

NEAR NEUTRAL PH TIN ELECTROPLATING SOLUTION

Background of the Invention

The present invention relates to the deposition of metals and more specifically to the deposition of tin or tin-lead alloys on objects or articles composed of an electroplatable substrate, such as metal, or a composite article having electroplatable and non-electroplatable portions. Of particular interest herein are electrical components such as surface mounted capacitors and resistors that have metal portions as well as ceramic, glass, or plastic portions.

The size of electronic components has been dramatically reduced in recent years. This reduction in size has made these components significantly more difficult to electroplate. Additionally, many surface mount technology (SMT) components have sensitive ceramic portions which can be damaged by highly acidic or highly alkaline solutions. To avoid this problem, neutral or near neutral pH electroplating solutions are desirable.

Neutral or near neutral pH tin and tin/lead alloy electrolytes have been made in the past in an attempt to be compatible with sensitive ceramic SMTs. Examples include US patents 4,163,700, 4,329,207, 4,640,746, 4,673,470, 4,681,670 and Japanese patent application H02-301588. The formulations described in these patents include complexing agents of components such as citrates, gluconates, ascorbates or pyrophosphates to complex the tin and/or lead and render them soluble in the solutions at the elevated pHs required. These disclosure are not entirely suitable for their intended purposes, and certainly are less than desirable for use with current SMTs.

For example, Japanese patent application H02-301588 discloses that the baths should be operable over a wide pH range of 2 to 9, but the examples illustrate near neutral baths (i.e., a pH of 6 to 7.5). The baths of these examples were found to not be stable at pH values above 5.0. U.S. patent 4,163,700 includes a significant amount of ammonia in its baths and this ingredient can attack ceramic or glass portions of SMTs. US patents 4,640,746 and 4,681,670 indicate that problems are encountered with deposit quality at pHs greater than 5.5. Thus, improvements in the stability and deposit quality of these baths when operating above a pH of 5.5 is desired.

The present invention now provides a near neutral electroplating solution and process that overcomes these problems.

Summary of the Invention

The present invention relates to a solution for use in connection with the deposition of tin or tin alloys on platable portions of substrates. This solution comprises water; tin ions in an amount sufficient to provide a tin deposit on platable portions of substrates; a complexing agent of an acid or salt thereof that is stable at a pH of above 5.5 and below 10 present in an amount sufficient to render the metal ion soluble in the solution; and a surfactant of an alkoxyated polyalcohol present in an amount sufficient to facilitate deposition of tin upon the platable portions of the substrates. Advantageously, the solution has a pH in the range of about 6 to about 8, which pH is adjusted, if necessary, by the addition of a suitable pH adjusting agent.

Preferably, the tin ions are present as a solution soluble salt selected from the group consisting of tin alkane sulfonates, tin sulfates, or tin chlorides, and the complexing agent is selected from the group consisting of gluconic acid, an alkali or alkaline earth metal gluconate, heptagluconic acid, an alkali or alkaline earth metal heptagluconate, pyrophosphoric acid or an alkali or alkaline earth metal pyrophosphate.

An important component is the surfactant, and preferred polyalkoxyated polyalcohols include liquid alkoxyated polyols primarily based on pentaerythritol, trimethylolpropane or neopentyl glycol or mixtures thereof reacted with ethylene oxide, propylene oxide or mixtures thereof.

Also, advantages are provided when the surfactant and metal ion are present in a concentration ratio of between about 2:1 and 9:1 in that agglomeration of the substrates during plating is reduced or minimized. Preferably, the surfactant is present in an amount of between 25 and 200 g/l and the tin ions are present in an amount of between 5 and 100 g/l but at a ratio within the stated range.

If desired, a divalent lead salt can be provided in an amount sufficient to deposit a tin-lead alloy from the solution. In addition, antioxidation agent may be included in an amount sufficient to inhibit oxidation of the tin ions in the solution. Another optional additive is a conductivity salt in an amount sufficient to increase the conductivity of the solution, such as an alkali or alkaline metal sulfate, sulfonate, or acetate compound.

The invention also relates to a method for electroplating a tin deposit on platable portions of substrates which comprises contacting such substrates with a solution as described herein and passing a current through the solution to provide tin deposits on the platable portions of the substrates without causing significant agglomeration of such substrates during electroplating. Preferably, the substrates include electroplatable and non-electroplatable

portions and which further comprises passing current through the solution to provide tin deposits on the electroplatable portions of the substrates without deleteriously affecting the non-electroplatable portions of the substrates.

5 Detailed Description of the Preferred Embodiments

It has now been discovered that propoxylated or ethoxylated polyalcohols surfactants are effective at providing a semibright deposit at high current efficiencies at pH values above 5.5 and most preferably at a pH of between 6 and 8. At the most preferred pH range, the solution is particularly useful for electroplating substrates of composite articles that have
10 electroplatable portions and non-electroplatable portions without deleteriously affecting the non-electroplatable portions. This is significant because conventional additives used in tin or tin/lead alloy plating fail to provide an acceptable deposit in this pH range and also suffer from poor current efficiencies. The polyalcohol surfactants are used in conjunction with complexing agents which form stable complexes with tin and/or lead at those pH values to
15 provide a practical near neutral pH electroplating solution.

Surfactants which are typically utilized in tin or tin alloy electrolytes, such as soluble alkylene oxide condensation compounds, solution soluble quaternary ammonium-fatty acid compounds, solution soluble amine oxide compounds, solution soluble tertiary amine compounds or mixtures thereof, have been found to be ineffective in the higher pH range of
20 the current invention. To improve deposit crystalline structure and improve deposit quality at high current densities ethoxylated or propoxylated polyalcohols have been found effective at the higher pH range of the current invention.

The preferred surfactants include liquid alkoxyated polyols based on pentaerythritol, trimethylolpropane or neopentyl glycol reacted with ethylene oxide or propylene oxide. These
25 surfactants can be used in an amount of about 0.01 to 20 g/l and more preferably in concentrations from 0.5 to 5 g/l. One of ordinary skill in the art can perform routine testing to determine the most appropriate surfactants of this class and preferred concentration for any particular plating solution of the present invention.

Tin metal is generally added to the solution as a stannous alkyl sulfonate salt, a
30 stannous sulfate salt, a stannous chloride salt, a stannous gluconate salt, or stannous oxide and is present in an amount of between about 5 and 100 g/l and preferably is from 10 to 50 g/l. When lead metal is added for the purpose of depositing a tin-lead alloy, it may be added to the solution as a divalent lead alkyl sulfonate salt, such as lead methane sulfonic acid, or gluconate salt and is present in an amount of between about 0.5 and 10 g/l.

Preferred complexing agents include gluconic acid, heptagluconic acid and pyrophosphate. Any of the complexing agents disclosed herein can be used in this invention. Salts of these acids can also be used, with the preferred salts being the alkali or alkaline metal salts. Any of these agents can be used at a typical amount of about 25 to 200 g/l. The most preferred complexing agent is gluconic acid or a gluconate salt because these compounds have a relatively low cost and are readily available.

The amount of complexing agent present should at a minimum be sufficient to render the metals present in the solution soluble at the given pH of the solution but should not greatly exceed this amount. As such the amount of complexing agent required is proportional to the metal concentration. At a tin concentration of 15 g/l, for example, the preferred gluconic acid concentration is about 50 to 120 g/l. A skilled artisan can readily determine by routine experimentation the appropriate amounts of metal and complexing agent for any particular bath formulation or specific plating application.

The complexing agent is present in the solution in a specific concentration ratio to the tin or lead ions such that only the amount of complexing agent is just sufficient to complex the metals without providing significant excess amounts. While a small excess of free complexing agent may be present in the plating solution, large excesses must be avoided in order to prevent agglomeration of the substrates during electroplating. The exact ratio will depend on the complexer used as well as the solution pH. Typically, the ratio is above 2:1 but is less than 10:1. Useful ratios range from about 3:1 to no more than 9:1. The ratio in any specific case may be established by routine experimentation.

Any electroplatable substrates can be plated using the solutions of the present invention. Generally, these substrates are made of a metal such as copper, nickel, steel or stainless steel. In today's commercial products, many parts that require electroplating are being made in smaller and smaller sizes. In particular, electronic components are a typical example of such parts. Furthermore, these parts are composite articles that have electroplatable and non-electroplatable portions. While the metal portions are metals or metallic, the non-electroplatable parts are typically ceramic, glass or plastic. The present solutions are particularly useful for electroplating such composite articles.

The electroplating solutions should have a pH above 5.5 but below 10 preferably between 6 and 8 and most preferably between 6.5 and 7.5 so that the solution is compatible with the electronic components that are to be plated. When the components have metallic and inorganic portions, the preferred pH range enables metal to be deposited on the metallic

portions without adversely affecting the inorganic portions. Generally, very high or very low pH solutions will damage the ceramic portions of the composite articles to be plated.

These solutions preferably do not contain appreciable amounts of free acid or free base, although essentially any acid or base can be used for pH adjustment. Generally, since
5 the solution is acidic, a base or basic component is utilized to convert free acid to its corresponding salt. Preferred bases for this purpose include sodium, potassium hydroxide, ammonium hydroxide as well as many others.

The solution is formulated to be compatible with the substrates to be plated, and preferably to have no adverse effect on the substrates. When composite articles that have
10 electroplatable and non-electroplatable portions are to be plated, the solution should be formulated to not attack or crack the non-electroplatable portions of the substrates. A simple test can be used to determine substrate/solution compatibility. The articles to be plated can simply be immersed in the proposed solution for a period of time that is equal to or longer than that which is to be used for the plating process. The temperature of the solution can be
15 that which approximates the temperature of the solution during the plating process, or an elevated temperature can be used for an accelerated test. The parts are immersed in the solution for a desired time and then are recovered and weighed to determine weight loss that occurs due to attack of the articles by the solution during immersion.

For example, composite articles used for capacitor manufacture now are being made
20 with a low-fired ceramic. These ceramics contain a larger proportion of glass than conventional ceramics, and are more prone to attack during the plating process. The present solutions at the preferred pH ranges are quite compatible with these components. A particularly useful device for electroplating such electrical components is disclosed in U.S. patent 6,193,858, and need not be described further herein. To the extent necessary, the entire
25 content of that patent is expressly disclosed herein by reference thereto.

Improvements to the previously patented system have been disclosed in Published International Application WO02/053809, the entire content of which is expressly incorporated herein by reference thereto. The immersion of the plating chamber into the electrolyte, as disclosed in this application, represents a significant improvement in that external soluble
30 electrodes can now be used.

It has been found that electrolytes which contain the complexing agents of the present invention are capable of electrodepositing tin or tin-lead alloys while minimizing the fusing or coupling of the electroplated parts, as well as without deleteriously affecting the non-electroplatable portions of the articles. In this regard, these electrolytes are superior to those

of the prior art, and in particular to baths that are citrate based. The complexing agent serves to maintain the tin and/or lead in solution at the pH of the electrolyte.

The conductivity of the solution maybe increased if necessary by the additional of a salt. If a pure tin solution is desired, a simple salt such as potassium sulfate may be used. If a tin-lead alloy is desired, potassium methanesulfonate or potassium acetate would be appropriate. Metal sulfide salts can also be used if desired. Any of these salts may be used to promote anode dissolution and assist in electrodeposition.

The pH can be raised by the addition of caustic, for example potassium hydroxide, ammonium hydroxide, sodium hydroxide or the like, or can be lowered with an acid such as sulfuric or methanesulfonic. An alkane or alkanol sulfonic acid, such as methanesulfonic acid, is preferred for tin-lead alloy solutions, since sulfuric acid can generate lead sulfate which is insoluble in the solution and which would tend to precipitate. Furthermore, the amount of complexing agent should not be in great excess to that needed to complex the tin in order to inhibit and minimize agglomeration.

Typical antioxidants used in tin and tin-lead solutions may be included in the solution of the present invention (e.g., catechol or hydroquinone as disclosed in US patent 4,871,429).

EXAMPLE

A pure tin electrodeposit is obtained from the following solution and under the following electroplating conditions.

Tin (as a methanesulfonic acid salt)	15 g/l	
Gluconic Acid	100 g/l	(Concentration ratio 6.67:1)
Propoxylated polyalcohol	3 g/l	
The pH was adjusted with KOH to 6.7.		
Temperature	110 F	

The above solution will deposit semi-bright tin at current densities of up to 20 ASF.

THE CLAIMS

What is claimed is:

- 5 1. A solution for use in connection with the deposition of tin or tin alloys on
platable portions of substrates, which comprises:
 water;
 tin ions in an amount sufficient to provide a tin deposit on platable portions of
substrates;
10 a complexing agent of an acid or salt thereof that is stable at a pH of above 5.5 and
below 10 present in an amount sufficient to render the metal ion soluble in the solution; and
 a surfactant of an alkoxyated polyalcohol present in an amount sufficient to facilitate
deposition of tin upon the platable portions of the substrates;
 wherein the solution has a pH in the range of above 5.5 to below 10, adjusted, if
15 necessary, by the addition of a suitable pH adjusting agent.
2. The solution of claim 1 wherein the tin ions are present as a solution soluble
salt selected from the group consisting of tin alkane sulfonates, tin sulfates, or tin chlorides.
- 20 3. The solution of claim 1 wherein the complexing agent is selected from the
group consisting of gluconic acid, an alkali or alkaline earth metal gluconate, heptagluconic
acid, an alkali or alkaline earth metal heptagluconate, pyrophosphoric acid or an alkali or
alkaline earth metal pyrophosphate.
- 25 4. The solution of claim 1 wherein the surfactant is a liquid alkoxyated polyol
based on a pentaerythritol, trimethylolpropane, neopentyl glycol or a mixture thereof reacted
with ethylene oxide, propylene oxide or mixtures thereof.
5. The solution of claim 1 wherein the surfactant is present in an amount of
30 between about 0.01 and about 20 g/l.
6. The solution of claim 1 having a pH of between 6 and 8.

7. The solution of claim 1 wherein the complexing agent and metal ion are present in a concentration ratio of between about 2:1 and 9:1 to reduce or minimize agglomeration of the substrates during plating.

5 8. The solution of claim 1 wherein the complexing agent is present in an amount of between 25 and 200 g/l and the tin ions are present in an amount of between 5 and 100 g/l.

9. The solution of claim 1 further comprising a divalent lead salt in an amount sufficient to deposit a tin-lead alloy from the solution.

10 10. The solution of claim 1 which further comprises an antioxidation agent in an amount sufficient to inhibit oxidation of the tin ions in the solution.

11. The solution of claim 1 which further comprises a conductivity salt in an
15 amount sufficient to increase the conductivity of the solution.

12. The solution of claim 11, wherein the conductivity salt is an alkali or alkaline metal sulfate, sulfonate, or acetate compound.

20 13. The solution of claim 1, further comprising an agent to promote anode dissolution.

14. The solution of claim 13, wherein the anode dissolution agent is potassium methane sulfonate, ammonium chloride or a metal sulfide salt.

25 15. A method for electroplating a tin deposit on platable portions of substrates which comprises contacting such substrates with the solution of claim 1 and passing a current through the solution to provide tin deposits on the platable portions of the substrates without causing significant agglomeration of such substrates during electroplating.

30 16. The method of claim 15 wherein the substrates include electroplatable and non-electroplatable portions and which further comprises passing current through the solution to provide tin deposits on the electroplatable portions of the substrates without deleteriously affecting the non-electroplatable portions of the substrates.