

Regeneration Method For A Plating Solution

Specification:

5 The invention relates to a method of depositing a layer of metal, more specifically a layer containing tin, above all for fabricating printed circuit boards and other electrical circuit carriers, and to a method of regenerating a solution containing metal ions in a high oxidation state, more specifically Sn(IV) ions. The plating method is mainly intended for utilization in the production of
10 solderable layers and etch-resist layers as well as in the deposition by cementation of layers of tin onto conductive patterns made of copper more specifically on the inner layers of printed circuit boards in order to bond said inner layers together.

15 For fabricating printed circuit boards, layers of tin and tin alloys, more specifically tin-lead coatings are deposited onto the copper surfaces to serve diverse purposes.

20 On the one side, tin-lead alloy coatings serve as solder pads on the surface of the printed circuit board at the places at which electronic component parts are to be soldered. In this case, such layers are deposited locally in those regions in which leads or other connecting elements of the component parts are to be electrically connected to the copper surface. After the solder regions are formed on the copper surfaces, the components are mounted on the solder
25 pads where they are bonded. Next, the solder is remelted in an oven to allow the electrical interconnections to form.

30 Layers of tin may also be used as etch-resist layers, e.g., to form metal patterns on the surfaces of the printed circuit boards. For this purpose, a negative image of the conductive pattern is at first formed on the copper surfaces by means of a photo-patternable resist. Then, the layers of tin or of

tin-lead alloy are deposited in the canals of the resist layer. After the resist is removed, bare copper may be removed by etching so that it is only the circuit traces and all the other metal patterns on the surfaces of the printed circuit board that remain below the layer of tin or tin-lead.

5

Furthermore, tin layers are also utilized as intermediate layers between the copper surfaces of the inner layers of multilayered circuit boards and the areas of the dielectric (usually glass fiber reinforced layers of resin). For to provide tight bonding of the copper areas with the dielectric, it is necessary to roughen the copper surfaces prior to pressing in order to achieve sufficient bonding strength between copper and resin. To accomplish this, the surfaces have heretofore been superficially oxidized by a so called black oxide treatment. However, the thereby formed oxide layer is not sufficiently resistant to acids so that the inner layers, which have been cut in the process of drilling the PCB material, are delaminated from the resin of the PCB material, forming delaminations. This problem is avoided when tin layers are used instead of the black oxide layers. For production, the tin layers are directly deposited by cementation onto the copper surfaces of the circuit traces. In post-treatment, if necessary, further bonding compounds are applied to the tin layers (e.g., a mixture of an ureidosilane and a disilane cross-linking agent (EP 0 545 216 A2)) before the inner layers are pressed together by action of heat and pressure.

10

15

20

25

30

Whereas, in the second application mentioned, the layers of tin or tin-lead alloy, respectively, can be electrolytically deposited as no electrically isolated metal regions have to be tin-plated, in the first and in the last mentioned case tin cannot be deposited by means of an electrolytic method since the copper areas to be metal plated usually are electrically mutually isolated so that it is hardly possible to establish an electric contact. For this reason, so called cementation baths are at hand for tin-plating.

A plating bath of this type is described in U.S. Patent No. 4,715,894. In addition

to a Sn(II) compound, this bath also contains a thiourea compound and an urea compound. According to EP 0 545 216 A2, thiourea, urea and the derivatives thereof may also be used as alternatives. Furthermore, the solution in accordance with U.S. Patent No. 4,715,894 also contains a complexing agent, a reducing agent and an acid. Accordingly, the Sn(II) compound used is SnSO₄ for example. According to EP 0 545 216 A2, the bath contains Sn(II) compounds of inorganic (mineral) acids, for example compounds of acids containing sulfur, phosphorus and halogen, or of organic acids such as Sn(II) formate and Sn(II) acetate for example. According to EP 0 545 216 A2, the Sn(II) salts of the acids containing sulfur are preferred i.e., the salts of sulfuric acid and of sulfamic acid. Furthermore, the bath may also contain alkali metal stannates such as sodium stannate or potassium stannate. Moreover, the thiourea and the urea compounds are, in the simplest case, the unsubstituted derivatives of thiourea and urea, respectively. According to EP 0 545 216 A2, Cu(I) ions complexed with thiourea are to form onto the copper surfaces when tin is deposited. Concurrently, metallic tin is deposited by reduction of Sn(II) ions. In this reaction, copper is dissolved, a tin coating being simultaneously formed on the copper surfaces.

EP 0 545 216 A2 reports that the Cu(I) thiourea complex enriches in the solution. Sn(IV) ions also enrich in the solution through oxidation of Sn(II) ions as oxygen from the air is carried into the solution. However, the concentrations of the Cu(I) thiourea complex and of the Sn(IV) ions do not exceed stationary concentration values when the printed circuit boards are merely immersed into the solution for treatment, since the bath solution is permanently drained away by the boards and diluted with water that has been carried over. If however, the bath fluid is sprayed onto the copper surfaces by way of spray nozzles, the rate of substance turnover, related to the volume of the bath, is considerably higher. Under these conditions, the concentration of the Cu(I) thiourea complex increases to such an extent that the limit of its solubility is reached and the complex precipitates as a deposit. The deposit clogs the nozzles and causes problems in the movable mechanical parts of the plant. In the plating bath,

Sn(IV) compounds are also increasingly formed by oxidation of the Sn(II) ions through oxygen from the air as air is carried to a greater extent into the bath solution by spraying the latter onto the printed circuit boards.

5 To mitigate these problems, the following provisions have been described in the publication mentioned: to reduce the concentration of the Cu(I) thiourea complex, part of the solution of the plating bath is taken from the treatment container to another tank where it is left to cool down so that a large part of the complex precipitates and can thus be separated. The solution, which is now
10 largely freed from the complex, may then be returned to the treatment container. To further lower the concentration of the Sn(IV) ions in the plating solution, there is provided a reservoir for the plating solution that contains metallic tin. The solution contained in said reservoir is sprayed onto the copper surfaces, the Sn(II) ions being reduced according to the reaction equation (1)
15 set forth below, and metallic copper simultaneously oxidizing to form Cu(I) ions according to reaction equation (2) which is also set forth below. A complex with thiourea or with the derivatives thereof, respectively, is formed thereby. Simultaneously, through the oxygen carried into the solution, part of the Sn(II) ions oxidizes to form Sn(IV) ions according to the reaction equation (3) set forth
20 below. The sprayed solution is next returned to the reservoir. There, the Sn(IV) ions react with the metallic tin to form the double quantity of Sn(II) ions according to the reaction equation (4) set forth below.

The method of regenerating tin-plating cementation baths described in
25 EP 0 545 216 A2 proved however to cause the concentration of tin contained in the solution to rise continuously. Therefore, the concentration of Sn(II) ions in the solution must be subjected to permanent analytic control. This is often not easily possible under manufacturing conditions and often readily causes the concentration to vary greatly. As a result thereof, the deposition of tin can
30 become uncontrollable. This is not acceptable. One approach to overcoming this problem could involve automated monitoring of the concentration of Sn(II) ions and permitting or obviating contact between the plating solution and

metallic tin in the reservoir when a predetermined range of reference values is exceeded or not reached, respectively. This is very complicated though and requires quite complicated devices.

5 It is therefore an object of the present invention to overcome the problems mentioned and to find means permitting tin plating of copper surfaces by cementation without variations of the Sn(II) ions content affecting the deposition of tin. It is aimed at making this possible without the use of complicated devices.

10

A solution to this object is the plating method of claim 1 and the regeneration method of claim 14. Preferred embodiments of the invention are indicated in the subordinate claims.

15 The plating method in accordance with the invention serves to produce layers of metal, more specifically layers containing tin and preferably layers of pure tin. The method can also be utilized for depositing layers consisting of a tin alloy. It involves the following method steps:

20 a. Providing a metal plating bath, more specifically a tin plating bath; containing metal ions in a low oxidation state, more specifically Sn(II) ions,

b. Depositing a metal layer from the metal plating bath onto a work piece;

25 c. Providing an electrolytic regeneration cell comprised of at least one auxiliary cathode and of at least one auxiliary anode;

d. Electrolytically depositing, in the electrolytic regeneration cell, metal serving for regeneration, more specifically metallic tin, from the metal plating bath onto the at least one auxiliary cathode;

30 e. Bringing the metal plating bath into contact with the metal serving for regeneration in an effort to reduce metal ions in a high oxidation state contained in the metal plating bath, more specifically Sn(IV) ions, to

metal ions in a low oxidation state, more specifically Sn(II) ions.

The regeneration method of the invention serves to regenerate solutions containing metal ions in a high oxidation state, more specifically Sn(IV) ions in order to reduce the metal ions in the high oxidation state to metal ions in a low oxidation state, more specifically to Sn(II) ions. This comprises the following method steps:

- a. Providing an electrolytic regeneration cell comprised of at least one auxiliary cathode and of at least one auxiliary anode;
- b. Electrolytically depositing, in the electrolytic regeneration cell, metal serving for regeneration, more specifically metallic tin, from the solution onto the at least one auxiliary cathode;
- c. Bringing the solution into contact with the metal serving for regeneration in an effort to reduce metal ions in the high oxidation state, more specifically Sn(IV) ions, to metal ions in the low oxidation state, more specifically Sn(II) ions.

When hereinafter layers containing tin, a tin plating bath or a tin plating solution, metallic tin, Sn(II) ions, Sn(IV) ions and a tin electrode or an electrode containing tin, respectively, are referred to, this should also apply generally and in lieu of to metal layers, a metal plating bath, metal, metal ions in a low oxidation state, metal ions in a high oxidation state, a metal electrode or an electrode containing metal, respectively.

The methods of the invention may more specifically be utilized for electroless deposition of tin or tin alloys utilizing a reduction agent, for the electrolytic deposition of tin and tin alloys and for the deposition by cementation of tin or tin alloys.

By a method of deposition by cementation a method is meant by which the metal to be deposited receives from the substrate metal the electrons needed

for the reduction to the oxidation state zero, said substrate metal concurrently oxidizing and being preferably dissolved thereby.

5 The method of the invention more specifically serves to coat copper surfaces on printed circuit boards or other circuit carriers with tin containing layers.

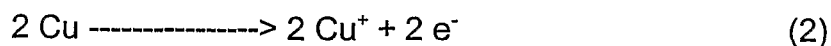
10 In the method described in EP 0 545 216 A2, metallic tin is added to the plating solution contained in the reservoir in order to convert Sn(IV) ions to Sn(II) ions. By contrast, with the method of the invention, the metallic tin utilized for regeneration is produced by electroplating it from the very tin plating bath. The method of the invention thus permits to avoid variations in the concentration of Sn(II) ions contained in the plating bath. This can be explained as follows:

15 When tin is deposited from an electroless, cementation or electrolytic tin bath, the following reaction takes place:



20 In electrolytic deposition, the electrons originate from an external source of electric current and are delivered to the Sn(II) ions via the cathode. In the case of electroless tin plating, the electrons needed for depositing the metal are provided by a reduction agent. In deposition by cementation, the electrons originate from the dissolving base metal, in the present case copper, onto which tin is deposited:

25



In an interfering side reaction, Sn(II) ions oxidize in these baths, through the oxygen from the air, to form Sn(IV) ions:

30



The Sn(IV) ions formed tend to precipitate tinstone (SnO_2). The problems related therewith are, *inter alia* that spray nozzles for delivering the plating solution to the copper surfaces may clog and that the function of movable parts in the processing plant may be impaired or the parts may even be damaged by precipitating solid matter. Furthermore, the Sn(IV) ions also have the disadvantageous property that the layer of tin, freshly deposited according to the reaction equation (1), is attacked by the Sn(IV) ions according to the reaction equation (4) set forth herein below, so that it may be dissolved again, at least partially.

In contacting the plating solution with metallic tin, Sn(IV) ions contained in the solution are reduced to Sn(II) ions according to the equation set forth below for this reaction, metallic tin being dissolved in the process (comproportionation):



This means that for each Sn(IV) ion formed, two Sn(II) ions are formed. As a result thereof, the concentration of tin contained in the plating solution increases gradually when the regeneration method according to EP 0 545 216 A2 is applied.

By contrast, in carrying out the method of the invention, the metallic tin used for reducing the Sn(IV) ions originates through electrolytic deposition from the very tin plating solution. As a result thereof, the tin balance of the bath is not disturbed by the regeneration according to equation (4). As the metallic tin used for regeneration is also formed from Sn(II) ions according to equation (1), and hence the concentration of the Sn(II) ions being lowered at first by electrolytic deposition, the Sn(II) ions consumed both through this reaction (1) and through the side reaction (3) are produced again by the regeneration reaction (4). The Sn(II) ions content therefore remains constant.

The method of the invention therefore permits to avoid the detrimental

consequences resulting from the formation of Sn(IV) ions and to concurrently regenerate the Sn(II) ions from the Sn(IV) ions without complicated devices and analytic expenditure.

- 5 The plating solution substantially contains at least one Sn(II) compound, at least one compound from the group comprising thiourea, urea and the derivatives thereof as well as at least one acid. If a tin alloy is deposited, the solution additionally contains at least one salt of the metal to be deposited additionally, e.g., one or more nickel, lead, mercury and/or gold salts.
- 10 Furthermore, the tin plating solution may also contain complexing agents, reducing agents as well as other component parts, like stabilizing agents for controlling deposition and for making sure that the plating solution be stable to decomposition, as well as surface-active agents. Usually, the solution is aqueous, i.e., the solvent contained in the solution consists of at least
- 15 50 percent by volume of water. It may also contain organic solvents like for example alcohols and ether esters.

The Sn(II) compound is preferably a Sn(II) salt of an inorganic (mineral) acid, e.g., of an acid containing sulfur, phosphorus and/or halogen; hydrogen halides

20 however should be avoided because of their corrosive effect and their tendency to incorporate tin halides into the deposited tin. Furthermore, the Sn(II) compound may also be the Sn(II) salt of an organic acid, e.g., of Sn(II) formate, Sn(II) acetate and the homologues thereof and the salt of an aromatic acid, more specifically of Sn(II) benzoate. The preferred salts are the Sn(II)

25 salts of the acids containing sulfur, i.e., the salts of the sulfuric acid and of the sulfamic acid (SnSO_4 and $\text{Sn}(\text{OSO}_2\text{NH}_2)_2$). The solution may furthermore contain alkali metal stannates such as sodium stannate or potassium stannate.

If a tin alloy is deposited, the tin plating solution additionally contains at least

30 one compound of the other alloying metals, for example a nickel, lead, mercury and/or gold salt; the anions of these salts can be the same as those utilized for the tin salts.

With respect to the Sn(II) compounds and to the compounds of other alloying metals, reference is made to U.S. Patent No. 4,715,894. The compounds disclosed therein are incorporated herein by reference as a disclosure.

5 The acid contained in the tin plating solution preferably is a mineral acid but may also be an organic acid, the anion of the acid being generally identical with that of the tin salt and, if necessary, with that of the salts of the other alloying metals.

10 The compounds of thiourea and urea used are more specifically the unsubstituted derivatives (thiourea, urea), the solution generally containing only thiourea and/or the derivatives thereof. U.S. Patent No. 4,715,894 indicates suitable derivatives of thiourea and of urea. The derivatives disclosed therein are incorporated herein by reference as a disclosure.

15 The tin plating solution can also contain complexing agents, those indicated in Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Edition, Volume 5, pages 339 - 368 being particularly suited. The complexing agents disclosed therein are incorporated herein as a disclosure. More specifically, amino
20 carboxylic acids and hydroxy carboxylic acids may be used. U.S. Patent No. 4,715,894 discloses certain examples of suitable compounds. The complexing agents disclosed therein are incorporated herein by reference as a disclosure.

25 The solution may also contain reducing agents, aldehydes, e.g., formaldehyde and acetaldehyde being more specifically utilized. Further reducing agents are indicated in U.S. Patent No. 4,715,894. The reducing agents disclosed therein are incorporated herein by reference as a disclosure.

30 Anionic, cationic and amphoteric surface-active agents may be used alike. It only matters that the surface-active agents are suited to reduce the surface tension of the plating solution sufficiently.

The metallic tin used for regeneration may be deposited onto an inert auxiliary cathode. By inert cathode, a separate electrode is meant which consists of a material that resists dissolution in the tin plating solution when the electrode is subjected to anodic polarization. More specifically, the auxiliary cathode can be made of platinized titanium.

The auxiliary cathode can be configured as a plate, a tube, expanded metal or as a formed body like for example a plate provided with ribs. The auxiliary cathode may also be shaped in smaller pieces, e.g., in the shape of spheres having for example a diameter of some few millimeters to some few centimeters. In the latter case, these pieces may be accommodated in a separate container for example, the plating solution flowing through said container. For this purpose, the pieces may for example be placed on a perforated bottom plate accommodated in a tower, the plating solution entering through said bottom plate and flowing through said tower. Configuring the auxiliary cathode in the form of smaller pieces permits to considerably increase the conversion rate of the Sn(IV) ions to Sn(II) ions.

If an inert auxiliary cathode is made use of, the maximum quantity of tin that can be dissolved again in the regeneration reaction according to reaction equation (4) is that amount that had been previously deposited from the bath. As a result thereof, the bath can be regenerated continuously without complicated analytical bath monitoring and, by contrast to the method according to EP 0 545 216 A2, the concentration of tin in the bath does not rise.

If, for depositing tin onto platinized titanium for example, the cathodic current density set for the auxiliary cathode is sufficiently high (e.g., 8 A/dm²), a tin coating in the form of flat scale crystals is obtained. This crystal shape has a very large surface which is well suited for the regeneration reaction according to equation (4) since it provides a very large surface referred to the weight of tin. As a result thereof, a large surface of deposited tin can be provided in a

predetermined volume of plating solution. A similar scale deposition is also observed when a high current density is produced on the auxiliary cathode when said auxiliary cathode is made of copper or of a copper alloy, for example with silver. The advantage of copper over inert materials, for example platinized titanium, is that copper is less expensive. The durable life of this material in a chemical tin plating solution is limited though.

The auxiliary cathode is in electric contact with the plating solution. An auxiliary anode, which is in direct electric contact with the plating solution or which is in electric contact with the plating solution via another solution, is also provided. By application of voltage between the auxiliary cathode and the auxiliary anode, a flow of current can be generated between these two electrodes, the auxiliary cathode being polarized cathodically and the auxiliary anode being polarized anodically when tin is to be deposited onto the auxiliary cathode. If tin deposited onto the auxiliary cathode is directly utilized to regenerate the tin plating solution, the auxiliary cathode is not to be polarized cathodically during the actual regeneration process in order to allow the tin to dissolve from the auxiliary cathode. Therefore, with this method, the auxiliary cathode is only polarized cathodic intermittently each time tin is to be deposited onto the auxiliary cathode. As soon as enough tin has been deposited onto the auxiliary cathode, the electrical connection between the auxiliary cathode and the auxiliary anode is interrupted in order to halt the deposition process. Then, the dissolution reaction according to equation (4) of this reaction takes place under these conditions, the plating solution having to be contacted with the auxiliary cathode. As soon as but a small amount of tin or no tin at all is left at the auxiliary cathode, tin can again be deposited onto said electrode.

For the regeneration reaction, metallic tin formed on the auxiliary cathode may either be used directly in contacting the plating solution with the auxiliary cathode coated with metallic tin or be removed mechanically from said electrode and be contacted with the tin plating solution after removal thereof.

To mechanically remove the tin deposited onto the auxiliary cathode, the auxiliary cathode is preferably taken out of the plant and the scales of metal that have grown thereon are stripped off. The removed tin may then be placed into the container for treating the printed circuit boards or into a reservoir that contains the tin plating solution. In the treatment container or in the reservoir, the tin dissolves to form Sn(II) ions, Sn(IV) ions being consumed in the process. As soon as the whole quantity or at least almost the whole quantity of tin placed in the container or in the reservoir has dissolved, further tin that has deposited onto the auxiliary cathode may be added.

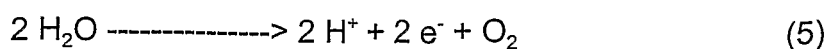
The rate at which tin from the very auxiliary cathode or metallic tin removed from the auxiliary cathode and placed into the treatment container or into a reservoir dissolves in the plating solution depends on a plurality of parameters: the dissolution rate of tin depends *inter alia* on the composition and on the temperature of the plating bath, on the morphology of electrolytically deposited tin, on the geometrical surface of the auxiliary cathode and on the flow conditions in immediate proximity to the dissolving tin. The rate may thus be optimized. A maximum dissolution rate is permanently aimed at since under these conditions Sn(IV) ions are actually quantitatively reduced to Sn(II) ions.

This makes it possible to minimize the concentration of Sn(IV) ions contained in the plating solution. The dissolution rate is the higher the higher the concentration of acid in the tin plating solution, the higher the temperature of the bath, the larger the surface of tin deposited onto the auxiliary cathode, referred to the weight of the tin, the larger the geometrical surface of the auxiliary cathode and the higher the convection of the plating solution in immediate proximity to the dissolving tin.

To optimize the method of the invention, the space surrounding the auxiliary anode (anode space) in the electrolytic regeneration cell can be separated from the space surrounding the auxiliary cathode (cathode space) by a membrane. The membrane is preferably configured in such a manner that cations (Sn(II) ions and Sn(IV) ions) cannot pass through. Therefore, the membrane may

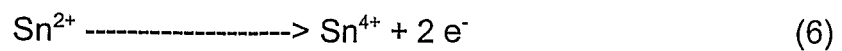
more specifically be an anion exchange membrane or a monoselective ion exchange membrane. In a particularly preferred embodiment of the method in accordance with the invention, there is an acid in the anode space. The acid contained in the plating solution in the cathode space and the acid contained in the anode space may be identical. However, a very good regeneration result is also obtained when the acid contained in the tin plating solution differs from the acid in the solution contained in the anode space. For example a tin plating solution containing methane sulfonic acid and a sulfuric acid solution contained in the cathode space yield good results. There is transfer of fluid between the cathode space and the region in which layers containing tin are deposited onto the printed circuit boards.

These further improvements of the method in accordance with the invention permit to prevent the tin plating bath from directly contacting the auxiliary anode. Sn(IV) ions are thus prevented from forming at the auxiliary anode, which would otherwise lower the efficiency of regeneration. The auxiliary anode may for example be immersed into an anode space that is separated from the cathode space surrounding the auxiliary cathode by an anion exchange membrane. The plating solution in the cathode space, which more specifically contains SnSO₄ and H₂SO₄ for example, cannot get near the auxiliary anode since the membrane prevents Sn(II) ions from passing through. A solution of the acid which is also contained in the cathode space is preferably also filled into the anode space. In the present example, the acid would be H₂SO₄. When the current flows between the two spaces, electroneutrality is guaranteed by the transfer of sulfate anions and by the corresponding electrode reactions, i.e., by the tin plating reaction at the auxiliary cathode according to equation (1) of this reaction and by an oxidation reaction at the auxiliary anode, in which oxygen is formed from water according reaction equation (5):



As the Sn(II) ions are prevented from contacting the auxiliary anode, oxidation

of Sn(II) ions according to the following equation:



5 cannot take place.

Alternatively, the auxiliary anode can also contact the tin plating solution directly. In order to also prevent in this case oxidation of the Sn(II) ions according to reaction equation (6), the concentration overvoltage must be high
10 enough for this reaction. This may be realized by an appropriate geometrical arrangement of the auxiliary anode relative to the auxiliary cathode for example: a depletion of the Sn(II) ions in the solution in the immediate proximity to the auxiliary cathode, which may lead to the concentration overvoltage, may also be achieved in that the anode space is accommodated in a container which is
15 separated from the cathode space, both spaces communicating through a pipe whose diameter is relatively small.

Concentration overvoltage in the above mentioned sense may also be achieved in considerably increasing the current density at the auxiliary anode so that
20 Sn(II) ions are virtually no longer available in the immediate proximity of the auxiliary anode. Under these conditions, Sn(II) ions do not oxidize to form Sn(IV) ions, but water oxidizes to form oxygen. The current density at the auxiliary anode may for example be increased by reducing the surface of the auxiliary anode relative to the surface of the auxiliary cathode.

25

In another embodiment of the invention, at least one electrode containing the tin to be deposited, i.e., an electrode of metallic tin for example, can be contacted with the tin plating bath. This tin electrode is polarized anodically relative to another electrode so that the tin electrode dissolves at least partially.
30 Such a soluble tin electrode may for example consist of poured balls which are located in a suitable container, e.g., in a titanium basket.

In this case, the tin electrode is at least intermittently polarized anodic relative to the other electrode so that metallic tin dissolves to form Sn(II) ions.

5 In using the soluble tin electrode, it is possible to produce the Sn(II) ions by dissolution consumed in the electrolytic deposition reaction so that the total amount of tin contained in the plating solution is kept constant. As soon as the desired concentration of Sn(II) ions contained in the solution is achieved in the process of anodic dissolution, the anodic dissolution reaction at the tin electrode can be halted by interrupting the flow of current. After the current is
10 no longer supplied to the soluble tin electrode, Sn(IV) ions may also be reduced at this electrode in causing them to react with the metallic tin of the electrode to form Sn(II) ions.

15 When using tin electrodes, the concentration of tin contained in the plating solution, namely the concentration of Sn(II) ions, must however be analytically monitored with accuracy since otherwise, the dissolution of the tin electrodes may cause the concentration of tin contained in the plating solution to exceed the reference value. In this case, dissolution of metallic tin of the tin electrode is not automatically limited which is the case when an inert auxiliary cathode is
20 exclusively used.

The tin plating solution may be contacted with the work in different ways: with conventional methods, the work is immersed into a bath of the plating solution, which is filled in a container. In this case, the arrangement with auxiliary
25 cathode and auxiliary anode is located either in the same container in a free space or in a separate container through which the plating solution flows. Fluid conduits in which the plating solution can be circulated between the treatment container and the regeneration container are provided for this purpose between the treatment container and this other regeneration container.

30 Furthermore, the work can be treated in a so called horizontal plant with a coating chamber. In this horizontal plant, the work is conveyed in horizontal

direction of transport through said chamber. In this case, the plating solution is delivered to the copper surfaces of the work by way of nozzles, e.g., spray nozzles, flow nozzles, jet nozzles or the like, while the work is conveyed through the chamber. For this purpose, the solution is kept in a reservoir from where it is delivered to the nozzles by means of pumps. After the plating solution has contacted the copper surfaces, it is drained into collecting tanks from where it is returned to the reservoir via fluid conduits. In this case, the arrangement with auxiliary cathode and auxiliary anode is accommodated either in the reservoir or in a separate regeneration container.

Thus a method of depositing a layer of metal and a method of regenerating a solution containing metal ions in a high oxidation state, especially a solution containing Sn(IV) ions, is described. Although specific embodiments, including specific equipment, method steps, method parameters, materials, solutions etc., have been described, various modifications to the disclosed embodiments will be apparent to those skilled in the art upon reading this disclosure.

Therefore, it is to be understood that such embodiments are merely illustrative of and not restrictive on the broad invention and that this invention is not limited to the specific embodiments described, but only by the scope of the appended claims.

Claims:

- 5 1. A method of depositing a metal layer, comprising the following method steps:
- a. Preparing a metal plating bath containing metal ions in a low oxidation state;
- 10 b. Depositing a metal layer from the metal plating bath onto a work piece;
- c. Bringing the metal plating bath in contact with the metal serving for regeneration in order to reduce metal ions in a high oxidation state contained in the metal plating bath to metal ions in a low oxidation state,
- 15 **wherein** an electrolytic regeneration cell comprised of at least one auxiliary cathode and of at least one auxiliary anode is provided and wherein the metal serving for regeneration is electrolytically deposited from the metal plating bath onto the at least one auxiliary cathode.
- 20 2. The method of claim 1, **wherein** the method serves for depositing tin containing layers, wherein the metal ions in the low oxidation state are Sn(II) ions and the metal ions in the high oxidation state are Sn(IV) ions and wherein the metal is metallic tin.
- 25 3. The method of any of claims 1 and 2, **wherein** the at least one auxiliary cathode is made of copper or of a copper alloy.
4. The method of any of claims 1 and 2, **wherein** the at least one auxiliary cathode is made of an inert material.
- 30 5. The method of claim 4, **wherein** the at least one auxiliary cathode is made of platinized titanium.

6. The method of any of claims 1 to 5, **wherein** the metal is deposited in scales onto the at least one auxiliary cathode by adjusting the cathodic current density.
- 5 7. The method of any of claims 1 to 6, **wherein** metal deposited onto the at least one auxiliary cathode is mechanically removed and wherein, after removal, the metal is contacted with the metal plating bath in order to reduce metal ions in a high oxidation state contained in the metal plating bath to metal ions in a low oxidation state.
- 10 8. The method of any of claims 1 to 7, **wherein** the at least one auxiliary anode is separated from the space surrounding the at least one auxiliary cathode by a membrane.
- 15 9. The method of claim 8, **wherein** the membrane is configured such that the metal ions may not permeate said membrane.
10. The method of any of claims 8 and 9, **wherein** said membrane is an anion exchange membrane or a monoselective ion exchange membrane.
- 20 11. The method of any of claims 8 to 10, **wherein** an acid is provided to the space surrounding the at least one auxiliary anode.
- 25 12. The method of any of claims 1 to 11, **wherein** at least one electrode containing the metal to be deposited is contacted with the metal plating bath and wherein the at least one electrode is polarized anodically relative to at least one further electrode so that the at least one electrode containing the metal to be deposited dissolves at least partially.
- 30 13. The method of any of claims 1 to 12, **wherein** the workpiece is conveyed in horizontal direction through a coating chamber for deposition of the metal layer.
14. A method of regenerating a solution containing metal ions in a high

oxidation state, in which method the solution is brought into contact with a metal serving for regeneration in order to reduce the metal ions in a high oxidation state to metal ions in a low oxidation state,

5 **wherein** an electrolytic regeneration cell comprised of at least one auxiliary cathode and of at least one auxiliary anode is provided and wherein the metal serving for regeneration is electrolytically deposited from the solution onto the at least one auxiliary cathode.

10 15. The method of claim 14, **wherein** the method serves for regenerating a tin containing solution, wherein the metal ions in the low oxidation state are Sn(II) ions and the metal ions in the high oxidation state are Sn(IV) ions and wherein the metal is metallic tin.