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(54) Plating bath and method

(57) Tin-containing electroplating baths having a combination of certain brightening agents provide tin-containing solder deposits having reduced void formation and smooth morphology.

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Description

[0001] The present invention relates generally to the field of electrolytic metal plating. In particular, the present invention relates to the field of electrolytic tin plating.

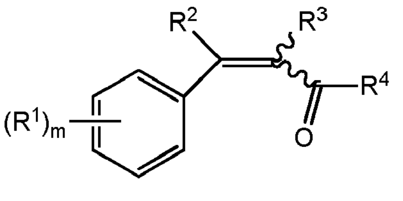
[0002] Metals and metal-alloys are commercially important, particularly in the electronics industry where they are often used as electrical contacts, final finishes and solders. The use of tin-lead, once the most common tin-alloy solder, has declined due to the increasing restrictions on lead. Lead-free solders, such as tin, tin-silver, tin-copper, tin-bismuth, tin-silver-copper, and others, are common replacements for tin-lead solders. These solders are often deposited on a substrate using a plating bath, such as an electroplating bath.

[0003] Methods for electroplating articles with metal coatings generally involve passing a current between two electrodes in a plating solution where one of the electrodes (typically the cathode) is the article to be plated. A typical tin plating solution comprises dissolved tin ions, water, an acid electrolyte such as methanesulfonic acid in an amount sufficient to impart conductivity to the bath, an antioxidant, and proprietary additives to improve the uniformity of the plating and the quality of the metal deposit. Such additives include surfactants and grain refiners, among others.

[0004] Certain applications for lead-free solder plating present challenges in the electronics industry. For example, when used as a capping layer on copper pillars, a relatively small amount of lead-free solder, such as tin-silver solder, is deposited on top of a copper pillar. In plating such small amounts of solder it is often difficult to plate a uniform height of solder composition on top of each pillar, both within a die and across the wafer. The use of known solder electroplating baths also results in deposits having a relatively rough surface morphology, for example, having a mean surface roughness (Ra) of about 800 nm or greater as measured by optical profilometry. Such relatively rough surface morphology often correlates with void formation in the solder after reflow, which ultimately creates concerns regarding solder joint reliability. Accordingly, there is interest in the industry for a pure tin or tin-alloy solder deposit which avoids the problem of a relatively rough surface morphology, and which provides improved within die uniformity.

[0005] Many tin electroplating baths are known. When lustrous surfaces are desired, brighteners are typically employed in the tin electroplating bath. Conventional brighteners include aldehydes, ketones, carboxylic acids, carboxylic acid derivatives, amines or mixtures thereof. For example, U.S. Pat. No. 4,582,576 discloses a tin or tin-lead electroplating bath containing at least one primary brightening agent selected from the group of aromatic aldehydes, acetophenones, and carbonyl compounds having the formula $Ar\text{-}C(H)=C(H)\text{-}C(O)\text{-}CH_3$ wherein Ar is phenyl, naphthyl pyridyl, thiophenyl or furyl, and at least one secondary brightening agent selected from the group of lower aliphatic aldehydes and substituted olefins of the formula $R_4C(R_3)=C(R_2)R_1$ wherein R_1 is a carboxy, carboxamide, alkali metal carboxylate, ammonium carboxylate, amine carboxylate or allyl carboxylate, and R_2, R_3 and R_4 are each independently hydrogen or lower alkyl groups. This patent discloses that such primary and secondary brightening agents are each used in relatively large amounts, that is, in tenths of grams or more per liter. When used in certain electronic applications, such conventional tin electroplating baths result in tin deposits having voids, such as when used to form a pure tin cap on a copper pillar, and/or result in tin deposits having unacceptable morphology, and/or result in deposits having a relatively high level of impurities. Accordingly, there remains a need in the industry for electroplating baths and methods for depositing a tin-containing solder layer, particularly as a cap on a copper pillar, that has both acceptable morphology and is substantially free of voids.

[0006] The present invention provides an electroplating composition comprising: a source of tin ions; an acid electrolyte; 0.0001 to 0.045 g/L of a first grain refiner; 0.005 to 0.75 g/L of an α,β-unsaturated aliphatic carbonyl compound as a second grain refiner; a nonionic surfactant; and water; wherein the first grain refiner is chosen from a compound of formula (1) or (2)



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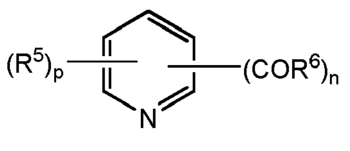


(2)

wherein each R^1 is independently $(C_{1\text{-}6})$alkyl, $(C_{1\text{-}6})$alkoxy, hydroxy, or halo; R^2 and R^3 are independently chosen from H and $(C_{1\text{-}6})$alkyl; R^4 is H, OH, $(C_1\text{-}_6)$alkyl or $O(C_1\text{-}_6)$alkyl; m is an integer from 0 to 2; each R^5 is independently $(C_{1\text{-}6})$alkyl; each R^6 is independently chosen from H, OH, $(C_1\text{-}_6)$alkyl, or $O(C_1\text{-}_6)$alkyl; n is 1 or 2; and p is 0, 1 or 2.

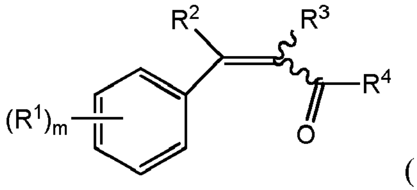
[0007] The present invention also provides a method of depositing a tin-containing layer on a semiconductor substrate comprising: providing a semiconductor wafer comprising a plurality of conductive bonding features; contacting the semiconductor wafer with the composition described above; and applying sufficient current density to deposit a tin-containing layer on the conductive bonding features.

[0008] Also provided by the present invention is a semiconductor device comprising a plurality of conductive bonding features and a tin-containing layer disposed on the bonding feature wherein the tin-containing layer is substantially free of voids as plated, and after reflow.

[0009] As used throughout this specification, the following abbreviations shall have the following meanings, unless the context clearly indicates otherwise: ASD = A/dm^2 = ampere per square decimeter; °C = degree Celsius; g = gram; mg = milligram; L = liter; Å = angstrom; nm = nanometer; μm = micron = micrometer; mm = millimeter; min = minute; DI = deionized; and mL = milliliter. All amounts are percent by weight ("wt%") and all ratios are weight ratios, unless otherwise noted. All numerical ranges are inclusive and combinable in any order, except where it is clear that such numerical ranges are constrained to add up to 100%.

[0010] As used throughout this specification, the term "plating" refers to metal electroplating. "Deposition" and "plating" are used interchangeably throughout this specification. "Pure tin" refers to a tin deposit that is not a tin-alloy, although such deposit may contain up to 5 atomic% of impurities. "Halide" refers to chloride, bromide, iodide and fluoride. The articles "a", "an" and "the" refer to the singular and the plural. "Alkyl" refers to linear, branched and cyclic alkyl. "Aryl" refers to aromatic carbocycles and aromatic heterocycles. The term "(meth)acrylic" refers to both "acrylic" and "methacrylic". When an element is referred to as being "disposed on" another element, it can be directly on the other element or intervening elements may be present therebetween. In contrast, when an element is referred to as being "disposed directly on" another element, there are no intervening elements present. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0011] Compositions of the present invention comprise: a source of tin ions; an acid electrolyte; 0.0001 to 0.045 g/L of a first grain refiner; 0.005 to 0.75 g/L of an α,β-unsaturated aliphatic carbonyl compound as a second grain refiner; a nonionic surfactant; and water; wherein the first grain refiner is chosen from a compound of formula (1) or (2)



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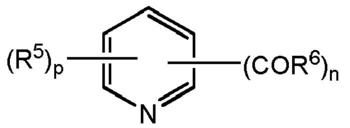


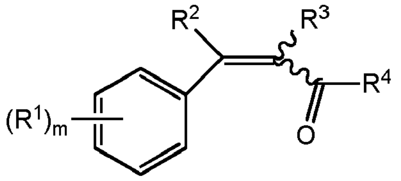
(2)

wherein each R^1 is independently (C_{1-6})alkyl, (C_{1-6})alkoxy, hydroxy, or halo; R^2 and R^3 are independently chosen from H and (C_{1-6})alkyl; R^4 is H, OH, (C_{1-6})alkyl or O(C_{1-6})alkyl; m is an integer from 0 to 2; each R^5 is independently (C_{1-6})alkyl; each R^6 is independently chosen from H, OH, (C_{1-6})alkyl, or O(C_{1-6})alkyl; n is 1 or 2; and p is 0, 1 or 2.

[0012] Any bath-soluble divalent tin salt may suitably be used as the source of tin ions. Examples of such tin salts include, but are not limited to, tin oxide and salts such as tin halides, tin sulfates, tin alkanesulfonate such as tin methanesulfonate and tin sulfonate, tin arylsulfonate such as tin phenylsulfonate, tin phenolsulfonate, tin cresolsulfonate, and tin toluenesulfonate, tin alkanolsulfonate, and the like. When tin halide is used, it is preferred that the halide is chloride. It is preferred that the tin compound is tin oxide, tin sulfate, tin chloride, tin alkanesulfonate or tin arylsulfonate. More preferably, the tin salt is the stannous salt of methanesulfonic acid, ethanesulfonic acid, propanesulfonic acid, 2-hydroxyethane-1-sulfonic acid, 2-hydroxypropane-1-sulfonic acid, 1-hydroxypropane-2-sulfonic acid, phenylsulfonic acid, toluenesulfonic acid, phenolsulfonic acid, or cresolsulfonic acid, and even more preferably methanesulfonic acid, phenylsulfonic acid or phenolsulfonic acid. Mixtures of tin salts may be used. The tin compounds useful in the present invention are generally commercially available from a variety of sources and may be used without further purification. Alternatively, the tin compounds useful in the present invention may be prepared by methods known in the literature. Typically, the amount of tin ions in the present composition is in the range of 10 to 300 g/L, preferably from 20 to 200 g/L, and more preferably from 30 to 100 g/L.

[0013] Any acid electrolyte that is bath-soluble and does not otherwise adversely affect the electrolyte composition may be used in the present invention. Suitable acid electrolytes include, but are not limited to: alkanesulfonic acids such as methanesulfonic acid, ethanesulfonic acid and propanesulfonic acid; arylsulfonic acids such as phenylsulfonic acid, toluenesulfonic acid, phenolsulfonic acid, and cresolsulfonic acid; alkanolsulfonic acids; sulfuric acid; sulfamic acid; and mineral acids such as hydrochloric acid, hydrobromic acid and fluoroboric acid. Alkanesulfonic acids and arylsulfonic acids are preferred acid electrolytes, and alkanesulfonic acids are more preferred. Methanesulfonic acid is particularly preferred. Mixtures of acid electrolytes are particularly useful, such as, but not limited to, mixtures of alkanesulfonic acids and sulfuric acid. Thus, more than one acid electrolyte may be used advantageously in the present invention. The acid electrolytes useful in the present invention are well-known and are generally commercially available and may be used without further purification. Alternatively, the acid electrolytes may be prepared by methods known in the literature. Typically, the amount of acid in the present compositions is in the range of 10 to 1000 g/L, preferably from 20 to 750 g/L, and more preferably from 30 to 500 g/L.

[0014] The present compositions comprise a mixture of a first grain refiner and a second grain refiner. The first grain refiner is chosen from a compound of formula (1) or (2)



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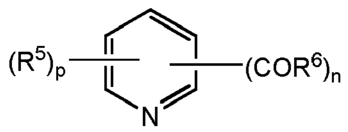


(2)

wherein each R^1 is independently (C_{1-6})alkyl, (C_{1-6})alkoxy, hydroxy, or halo; R^2 and R^3 are independently chosen from H and (C_{1-6})alkyl; R^4 is H, OH, (C_{1-6})alkyl or $O(C_{1-6})$alkyl; m is an integer from 0 to 2; each R^5 is independently (C_{1-6})alkyl; each R^6 is independently chosen from H, OH, (C_{1-6})alkyl, or $O(C_{1-6})$alkyl; n is 1 or 2; and p is 0, 1 or 2. Preferably, each R^1 is independently (C_{1-6})alkyl, (C_{1-3})alkoxy, or hydroxy, and more preferably (C_{1-4})alkyl, (C_{1-2})alkoxy, or hydroxy. It is preferred that R^2 and R^3 are independently chosen from H and (C_{1-3})alkyl, and more preferably H and methyl. Preferably, R^4 is H, OH, (C_{1-4})alkyl or $O(C_{1-4})$alkyl, and more preferably H, OH, or (C_{1-4})alkyl. It is preferred that R^5 is (C_{1-4})alkyl, and more preferably (C_{1-3})alkyl. Each R^6 is preferably chosen from H, OH, or (C_{1-6})alkyl, more preferably H, OH, or (C_{1-3})alkyl, and yet more preferably H or OH. It is preferred that m is 0 or 1, and more preferably m is 0. Preferably, n = 1. It is referred that p is 0 or 1, and more preferably p = 0. A mixture of first grain refiners may be used, such as 2 different grain refiners of formula 1, 2 different grain refiners of formula 2, or a mixture of a grain refiner of formula 1 and a grain refiner of formula 2. It is preferred that the first grain refiner is a compound of formula (1).

[0015] Exemplary compounds useful as the first grain refiner include, but are not limited to, cinnamic acid, cinnamaldehyde, benzylidene acetone, picolinic acid, pyridinedicarboxylic acid, pyridinecarboxaldehyde, pyridinedicarboxaldehyde, or mixtures thereof. Preferred first grain refiners include cinnamic acid, cinnamaldehyde, and benzylidene acetone.

[0016] The first grain refiner is present in the plating baths of the invention in an amount of 0.0001 to 0.045 g/L. Preferably, the first grain refiner is present in an amount of 0.0001 to 0.04 g/L, more preferably in an amount of 0.0001 to 0.035 g/L, and yet more preferably from 0.0001 to 0.03 g/L. Compounds useful as the first grain refiners are generally commercially available from a variety of sources and may be used as is or may be further purified.

[0017] The second grain refiner useful in the present plating baths is an α,β-unsaturated aliphatic carbonyl compound. Suitable α,β-unsaturated aliphatic carbonyl compound include, but are not limited to, α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid esters, α,β-unsaturated amides, and α,β-unsaturated aldehydes. Preferably, the second grain refiner is chosen from α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid esters, and α,β-unsaturated aldehydes, and more preferably α,β-unsaturated carboxylic acids, and α,β-unsaturated aldehydes. Exemplary α,β-unsaturated aliphatic carbonyl compounds include (meth)acrylic acid, crotonic acid, (C_{1-6})alkyl (meth)acrylate, (meth)acrylamide, (C_{1-6})alkyl crotonate, crotonamide, crotonaldehyde, (meth)acrolien, or mixtures thereof. Preferred α,β-unsaturated aliphatic carbonyl compounds are (meth)acrylic acid, crotonic acid, crotonaldehyde, (meth)acrylaldehyde or mixtures thereof.

[0018] The second grain refiner is present in the plating baths of the invention in an amount of 0.005 to 0.75 g/L. Preferably, the second grain refiner is present in an amount of 0.005 to 0.5 g/L, more preferably in an amount of 0.005 to 0.25 g/L, and yet more preferably from 0.01 to 0.25 g/L. Compounds useful as the second grain refiners are generally commercially available from a variety of sources and may be used as is or may be further purified.

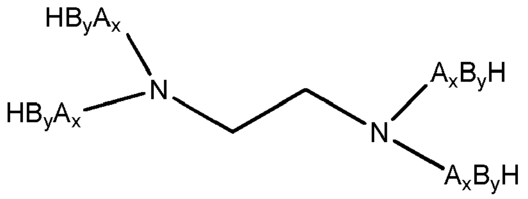
[0019] One or more nonionic surfactants are used in the present compositions. Typically, the nonionic surfactants have an average molecular weight of from 200 to 100,000, preferably from 500 to 50,000, more preferably from 500 to 25,000, and yet more preferably from 750 to 15,000. Such nonionic surfactants are typically present in the electrolyte compositions in a concentration of from 1 to 10,000 ppm, based on the weight of the composition, and preferably from 5 to 10,000 ppm. Preferred alkylene oxide compounds include polyalkylene glycols, including ethylene oxide/propylene oxide ("EO/PO") copolymers alkylene oxide condensation products of an organic compound having at least one hydroxy group and 20 carbon atoms or less, and tetrafunctional polyethers derived from the addition of different alkylene oxides to ethylenediamine compounds prepared by adding oxypropylene to polyoxyethylene glycol.

[0020] Typically, the polyalkylene glycols useful in the compositions are those having an average molecular weight in the range of 200 to 100,000, and preferably from 900 to 20,000. Preferred polyalkylene glycols are polyethylene glycol, and polypropylene glycol. Such polyalkylene glycols are generally commercially available from a variety of sources and may be used without further purification. Capped polyalkylene glycols where one or more of the terminal hydrogens are replaced with a hydrocarbyl group may also be suitably used. Examples of suitable polyalkylene glycols are those of the formula $R\text{-}O\text{-}(CXYCX'Y'O)_nR'$ where R and R' are independently chosen from H, (C_{2-20})alkyl group and (C_{6-20})aryl group; each of X, Y, X' and Y' is independently selected from hydrogen, alkyl such as methyl, ethyl or propyl, aryl such as phenyl, or aralkyl such as benzyl; and n is an integer from 5 to 100,000. Typically, one or more of X, Y, X' and Y' is hydrogen.

[0021] Suitable EO/PO copolymers generally have a weight ratio of EO:PO of from 10:90 to 90:10, and preferably from 10:90 to 80:20. Such EO/PO copolymers preferably have an average molecular weight of from 1000 to 15,000. Preferred EO/PO copolymers are block copolymers having the structure of EO/PO/EO or PO/EO/PO. Such EO/PO copolymers are available from a variety of sources, such as those available from BASF under the PLURONIC brand.

[0022] Suitable alkylene oxide condensation products of an organic compound having at least one hydroxy group and 20 carbon atoms or less include those having an aliphatic hydrocarbon of from one to seven carbon atoms, an unsubstituted aromatic compound or an alkylated aromatic compound having six carbons or less in the alkyl moiety, such as those disclosed in U.S. Pat. No. 5,174,887. The aliphatic alcohols may be saturated or unsaturated. Suitable aromatic compounds are those having up to two aromatic rings. The aromatic alcohols have up to 20 carbon atoms prior to derivatization with ethylene oxide. Such aliphatic and aromatic alcohols may be further substituted, such as with sulfate or sulfonate groups. Such suitable alkylene oxide compounds include, but are not limited to: ethoxylated polystyrenated phenol having 12 moles of EO, ethoxylated butanol having 5 moles of EO, ethoxylated butanol having 16 moles of EO, ethoxylated butanol having 8 moles of EO, ethoxylated octanol having 12 moles of EO, ethoxylated beta-naphthol having 13 moles of EO, ethoxylated bisphenol A having 10 moles of EO, ethoxylated sulfated bisphenol A having 30 moles of EO and ethoxylated bisphenol A having 8 moles of EO.

[0023] Formulae 3 and 4 represent nonionic surfactants which are tetrafunctional polyethers derived from the addition of different alkylene oxides to ethylenediamine:



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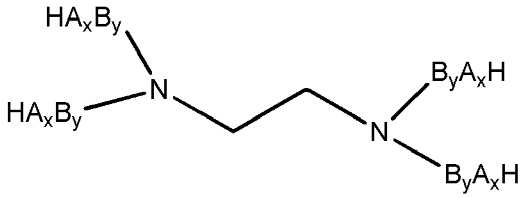

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where A and B represent different alkyleneoxy moieties, and x and y represent the number of repeat units of each alkylene oxide, respectively. Preferably, A and B are chosen from (C_{2-4})alkylene oxides, and more preferably from propyleneoxide and ethyleneoxide. The alkyleneoxy moieties in the compounds of formulae 1 and 2 may be in block, alternating or random arrangements. The mole ratio of x:y in formulae 3 and 4 is typically from 10:90 to 90:10, and preferably from 10:90 to 80:20. Such tetrafunctional polyethers are generally commercially available, such as from BASF (Ludwigshafen, Germany) under the TETRONIC brand.

[0024] In general, the present compositions contain water. The water may be present in a wide range of amounts. Any type of water may be used, such as distilled, DI or tap.

[0025] The present compositions may optionally include one or more additives, such as antioxidants, organic solvents, alloying metals, conductivity acids, complexers, and mixtures thereof. While additional grain refiners may be used in the present plating baths, it is preferred that the plating baths comprise only the first and second grain refiners as discussed above.

[0026] Antioxidants may optionally be added to the present composition to assist in keeping the tin in a soluble, divalent state. It is preferred that one or more antioxidants are used in the present compositions. Exemplary antioxidants include, but are not limited to, hydroquinone, and hydroxylated aromatic compounds, including sulfonic acid derivatives of such aromatic compounds, and preferably are: hydroquinone; methylhydroquinone; resorcinol; catechol; 1,2,3-trihydroxybenzene; 1,2-dihydroxybenzene-4-sulfonic acid; 1,2-dihydroxybenzene-3,5-disulfonic acid; 1,4- dihydroxybenzene-2-sulfonic acid; 1,4-dihydroxybenzene-2,5-disulfonic acid; and 2,4-dihyroxybenzene sulfonic acid. Such antioxidants are disclosed in U.S. Pat. No. 4,871,429. Other suitable antioxidants or reducing agents include, but are not limited to, vanadium compounds, such as vanadylacetylacetonate, vanadium triacetylacetonate, vanadium halides, vanadium oxyhalides, vanadium alkoxides and vanadyl alkoxides. The concentraion of such reducing agent is well known to those skilled in the art, but is typically in the range of from 0.1 to 10 g/L, and preferably from 1 to 5 g/L. Such antioxidants are generally commercially available from a variety of sources.

[0027] Optional organic solvents may be added to the present tin electroplating composition. Typical solvents useful in the present compositions are aliphatic alcohols. Preferred organic solvents are methanol, ethanol, n-propanol, isoproponol, n-butanol, and iso-butanol. Such solvent may be used in the present tin electroplating compositions in an amount if from 0.05 to 15 g/L, and preferably from 0.05 to 10 g/L.

[0028] Optionally, the present plating baths may contain one or more sources of alloying metal ions. Suitable alloying metals include, without limitation, silver, gold, copper, bismuth, indium, zinc, antimony, manganese and mixtures thereof.

Preferred alloying metals are silver, copper, bismuth, indium, and mixtures thereof, and more preferably silver. It is preferred that the present compositions are free of lead. Any bath-soluble salt of the alloying metal may suitably be used as the source of alloying metal ions. Examples of such alloying metal salts include, but are not limited to: metal oxides; metal halides; metal fluoroborate; metal sulfates; metal alkanesulfonates such as metal methanesulfonate, metal ethanesulfonate and metal propanesulfonate; metal arylsulfonates such as metal phenylsulfonate, metal toluenesulfonate, and metal phenolsulfonate; metal carboxylates such as metal gluconate and metal acetate; and the like. Preferred alloying metal salts are metal sulfates; metal alkanesulfonates; and metal arylsulfonates. When one alloying metal is added to the present compositions, a binary alloy deposit is achieved. When 2, 3 or more different alloying metals are added to the present compositions, tertiary, quaternary or higher order alloy deposits are achieved. The amount of such alloying metal used in the present compositions will depend upon the particular tin-alloy desired. The selection of such amounts of alloying metals is within the ability of those skilled in the art. It will be appreciated by those skilled in the art that when certain alloying metals, such as silver, are used, an additional complexing agent may be required. Such complexing agents (or complexers) are well-known in the art and may be used in any suitable amount.

[0029] Conductivity acids may optionally be added to the present compositions. Such conductivity acids include, but are not limited to, boric acid, alkanoic acids, hydroxyalkanoic acids, and salts of these acids to the extent they are water-soluble. Preferred are formic acid, acetic acid, oxalic acid, citric acid, malic acid, tartaric acid, gluconic acid, glucaric acid, glucuronic acid, and salts of these acids. When used, such conductivity acids and salts are employed in conventional amounts.

[0030] The electroplating compositions of the invention may be prepared by any suitable method known in the art. Typically, they are prepared by adding the acid electrolyte to a vessel, followed by one or more tin compounds, one or more surfactants, one or more grain refiners, optionally water and any other optional components. Other orders of addition of the components of the compositions may be used. Once the composition is prepared, any undesired material is removed, such as by filtration, and then water is added to adjust the final volume of the composition. The composition may be agitated by any known means, such as stirring, pumping, sparging or jetting the composition, for increased deposition speed.

[0031] Plating baths of the invention are acidic, that is, they have a pH of < 7. Typically, the pH of the present plating baths is from -1 to < 7, preferably from -1 to 6.5, more preferably from -1 to 5, and yet more preferably from -1 to 2.

[0032] The present electroplating compositions are suitable for depositing a tin-containing layer, which may be a pure tin layer or a tin-alloy layer. Exemplary tin-alloy layers include, without limitation, tin-silver, tin-silver-copper, tin-silver-copper-antimony, tin-silver-copper-manganese, tin-silver-bismuth, tin-silver-indium, tin-silver-zinc-copper, and tin-silver-indium-bismuth. Preferably, the present electroplating compositions deposit pure tin, tin-silver, tin-silver-copper, tin-silver-bismuth, tin-silver-indium, and tin-silver-indium-bismuth, and more preferably pure tin, tin-silver or tin-silver-copper. Alloys deposited from the present electroplating bath contain an amount of tin ranging from 0.01 to 99.99 wt%, and an amount of one or more alloying metals ranging from 99.99 to 0.01 wt%, based on the weight of the alloy, as measured by either atomic adsorption spectroscopy (AAS), X-ray fluorescence (XRF), inductively coupled plasma (ICP) or differential scanning calorimetry (DSC). Preferably, the tin-silver alloys deposited using the present invention contain from 75 to 99.99 wt % tin and 0.01 to 10 wt % of silver and any other alloying metal. More preferably, the tin-silver alloy deposits contain from 95 to 99.9 wt % tin and 0.1 to 5 wt % of silver and any other alloying metal. Tin-silver alloy is the preferred tin-alloy deposit, and preferably contains from 90 to 99.9 wt% tin and from 10 to 0.1 wt% silver. More preferably, the tin-silver alloy deposits contain from 95 to 99.9 wt% tin and from 5 to 0.1 wt% silver. For many applications, the eutectic composition of an alloy may be used. Alloys deposited according to the present invention are substantially free of lead, that is, they contain ≤ 1 wt% lead, more preferably ≤ 0.5 wt%, and yet more preferably ≤ 0.2 wt%, and still more preferably are free of lead.

[0033] The plating compositions of the present invention are useful in various plating methods where a tin-containing layer is desired, and particularly for depositing a tin-containing solder layer on a semiconductor wafer comprising a plurality of conductive bonding features. Plating methods include, but are not limited to, horizontal or vertical wafer plating, barrel plating, rack plating, high speed plating such as reel-to-reel and jet plating, and rackless plating, and preferably horizontal or vertical wafer plating. A wide variety of substrates may be plated with a tin-containing deposit according to the present invention. Substrates to be plated are conductive and may comprise copper, copper alloys, nickel, nickel alloys, nickel-iron containing materials. Such substrates may be in the form of electronic components such as lead frames, connectors, chip capacitors, chip resistors, and semiconductor packages; plastics such as circuit boards; and semiconductor wafers; and preferably are semiconductor wafers. Accordingly, the present invention also provides a method of depositing a tin-containing layer on a semiconductor wafer comprising: providing a semiconductor wafer comprising a plurality of conductive bonding features; contacting the semiconductor wafer with the composition described above; and applying sufficient current density to deposit a tin-containing layer on the conductive bonding features. Preferably, the bonding features comprise copper, which may be in the form of a pure copper layer, a copper alloy layer, or any interconnect structure comprising copper. Copper pillars are one preferred conductive bonding feature. Optionally, the copper pillars may comprise a top metal layer, such as a nickel layer. When the conductive bonding features have a top metal layer, then the pure tin solder layer is deposited on the top metal layer of the bonding feature. Conductive bonding features, such as bonding pads, copper pillars, and the like, are well-known in the art, such as described in U.S. Pat. No. 7,781,325, and in U.S. Pat. Pub. Nos. 2008/0054459, 2008/0296761, and 2006/0094226.

[0034] As used herein, the term "semiconductor wafer" is intended to encompass "an electronic device substrate," "a semiconductor substrate," "a semiconductor device," and various packages for various levels of interconnection, including a single-chip wafer, multiple-chip wafer, packages for various levels, or other assemblies requiring solder connections. Particularly suitable substrates are patterned wafers, such as patterned silicon wafers, patterned sapphire wafers and patterned gallium-arsenide wafers. Such wafers may be any suitable size. Preferred wafer diameters are 200 mm to 300 mm, although wafers having smaller and larger diameters may be suitably employed according to the present invention. As used herein, the term "semiconductive substrates" includes any substrate having one or more semiconductor layers or structures which include active or operable portions of semiconductor devices. The term "semiconductor substrate" is defined to mean any construction comprising semiconductive material, including but not limited to bulk semiconductive material such as a semiconductive wafer, either alone or in assemblies comprising other materials thereon, and semiconductive material layers, either alone or in assemblies comprising other materials. A semiconductor device refers to a semiconductor substrate upon which at least one microelectronic device has been or is being batch fabricated.

[0035] A substrate is plated with a tin-containing layer by contacting the substrate with the present compositions and applying a current density for a period of time to deposit the tin-containing layer on the substrate. Such contact is may be by placing the substrate to be plated in the plating bath composition, or pumping the plating bath composition onto the substrate. The substrate is conductive and is the cathode. The plating bath contains an anode, which may be soluble or insoluble. Potential is typically applied to the cathode. Sufficient current density is applied and plating performed for a period of time sufficient to deposit a tin-containing layer having a desired thickness on the substrate. Semiconductor wafers comprising a plurality of bonding features are electroplated by contacting the wafer with a plating bath of the present invention and applying a current density for a period of time to deposit a tin-containing layer on the plurality of bonding features. The semiconductor wafer functions as the cathode.

[0036] The particular current density used to deposit the tin-containing layer depends on the particular plating method, the substrate to be plated, and whether a pure tin or tin-alloy layer is to be deposited. Suitable current density is from 0.1 to 200 A/dm^2. Preferably the current density is from 0.5 to 100 A/dm^2, more preferably from 0.5 to 30 A/dm^2, even more preferably from 0.5 to 20 A/dm^2, and most preferably from 2 to 20 A/dm^2. Other current densities may be useful depending upon the particular bonding feature to be plated, as well as other considerations known to those skilled in the art. Such current density choice is within the abilities of those skilled in the art.

[0037] Tin-containing layers may be deposited at a temperature of 10° C or higher, preferably in the range of from 10 to 65° C, and more preferably from 15 to 40° C. In general, the longer the time the substrate is plated the thicker the deposit while the shorter the time the thinner the deposit for a given temperature and current density. Thus, the length of time a substrate remains in a plating composition may be used to control the thickness of the resulting tin-containing deposit. In general, metal deposition rates may be as high as 15 μm/min. Typically, deposition rates may range from 0.5 to 15 μm/min, and preferably from 1 to 10 μm/min.

[0038] While the present electrolyte compositions may be used for a variety of applications as described above, an exemplary application is for interconnect bump (solder bump) formation for wafer-level-packaging. This method involves providing a semiconductor die (wafer die) having a plurality of conductive bonding features (such as interconnect bump pads), forming a seed layer over the bonding features, depositing a tin-containing interconnect bump layer over the bonding features by contacting the semiconductor die with the present electroplating composition and passing a current through the electroplating composition to deposit the tin-containing interconnect bump layer on the substrate, and then reflowing the interconnect bump layer to form a solder bump. The conductive interconnect bump pad may be one or more layers of a metal, composite metal or metal alloy typically formed by physical vapor deposition (PVD) such as sputtering. Typical conductive bonding features comprise, without limitation, aluminum, copper, titanium nitride, and alloys thereof.

[0039] A passivation layer is formed over the bonding features and openings extending to the bonding features are formed therein by an etching process, typically by dry etching. The passivation layer is typically an insulating material, for example, silicon nitride, silicon oxynitride, or a silicon oxide, such as phosphosilicate glass. Such materials may be deposited by chemical vapor deposition (CVD) processes, such as plasma enhanced CVD. An under bump metallization (UBM) structure formed typically of a plurality of metal or metal alloy layers, is deposited over the device. The UBM acts as an adhesive layer and electrical contact base (seed layer) for an interconnect bump to be formed. The layers forming the UBM structure may be deposited by PVD, such as sputtering or evaporation, or CVD processes. Without limitations, the UBM structure may be, for example, a composite structure including in order, a bottom chrome layer, a copper layer, and an upper tin layer. Nickel is one metal used in UBM applications.

[0040] In general, a photoresist layer is applied to a semiconductor wafer, followed by standard photolithographic exposure and development techniques to form a patterned photoresist layer (or plating mask) having openings or vias therein (plating vias). The dimensions of the plating mask (thickness of the plating mask and the size of the openings in the pattern) defines the size and location of the tin-silver layer deposited over the I/O pad and UBM. The diameters of such deposits typically range from 5 to 300 μm, preferably from 10 to 150 μm. The height of such deposits typically range from 10 to 150 μm, preferably from 15 to 150 μm, and more preferably from 20 to 80μm. Suitable photoresist materials are commercially available (such as from Dow Electronic Materials, Marlborough, Massachusetts, USA) and are well-known in the art.

[0041] The interconnect bump material is deposited on the device by an electroplating process using the above-described electroplating compositions. Interconnect bump materials include, for example, pure tin or any suitable tin alloys. Exemplary tin alloys are those described above. It may be desired to use such alloys at their eutectic compositions, or at any other suitable compositions. The bump material is electrodeposited in the areas defined by the plating via. For this purpose, a horizontal or vertical wafer plating system, for example, a fountain plating system, is typically used with a direct current or pulse-plating technique. In the plating process, the interconnect bump material completely fills the via extending above and on a portion of the top surface of the plating mask, resulting in a mushroom-shaped metal deposit. This ensures that a sufficient volume of interconnect bump material is deposited to achieve the desired ball size after reflow. In the via plating process, the photoresist has a sufficient thickness such that the appropriate volume of interconnect bump material is contained within the plating mask via. A layer of copper or nickel may be electrodeposited in the plating via prior to plating the interconnect bump material. Such a layer may act as a wettable foundation to the interconnect bump upon reflow.

[0042] Following deposition of the interconnect bump material the plating mask is stripped using an appropriate solvent or other remover. Such removers are well known in the art. The UBM structure is then selectively etched using known techniques, removing all metal from the field area around and between interconnect bumps.

[0043] Alternatively, after plating vias are formed in the photoresist layer, a metal interconnect structure, such as a pillar, that is free of tin, may be deposited on the bonding features. Copper pillars are conventional. Typically, such metal deposition will stop before the plating via is completely filled. Such interconnect structures, such as copper pillars, may then be capped by a tin-containing layer by an electroplating process using the above-described electroplating compositions. The tin-containing layer is electrodeposited in the areas defined by the plating via. For this purpose, a horizontal or vertical wafer plating system, for example, a fountain plating system, is typically used with a direct current or pulse-plating technique. A layer of a top metal, such as nickel, may be electrodeposited in the plating via on top of the copper pillar prior to plating the tin-containing layer. Such a top metal layer may act as a wettable foundation to pure tin solder layer, and/or provide a barrier layer. The height of such tin-containing layer may range from 20 to 50 μm although other heights may be suitable, and has a diameter substantially equal to that of the interconnect structure on which it is deposited. Following deposition of the tin-containing solder layer, the plating mask is stripped using an appropriate solvent or other remover. Such removers are well known in the art. The UBM structure is then selectively etched using known techniques, removing all metal from the field area around and between interconnect bumps.

[0044] The wafer is then optionally fluxed and is heated in a reflow oven to a temperature at which the tin-containing solder layer melts and flows into a truncated substantially spherical shape. Heating techniques are known in the art, and include, for example, infrared, conduction, and convection techniques, and combinations thereof. The reflowed interconnect bump is generally coextensive with the edges of the UBM structure. The heat treatment step may be conducted in an inert gas atmosphere or in air, with the particular process temperature and time being dependent upon the particular composition of the interconnect bump material.

[0045] Tin-containing solders electodeposited from the present compositions are substantially free of voids when deposited (or plated), preferably these solders are substantially free of voids after one reflow cycle and preferably after repeated reflow cycles, such as after 3 reflow cycles, and more preferably after 5 reflow cycles. A suitable reflow cycle uses a Falcon 8500 tool from Sikama International, Inc., having 5 heating and 2 cooling zones, using temperatures of 140/190/230/230/260° C, with a 30 second dwell time, and a conveyor rate of ca. 100 cm/min. and a nitrogen flow rate of 40 cubic feet/hour. Alpha 100-40 flux (Cookson Electronics, Jersey City, New Jersey, USA) is a suitable flux used in this reflow process. As used herein, the term "voids" refers to both interfacial voids and voids within the bulk tin-containing layer. By "substantially free of voids" is meant that no void of a diameter larger than 3 μm, preferably 2 μm, and more preferably 1 μm, is visible using a Cougar microfocus X-ray system (YXLON International GmbH, Hamburg, Germany).

[0046] The present electroplating compositions also provide tin-containing solder deposits having a relatively smooth surface as plated, that is, the surface as plated has a mean surface roughness (R_a) of ≤ 200 nm, preferably ≤ 150 nm and even more preferably ≤ 100 nm, as measured using an optical profilometer (Leica DCM3D, Leica Microsystems GmbH, Wetzlar, Germany).

[0047] Example 1: An electroplating composition for depositing pure tin was prepared by combining 75 g/L tin (from tin methanesulfonate), 140 g/L methanesulfuonic acid, 8.8 g/L of an ethoxylated beta-naphthol nonionic surfactant, 9.7 g/L of an ethoxylated bisphenol A nonionic surfactant, 0.0166 g/L of benzylidene acetone as the first grain refiner, 0.1 g/L of methacrylic acid as the second grain refiner, 1.5 g/L of alcohol solvent, 1 g/L of a commercial antioxidant, and DI water (balance). The pH of the composition was < 1.

[0048] Example 2: The composition of Example 1 was used to deposit pure tin on a conductive bonding feature. Wafer segments of 4 cm x 4 cm with photoresist patterned vias of 75 μm (diameter) x 50 μm (depth) and pre-formed copper pillars of 37 μm height were immersed in a plating cell containing the composition of Example 1 and plated with a pure tin layer. Samples were plated in the bath at 8 A/dm^2. The temperature of the bath was at 25° C. An insoluble platinized titanium electrode was used as the anode, and the wafer segment was the cathode. Electroplating was done until a mushroom shaped tin cap of 23 μm height was plated on top of copper pillars. Morphology of the resulting tin layer was inspected with a Hitachi S2460™ scanning electron microscope. The pure tin deposits were uniform, smooth, compact, and free of nodules.

[0049] Example 3: An electroplating composition for depositing a tin-silver alloy was prepared by combining 75 g/L tin (from tin methanesulfonate), 0.65 g/L silver (from silver methanesulfonate), 104 g/L methanesulfuonic acid, 5 g/L of a tetrafunctional block copolymer derived from the sequential addition of EO and PO to ethylenediamine nonionic surfactant (EO:PO of approximately 40:60, TETRONIC 90R4), 0.0166 g/L of benzylidene acetone as the first grain refiner, 0.1 g/L of methacrylic acid as the second grain refiner, 0.6 g/L of a dithiaalkyldiol as a first silver complexing agent, 3.1 g/L of a mercaptotetrazole derivative as a second silver complexing agent, 1.5 g/L of alcohol solvent, 1 g/L of a commercial antioxidant, and DI water (balance). The pH of the composition was < 1.

[0050] Wafer segments of 4 cm x 4 cm with photoresist patterned vias of 75 μm (diameter) x 72 μm (depth) and a copper seed layer were immersed in a plating cell containing the tin-silver electroplating composition and plated with tin-silver bumps. Samples were plated in the bath at 8 A/dm^2. The temperature of the bath was at 25° C. An insoluble platinized titanium electrode was used as the anode. Electroplating was done until a bump of 60 μm was plated. The resulting tin-silver solder bump deposit was flat and had a smooth morphology with a mean surface roughness of 150 nm as measured using a Leica DCM3D optical profilometer. The tin-silver solder deposit was reflowed using a Falcon 8500 tool (Sikama International, Inc.) having 5 heating and 2 cooling zones, using temperatures of 140/190/230/230/260° C, with a 30 second dwell time, and a conveyor rate of ca. 100 cm/min. and a nitrogen flow rate of 40 cubic feet/hour. The solder deposits were fluxed with Alpha 100-40 flux. The reflowed tin-silver deposit was evaluated using a Cougar microfocus X-ray system (YXLON International GmbH, Hamburg, Germany) and was found to be free of voids.

[0051] Example 4: Various tin-alloy electroplating compositions are prepared by repeating the procedure of Example 3 and replacing the source of silver ions with the sources of metal ions listed in Table 1.

Table 1

Sample	Alloy	Source of Alloying Metal Ions
4-1	Sn-Bi	Bismuth methansulfonate (10 g/L Bi)
4-2	Sn-Cu	Copper methanesulfonate (0.3 g/L Cu)
4-3	Sn-Ag-Cu	Silver methanesulfonate (0.6 g/L Ag) Copper methanesulfonate (0.2 g/L Cu)
4-4	Sn-In	Indium methanesulfonate (50 g/L In)

[0052] Example 5: The electroplating composition of Examples 1 and 3 are repeated except that the grain refiners shown in Table 2 are used.

Table 2

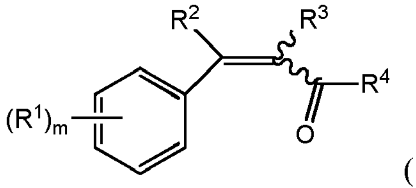
Sample	First Grain Refiner	Second Grain Refiner
5-1	Picolinic Acid (0.015 g/L)	Methacrylic acid (0.1 g/L)
5-2	Cinnamaldehyde (0.022 g/L)	Methacrylic acid (0.15 g/L)
5-3	Benzylidene Acetone (0.013 g/L)	Crotonic acid (0.25 g/L)
5-4	Cinnamaldehyde (0.008 g/L)	Methacrolein (0.35 g/L)
5-5	Pyridinycarboxaldehyde (0.005 g/L)	Methacrylic acid (0.35 g/L)
5-6	Cinnamic acid (0.025 g/L)	Acrolein (0.08 g/L)
5-7	Benzylidene Acetone (0.022 g/L)	Methacrolein (0.13 g/L)
5-8	Pyridinedicarboxylic acid (0.0075 g/L)	Crotonaldehyde (0.32 g/L)
5-9	Benzylidene Acetone (0.005 g/L)	Acrylic acid (0.4 g/L)

[0053] Comparative Example 1: The procedure of Example 3 was repeated except that the amount of the first grain refiner, benzylidene acetone, was 0.166 g/L. The resulting tin-silver bump deposit was significantly concave, and skewed to one side of the bump. Evaluation of the deposit by microfocus X-ray showed the formation of voids (> 3 μm) after one reflow of the deposit.

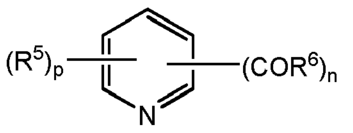
[0054] Comparative Example 2: The procedure of Example 3 was repeated except that no first grain refiner was used. The resulting tin-silver bump deposit was unacceptably rough, having a mean surface roughness (Ra) over 800 nm as measured by a Leica DCM3D optical profilometer.

Claims

1. An electroplating composition comprising: a source of tin ions; an acid electrolyte; 0.0001 to 0.045 g/L of a first grain refiner; 0.005 to 0.75 g/L of an α,β-unsaturated aliphatic carbonyl compound as a second grain refiner; a nonionic surfactant; and water; wherein the first grain refiner is chosen from a compound of formula (1) or (2)



(1)



(2)

wherein each R^1 is independently (C_{1-6})alkyl, (C_{1-6})alkoxy, hydroxy, or halo; R^2 and R^3 are independently chosen from H and $(C_1\text{-}_6)$alkyl; R^4 is H, OH, $(C_1\text{-}_6)$alkyl or $O(C_1\text{-}_6)$alkyl; m is an integer from 0 to 2; each R^5 is independently $(C_1\text{-}_6)$alkyl; each R^6 is independently chosen from H, OH, $(C_1\text{-}_6)$alkyl, or $O(C_1\text{-}_6)$alkyl; n is 1 or 2; and p is 0, 1 or 2.

2. The composition of claim 1 further comprising a source of alloying metal ions.

3. The composition of claim 1 wherein the α,β-unsaturated aliphatic carbonyl compound is chosen from α,β-unsaturated carboxylic acids, α,β-unsaturated carboxylic acid esters, α,β-unsaturated amides, and α,β-unsaturated aldehydes.

4. The composition of claim 3 wherein the α,β-unsaturated aliphatic carbonyl compound is chosen from (meth)acrylic acid, crotonic acid, $(C_1\text{-}_6)$alkyl (meth)acrylate, (meth)acrylamide, $(C_1\text{-}C_6)$alkyl crotonate, crotonamide, crotonaldehyde, or mixtures thereof.

5. The composition of claim 1 wherein the first grain refiner is chosen from cinnamic acid, cinnamaldehyde, benzylidene acetone, picolinic acid, pyridinedicarboxylic acid, pyridinecarboxaldehyde, pyridinedicarboxaldehyde, or mixtures thereof.

6. The composition of claim 1 wherein the first grain refiner is present in an amount of 0.001 to 0.04 g/L.

7. The composition of claim 1 wherein the nonionic surfactant comprises an alkoxylated amine moiety.

8. A method of depositing a tin-containing layer on a semiconductor substrate comprising: providing a semiconductor wafer comprising a plurality of conductive bonding features; contacting the semiconductor wafer with the composition of claim 1; and applying sufficient current density to deposit a tin-containing layer on the conductive bonding features.

9. The method of claim 8 wherein the bonding features comprise copper.

10. The method of claim 8 wherein the tin-containing layer on the bonding features is substantially free of voids as plated and after one reflow cycle.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4582576 A **[0005]**
- US 5174887 A **[0022]**
- US 4871429 A **[0026]**
- US 7781325 B **[0033]**
- US 20080054459 A **[0033]**
- US 20080296761 A **[0033]**
- US 20060094226 A **[0033]**