control.

[0028] The indium layers range in thickness from > 0.1 μm, preferably, from 0.2 μm to 10μm, more preferably, from 0.2μm to 5μm, most preferably, from 0.2μm to 1μm.

[0029] Apparatus used to deposit indium metal or indium alloys directly adjacent to nickel is conventional. Preferably, conventional soluble indium electrodes are used as the anode. Current densities can vary depending on the concentration of indium ions in the electroplating composition and bath agitation. Preferably, current densities range from 0.1 ASD or greater (e.g. 0.1-50 ASD, 0.1-30 ASD or 0.1-20 ASD), more preferably, 0.5 ASD to 50 ASD (e.g. 0.5-40 ASD, 1-20 ASD or 1-10 ASD).

[0030] The temperatures of the indium compositions during indium metal or indium alloy electroplating can range from room temperature to 60 °C. Preferably, the temperatures range from room temperature to 55 °C, more preferably, from room temperature to 50 °C, most preferably, from 30-45 °C.

[0031] The indium plating speed of the aqueous acid indium electroplating compositions of the present invention can range from ≥ 0.2μm/min., ≥ 0.5μm/min., > 1μm/min., > 2.3μm/min., or > 3μm/min., at 1, 2, 4, 8 or 10 ASD, respectively.

[0032] Optionally, the indium or indium alloy plated nickel and copper or copper alloy substrates are reflowed. Reflow tests are preferably done at temperatures of ≥ 150 °C, more preferably, at temperatures of ≥ 200 °C, most preferably, from 200-350 °C. Reflow can be done in conventional reflow ovens used for metal substrates. The reflowed indium plated nickel substrates show minor to substantially no dewetting.

[0033] Although the aqueous acid indium electroplating compositions of the present invention are preferably used to deposit indium metal or indium alloy directly adjacent a nickel layer, wherein the nickel layer is directly adjacent copper or copper alloy, such as for connector pins in IC electronic devices, it is envisioned that the aqueous acid indium electroplating compositions of the present invention can be used to deposit indium metal or indium alloys directly adjacent other metals, such as copper and copper alloys. It is preferred that indium metal is deposited directly adjacent other metals, such as nickel, copper or copper alloys, most preferably, indium metal is deposited directly adjacent nickel, wherein the nickel is directly adjacent copper or copper alloy.

[0034] The following examples are intended to illustrate the present invention, but are not intended to limit the inventions scope.

Examples 1-10

Hull Cell Electroplating Performance of Aqueous Acid Indium Electroplating Compositions of the Present Invention

[0035] The following aqueous, acid indium electroplating compositions were prepared:

Table 1

Example	Indium Ion Concentration	Amino Acid	Acid	pH	Plating Temperature °C
1	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	Sulfamic acid 50 g/L	2.1	30
2	30 g/L Indium ions (from indium sulfate)	Glycine 50 g/L	Sulfamic acid 100 g/L	1.1	50
3	30 g/L Indium ions (from indium sulfate)	Glycine 50 g/L	Sulfamic acid 100 g/L	2	50

(continued)

Example	Indium Ion Concentration	Amino Acid	Acid	pH	Plating Temperature °C
4	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L + Arginine 40 g/L	Sulfuric acid 28 g/L	2.4	40
5	30 g/L Indium ions (from indium sulfate)	Glycine 120 g/L	Methane Sulfonic acid 160 g/L	2.2	30
6	30 g/L Indium ions (from indium sulfate)	Lysine 100 g/L	Sulfamic acid 50 g/L	2.1	35
7	30 g/L Indium ions (from indium sulfate)	Glutamine 100 g/L	Sulfamic acid 50 g/L	2.1	40
8	30 g/L Indium ions (from indium sulfate)	Histidine 100 g/L	Sulfamic acid 50 g/L	2.1	35
9	30 g/L Indium ions (from indium sulfate)	Serine 100 g/L	Sulfamic acid 50 g/L	2.1	35
10	30 g/L Indium ions (from indium sulfate)	Asparagine 100 g/L	Sulfamic acid 50 g/L	2.1	35

The solvent of the foregoing indium electroplating compositions was water and the pH of the indium electroplating compositions was adjusted with potassium hydroxide.

[0036] 250 mL of each indium composition was placed in separate Hull cells. A brass (copper-zinc alloy) panel coated with nickel was used as the cathode. Indium metal was used as a soluble anode. The rectifier was set as 2 A. During plating, the indium compositions were agitated using a common laboratory paddle agitator. Indium electroplating was done for 3 min. Current densities ranged from 0.1-10 ASD. The indium metal deposit was measured at current densities of 1, 2, 3, 4, 6, 8 and 10 ASD using a Fischerscope X-Ray XDV-SD XRF apparatus. The plating rate was determined by dividing the thickness at each current density by the plating time in minutes.

[0037] As the current density increased, the plating rate of the indium deposition on the nickel also increased. Plating rates ranged from a low of 0.5μm/min. at 1 ASD to a high of 3.2μm/min. at 10 ASD. After electroplating was completed, the indium deposits were examined for the quality of the deposits. All the indium deposits appeared smooth, matte and uniform. No deposit defects were observed.

Examples 11-12

Reflow Test of Indium Metal on Nickel

[0038] The following aqueous, acid indium electroplating compositions were prepared:

Table 2

Example	Indium Ion Concentration	Amino Acid	Copolymer	Acid	pH	Plating Temperature °C
11	30 g/L Indium ions (from indium sulfate	Glycine 100 g/L	-----------	Sulfamic acid 50 g/L	2.1	30
12 (comparative)	30 g/L Indium (from indium sulfate)	-----------	Imidazole-epichlorohydrin[1] 130 g/L	Methane sulfonic acid 4.4 g/L	1.1	50
[1] LUGALVAN™ IZE, available from BASF (IZE contains 48-50wt% copolymer).						

[0039] Each aqueous, acid indium electroplating composition was used to plate indium on nickel coated brass (copper-zinc alloy). The counter electrode was an indium soluble anode. Plating of indium on the nickel of the substrate was done for 3 min. at a current density of 5ASD. The indium electroplating compositions were agitated throughout plating.

[0040] After plating, the indium plated substrates were rinsed with DI water, dried and observed for plating performance. The indium deposit on the nickel appeared uniform, matte and smooth on both substrates.

[0041] The substrates were then reflowed/heated using a conventional reflow oven. Reflow was done at 200 °C for 3 min. The reflowed substrates were removed from the oven and the quality of their surfaces was analyzed. The substrate which was plated with the indium composition of Example 11 showed no indication of dewetting. In contrast, the substrate plated with the indium composition of Example 12 showed significant dewetting: nickel was exposed on some areas which were covered by the indium before reflow.

Examples 13-14

Hull Cell Plating Performance of Aqueous Acid Indium Plating Compositions Containing Amino Acid Cysteine or Amino Acid Glycine

[0042] The following aqueous acid indium electroplating compositions were prepared:

Table 3

Example	**Indium Ion Concentration**	**Amino Acid**	**Acid**	**pH**	**Plating Temperature °C**
13 (comparative)	30 g/L Indium ions (from indium sulfate)	L-cysteine 100 g/L	Sulfamic Acid (sufficient amount to provide desired pH)	2	35
14	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	Sulfamic Acid (sufficient amount to provide desired pH)	2	35

250 mL of each aqueous acid indium composition was placed in a Hull cell. A nickel coated brass (copper-zinc alloy) substrate was used as a cathode. The plating was done at a current of 2A for 3 min. under paddle agitation. The counter electrode was a soluble indium anode. The coating appearance and thickness were evaluated at the current density ranging from 0.1-10 ASD. For comparative Example 13 there was no indication of indium plating as the lower current densities of 0.1-3 ASD. The indium deposit was very thin (less than 0.4μm) and non-uniform at current densities above 3 ASD. Substantial gas evolution was observed during plating (observed by gas bubbling from the cathode with the naked eye).

[0043] In contrast, the indium deposit of Example 14 appeared uniform, matte and smooth from 0.1-10 ASD. The plating speed was comparable to the plating speeds of Examples 1-5, above.

Examples 15-17

Hull Cell Plating Performance of Aqueous Acid Indium Plating Compositions The following aqueous acid indium electroplating compositions were prepared:

[0044]

Table 4

Example	**Indium Ion Concentration**	**Amino Acid**	**Copolymer**	**Acid**	**pH**	**Plating Temperature °C**
15	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	-----------	Sulfamic acid 50 g/L	2	35
16 (comparative)	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	Imidazole-epichlorohydrin[1] 5 g/L	Sulfamic acid 50 g/L	2	35

(continued)

Example	Indium Ion Concentration	Amino Acid	Copolymer	Acid	pH	Plating Temperature °C
17 (comparative)	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	Imidazole-epichlorohydrin[1] 15 g/L	Sulfamic acid 50 g/L	2	35

[1] LUGALVAN™ IZE, available from BASF (IZE contains 48-50wt% copolymer).

[0045] 250 mL of each aqueous acid indium composition was placed in a Hull cell. A nickel coated brass (copper-zinc alloy) substrate was used as a cathode. The plating was done at a current of 2 A. Plating was done under paddle agitation for 3 min. The counter electrode was an indium soluble anode. The indium coating appearances and thicknesses were evaluated at current densities ranging from 0.1-10 ASD.

[0046] The substrate plated with indium from Example 15 had a uniform, matte and smooth indium deposit. The plating rate was good and was substantially the same as in Examples 1-5 above over the current density range of 0.1-10 ASD. There were no observable defects.

[0047] In contrast, the substrates plated with the indium compositions of Examples 16-17 showed no substantial indium deposited on the substrate. XRF analysis of the substrates from Examples 16-17 showed 0.1-0.6μm indium clusters at some areas of the substrates. Substantial gas evolution was observed during the plating of the substrates of Examples 16-17. It was determined that the imidazole/epihalohydrin copolymer was not suitable for indium metal electroplating.

Example 18

Hydrogen Gas Generation and Reflow Test of Indium on Nickel

[0048] The indium plating compositions of Examples 15, 16 and 17 of Table 4 above were added to separate one liter glass beakers. Two indium soluble anodes were placed in each beaker. A nickel coated brass coupon was used in each beaker as a cathode. The electrodes were connected to a rectifier. A current density of 4 ASD was applied to each composition. Plating was done over 2 min. The indium electroplating compositions were agitated using a magnetic stirrer throughout plating. After plating, each coupon was removed from the beaker and rinsed with DI water, dried and analyzed for indium plating performance.

[0049] The coupon from Example 15 had a uniform, matte and smooth indium deposit 2.2μm thick. In contrast, the indium deposits from the plating compositions of Examples 16-17 were very thin. XRF analysis measured an indium deposit of only 0.2μm thick for the coupon plated with the indium composition from Example 16 and an indium deposit of 0.1 μm thick from the composition of Example 17. Substantial gas evolution was observed during plating for Examples 16-17.

[0050] The above experiment was repeated using a current density of 8 ASD with a plating time of 1 min. 30 sec. The indium deposit from Example 15 was uniform, matte and smooth in appearance with a 3.7μm thick indium deposit. The indium deposit from the compositions of Examples 16-17 had indium thicknesses of 0.55μm and 0.35μm, respectively.

Examples 19-21

Hydrogen Gas Generation and Reflow Test of Indium on Nickel

[0051] The following aqueous acid indium electroplating compositions were prepared:

Table 5

Example	Indium Ion Concentration	Amino Acid	Copolymer	Acid	pH	Plating Temperature °C
19	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	----------	Sulfamic acid 50 g/L	2	35

(continued)

Example	Indium Ion Concentration	Amino Acid	Copolymer	Acid	pH	Plating Temperature °C
20 (comparative)	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	Imidazole-epichlorohydrin[1] 5 g/L	Sulfamic acid 50 g/L	2	35
21 (comparative)	30 g/L Indium ions (indium sulfate)	Glycine 100 g/L	Imidazole-epichlorohydrin[1] 15 g/L	Sulfamic acid 50 g/L	2	35
[1]LUGALVAN™ IZE, available from BASF (IZE contains 48-50wt% copolymer).						

[0052] Each of the indium plating compositions of Examples 19-20 were added to separate glass one liter beakers. Two indium anodes were placed in each beaker and a nickel coated coupon was used in each beaker as a cathode. The electrodes were connected to a rectifier. A current density of 4 ASD was applied for 2 min. of plating. The plating compositions were agitated throughout plating. During indium plating substantial hydrogen gas evolution was observed for Examples 20-21. In contrast, insignificant hydrogen gas evolution was observed for Example 19.

[0053] After plating, the indium plated substrates were rinsed with DI water, dried and observed for plating performance. The indium deposit on the nickel plated from the indium compositions of Example 19 appeared uniform, matte and smooth. The average indium thickness was 2.2μm.

[0054] In contrast, substantially no indium was deposited on the nickel from the indium compositions of Examples 20 and 21. The average indium thickness on the nickel plated with the indium composition of Example 20 was only 0.55μm and the average thickness on the nickel plated with indium with the composition of Example 21 was only 0.35μm.

[0055] The substrates with the indium deposits adjacent the nickel were then reflowed using a conventional reflow oven. Reflow was done at 200 °C for 3 min. The reflowed substrates were removed from the oven and the quality of their surfaces was analyzed. The substrate which was plated with the indium composition of Example 19 showed no indication of dewetting. In contrast, the substrates plated with the indium compositions of Examples 20-21 showed several dewetting spots spread over the surface of the indium layer.

Examples 22-27

Aqueous Acid Indium Electroplating Composition Stability

[0056] The following aqueous acid indium electroplating compositions were prepared:

Table 6

Example	Indium Ion Concentration	Amino Acid	Acid	pH	pH Adjuster
22 (comparative)	30 g/L Indium ions (from indium sulfate)	-----------	Sulfamic acid 50 g/L	2	Potassium hydroxide
23	30 g/L Indium ions (from indium sulfate)	Glycine 25 g/L	Sulfamic acid 50 g/L	2	Potassium hydroxide
24	30 g/L Indium ions (from indium sulfate)	Glycine 50 g/L	Sulfamic acid 50 g/L	2	Potassium hydroxide
25	30 g/L Indium ions (from indium sulfate)	Glycine 75 g/L	Sulfamic acid 50 g/L	2	Potassium hydroxide
26	30 g/L Indium ions (from indium sulfate)	Glycine 100 g/L	Sulfamic acid 50 g/L	2	Sulfamic acid
27	30 g/L Indium ions (from indium sulfate)	Glycine 150 g/L	Sulfamic acid 50 g/L	2	Sulfuric acid

[0057] After initial make-up at room temperature, all the foregoing indium plating compositions appeared colorless. All the indium plating compositions idled at room temperature for one day. The indium plating composition of Example 22 was significantly turbid. White precipitate was observed at the bottom of the glass beaker. The white precipitate indicated that an indium salt precipitated from the composition.

[0058] In contrast, the indium plating compositions of Examples 23-27 remained colorless indicating good stability. The compositions of Examples 23-27 remained colorless indicating stable indium compositions over several weeks. No turbidity or precipitation was observed even after one month.

Claims

1. An indium electroplating composition consisting of water; one or more sources of indium ions; one or more acids selected from the group consisting of inorganic acids, alkane sulfonic acids, and salts of the acids, wherein the inorganic acids are selected from the group consisting of sulfamic acid and sulfuric acid; and one or more amino acids selected from the group consisting alanine, arginine, aspartic acid, asparagine, glutamic acid, glycine, glutamine, leucine, histidine, lysine, threonine, isoleucine, serine, and valine; optionally one or more alloying metal; and optionally one or more pH adjuster.

2. The indium electroplating composition of claim 1, wherein the one or more amino acids are selected from the groups consisting of glycine, arginine, lysine, glutamine, serine, histidine and asparagine.

3. The indium electroplating composition of claim 1, wherein the one or more amino acids are in amounts of at least 5 g/L.

4. The indium electroplating composition of claim 3, wherein the one or more amino acids are in amounts of 10 g/L to 200 g/L.

5. The indium electroplating composition of claim 1, wherein the one or more acids are inorganic acids selected from the group consisting of sulfamic acid and sulfuric acid.

6. The indium electroplating composition of claim 1, wherein the one or more alloying metals is selected from the group consisting of tin, silver, bismuth and copper.

7. A method of electroplating indium on nickel comprising:

   a. providing a substrate comprising a nickel layer adjacent to a copper or copper alloy layer;
   b. contacting the substrate comprising the nickel layer adjacent to the copper or the copper alloy layer with an indium electroplating composition consisting of water; one or more sources of indium ions; one or more acids selected from the group consisting of inorganic acids, alkane sulfonic acids, and salts of the acids, wherein the inorganic acids are selected from the group consisting of sulfamic acid and sulfuric acid; and one or more amino acids selected from the group consisting alanine, arginine, aspartic acid, asparagine, glutamic acid, glycine, glutamine, histidine, leucine, lysine, threonine, isoleucine, serine, and valine; optionally one or more alloying metal; and one or more pH adjuster; and
   c. electroplating an indium layer adjacent to the nickel layer of the substrate with the indium electroplating composition.

8. The method of electroplating indium on nickel of claim 7, wherein the indium layer is greater than 0.1μm.

9. The method of electroplating indium on nickel of claim 8, wherein the indium layer is 0.2-1 μm.

10. The method of electroplating indium or indium alloy of claim 7, wherein the one or more amino acids are selected from the groups consisting of glycine, lysine, glutamine, histidine, serine, asparagine and arginine.

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EUROPEAN SEARCH REPORT

Application Number
EP 20 15 3749

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	T. S. DOBROVOLSKA ET AL: "Electrodeposition of gold-indium alloys", TRANSACTIONS OF THE INSTITUTE OF METAL FINISHING., vol. 93, no. 6, 2 November 2015 (2015-11-02), pages 321-325, XP055704843, GB ISSN: 0020-2967, DOI: 10.1080/00202967.2015.1117260	1-6	INV. C25D3/54 C25D3/56 C25D5/12 C25D5/50
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A	US 2018/298511 A1 (VAZHENIN GRIGORY [DE] ET AL) 18 October 2018 (2018-10-18) * paragraphs [0054] - [0077] * * examples 1,2 * -----	1-10	
A	US 9 809 892 B1 (QIN YI [US] ET AL) 7 November 2017 (2017-11-07) * column 3, line 33 - column 4, line 54 * * claim 1 * -----	1-10	**TECHNICAL FIELDS SEARCHED (IPC)** C25D
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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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