

(19)



(11)

EP 4 563 729 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.06.2025 Bulletin 2025/23

(51) International Patent Classification (IPC):
C25D 3/60 (2006.01)

(21) Application number: **23212743.1**

(52) Cooperative Patent Classification (CPC):
C25D 3/60

(22) Date of filing: **28.11.2023**

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

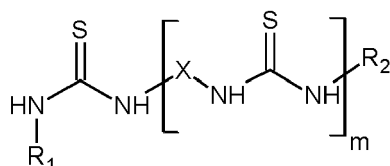
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(54) **AQUEOUS COMPOSITION FOR DEPOSITING A TIN SILVER ALLOY AND METHOD FOR ELECTROLYTICALLY DEPOSITING SUCH AN ALLOY**

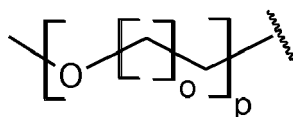
(57) The present invention refers to aqueous composition for depositing a tin silver alloy, the composition comprising

- (a) tin ions,
- (b) silver ions,
- (c) at least a complexing agent according to the following formula (I)



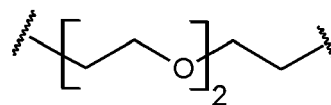
(I)

or a salt thereof;
wherein independently:
 $m = 0, 1, 2$, preferably $m = 1, 2$;
 R_1, R_2 denotes a substituent according to the following formula (II)



(II),

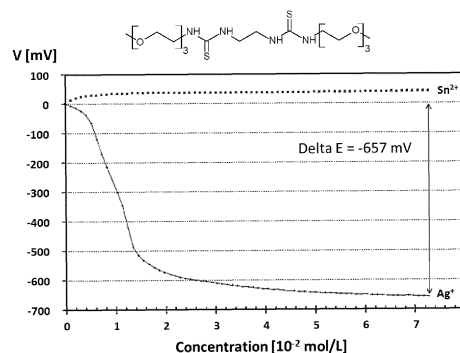
wherein $o = 1, 2$ and $p = 1 - 12$, preferably $p = 1 - 3$;
 X denotes a C2-C4 alkanediyl or a moiety according to the following formula (III)



(III).

Furthermore, the present invention refers to a method for electrolytically depositing a tin silver alloy onto a substrate, the use of the inventive aqueous composition for electrolytically depositing tin silver alloys and a compound according to formula (I).

Figure 1



Description**Field of the Invention**

[0001] The present invention relates to an aqueous composition for depositing a tin silver alloy, a method for electrolytically depositing such an alloy onto a substrate, the use of said composition for electrolytically depositing tin silver alloys and a compound according to formula (I).

Background of the Invention

[0002] In modern packaging technologies a clear trend toward decreasing sizes is observed to address increased performance and improved functionality for electronic devices. Solder caps on copper pillars have turned out to be an interesting and promising alternative to conventional solder ball applications, in particular for Flip-Chip applications in microelectronic devices.

[0003] Solder caps on copper pillars typically consist of two elements: (i) a structural element made of copper forming the pillar, e.g. a cylinder and (ii) a solder cap on top of said pillar. A large number of such capped copper pillars are typically arranged on a die, which is part of a wafer. Compared to conventional solder ball applications, solder caps on copper pillars provide an improved thermal and electrical behaviour due to the comparatively large volume of copper in the capped pillar, which provides an excellent electrical connection and increased conductivity. The solder cap provides an electrical as well as mechanical connection between the respective pillar and a corresponding feature, for example a pillar of another die.

[0004] An additional advantage of solder caps on copper pillars is the slim shape of the pillars compared to ball-like conventional solder ball applications. This allows a reduced distance (also called pitch) between two neighbouring pillars, which is a key element for higher packaging.

[0005] The solder cap typically includes tin and in many cases is a tin silver alloy; typically being free of lead. Such an alloy usually provides an excellent solderability and is a suitable alternative to previously used lead-containing solder caps and solder balls, respectively.

[0006] Depositing such tin silver alloys is known in the art. For example, JP 2006-265573 A discloses a tin silver alloy plating bath without cyanide, which improves solderability and appearance of an electrodeposition film obtained from the tin silver bath.

[0007] EP 0 854 206 B1 relates to an acidic tin silver alloy plating bath, which is substantially free of cyanide, and a method for electroplating tin silver alloy onto a substrate.

[0008] US 2014/0251818 A1 refers to a cyanide-free tin alloy plating solution having outstanding serial stability as well as a method of plating tin alloy onto an electroconductive object using the tin alloy plating solution. The tin alloy plating solution contains tin ions and one or more additional metal ions of silver, copper, bismuth, indium, palladium, lead, zinc, or nickel, and peptides with cysteine residues.

[0009] WO 03/046260 A2 relates to an electrolysis bath for electrodepositing silver-tin alloys that, in addition to water serving as a solvent with a pH value of less than 1.5, contains a water-soluble silver compound, a water-soluble tin compound and an organic complexing agent. In order to obtain a stable electrolysis bath that enables the homogenous deposition of a compact tin silver alloy with any type of composition, an aliphatic complexing agent having a sulfide group and an amino group is used as a complexing agent, whereby said functional groups are bound to different carbon atoms.

[0010] EP 1 553 211 B1 relates to a tin-silver-copper plating solution comprising 30-90 wt% of water, a sulfonic acid, tin ions, copper ions and silver ions, wherein the concentration of the silver ions is 0.01 to 0.1 mol/L, the concentration of the tin ions is 0.21 to 2 mol/L, the concentration of the copper ions is 0.002 to 0.02 mol/L and the mole ratio of the silver-ions to the copper ions is in the range of 4.5 to 5.58.

[0011] US 6,607,653 B1 relates to a tin-copper alloy plating bath, tin-copper-bismuth alloy plating bath or tin-copper-silver alloy plating bath containing a soluble metal compound and a specific sulfur-containing compound.

[0012] EP 2 221 396 A1 relates to a composition comprising one or more sources of tin ions, one or more sources of alloying metal ions, the metal ions are selected from the group consisting of silver ions, copper ions and bismuth ions, one or more flavone compounds, and one or more compounds having a formula: $\text{HOR}(\text{R}')\text{SR}'\text{SR}(\text{R}')\text{OH}$ wherein R, R' and R'' are the same or different and are alkylene radicals having 1 to 20 carbon atoms.

[0013] Despite known approaches, depositing a tin silver alloy, typically carried out by means of electrolytic deposition, requires highly sophisticated, accurate and stable bath compositions, in order to obtain coatings with a high measure of uniformity. In addition, besides the obtainable deposition quality as such, it is advantageous and especially ecologically friendly, that such aqueous compositions comprise a long shelf life and do not significantly alter their properties as a function of storage or application time. Suitable compositions and methods, respectively, to obtain homogeneous silver/tin coatings even at long storage periods are still missing and highly demanded to increase the usability of the coating compositions.

Objective of the present Invention

[0014] It is an objective of the present invention to provide an aqueous composition for depositing tin silver alloys, which overcome the above-mentioned problems. It is in particular an objective of the present invention to provide very stable aqueous silver tin compositions showing no or only very small tendencies of silver precipitation at longer storage times. In addition, it is an objective of the present invention to provide a way to obtain very uniform tin silver alloys such that, for example, very uniform solder caps on pillars are formable therefrom. It is furthermore an objective that said tin silver alloy can also be utilized in advanced packaging in Fan-Out-Wafer-Level-Packaging (FOWLP) or Flip-Chip applications.

[0015] It is an additional objective of the present invention to provide also a respective method for electrolytically depositing such a tin silver alloy, in particular for electrolytically depositing homogeneous tin silver alloys such that the bath compositions show a remarkable stability with respect to silver precipitation.

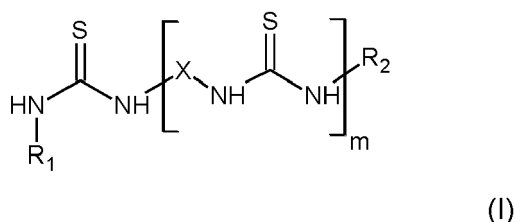
Summary of the Invention

[0016] These objectives are solved by an aqueous composition for depositing a tin silver alloy, the composition comprising

(a) tin ions,

(b) silver ions,

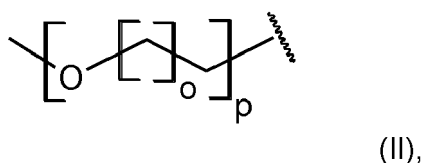
(c) at least a complexing agent according to the following formula (I)



or a salt thereof;
wherein independently:

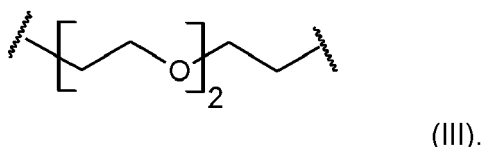
$m = 0, 1, \text{ or } 2$, preferably 1 or 2;

R_1, R_2 denotes a substituent according to the following formula (II)



wherein $o = 1, 2$ and $p = 1 - 12$, preferably $p = 1 - 3$;

X denotes a C2-C4 alkanediyl or a moiety according to the following formula (III)



[0017] Furthermore, the additional objective is solved by a method for electrolytically depositing a tin silver alloy onto a substrate, the method comprising the steps

(A) providing the substrate,

(B) providing an aqueous composition according to the present invention, preferably as described throughout the text as being preferred,

(C) contacting said substrate with said aqueous composition and supplying an electrical current such that said tin silver alloy is electrolytically deposited onto the substrate.

[0018] In addition, the objectives are solved by the use of an aqueous composition according to the present invention, preferably as described as being preferred throughout the present text, for electrolytically depositing tin silver alloys, tin silver alloy solder bumps or tin silver alloy solder caps onto metal pillars, preferably for electrolytically depositing tin silver alloy solder caps onto copper pillars. Furthermore, compounds according to formula (I) are within the scope of the invention.

Brief description of the figures

[0019]

Figure 1 is a diagram showing the complexing properties of the complexing compound 12,17-dithioxo-2,5,8,21,24,27-hexaoxa-11,13,16,18-tetraazaocacosane according to the invention for silver ions. On the x-axis the concentration in mol/L is given, wherein on the y-axis the overpotential in mV as a function of the compound's concentration is given.

Figure 2 is a diagram showing the complexing properties of the complexing compound 6,12-dithioxo-2,16-dioxo-5,7,11,13-tetraazaheptadecane according to the invention for silver ions. On the x-axis the concentration in mol/L is given, wherein on the y-axis the overpotential in mV as a function of the compound's concentration is given.

Figure 3 is a diagram showing the complexing properties of the complexing compound 1,3-bis(2-methoxyethyl)thiourea according to the invention for silver ions. On the x-axis the concentration in mol/L is given, wherein on the y-axis the overpotential in mV as a function of the compound's concentration is given.

Figure 4 is a diagram showing the complexing properties of the complexing compound 1,3-bis(2-methoxypropyl)thiourea according to the invention for silver ions. On the x-axis the concentration in mol/L is given, wherein on the y-axis the overpotential in mV as a function of the compound's concentration is given.

Detailed Description of the Invention

[0020] Own experiments show that the aqueous composition, the method, and the use as defined above, result in excellent uniform tin silver alloys, wherein the alloys are especially suitable for solder caps. These caps can be excellently utilized for metal pillars, in particular copper pillars. Furthermore, the aqueous compositions are very stable for long storage and use times, proving the remarkable capability of the inventive group of complexing compounds to stabilize silver tin baths against silver precipitation. Surprisingly, it was also found, that these compounds are able to achieve large shifts in the $\text{Ag}^+/\text{Sn}^{2+}$ -overpotential in the range of or even above 600 mV at very reasonable concentrations. This is a clear indicator for a stronger silver-ion complexation and the stronger complexation provides additional stability by hindering oxidation of Sn^{2+} -ions and reduction of Ag^{1+} -ions.

[0021] In the context of the present invention, the term "at least one" denotes (and is exchangeable with) "one, two, three or more than three".

[0022] The term "independently" denotes for example that in the group definitions of X, R^1 , and R^2 in formula (I) each substituent can be selected from the defined group, wherein the selection does not exclude or guide the selection from this group for the other substituents.

[0023] The composition of the present invention is an aqueous composition, which means that water is the primary component. Thus, more than 50 wt-% of the aqueous composition is water, based on the total weight of the aqueous composition, preferably at least 60 wt-%, even more preferably at least 70 wt-%, most preferably 80 wt-% or more. It is preferred that the aqueous composition is substantially free of organic solvents; more preferably does not contain organic solvents at all. Furthermore, the aqueous composition is preferably an aqueous solution, i.e. is homogeneous and thus preferably does not contain any particles.

[0024] In the context of the present invention, the term "at least" in combination with a particular value denotes (and is exchangeable with) this value or more than this value. For example, "at least 70 wt-%" denotes (and is exchangeable with) "70 wt-% or more than 70 wt-%".

[0025] In the context of the present invention, the term "substantially free" of a subject-matter (e.g. a compound, a material, etc.) independently denotes that said subject-matter is not present at all or is present only in (to) a very little and

undisturbing amount (extent) without affecting the intended purpose of the invention. For example, such a subject-matter might be added or utilized unintentionally, e.g. as unavoidable impurity. "Substantially free" preferably denotes 0 (zero) ppm to 50 ppm, based on the total weight of the aqueous composition of the present invention, if defined for said aqueous composition, or based on the total weight of the tin silver alloy, if defined for said alloy; preferably 0 ppm to 25 ppm, more preferably 0 ppm to 10 ppm, even more preferably 0 ppm to 5 ppm, most preferably 0 ppm to 1 ppm. Zero ppm denotes that a respective subject-matter is not at all comprised.

[0026] Preferred is an aqueous composition of the present invention, wherein the composition is acidic, preferably the composition has a pH in the range from -2 to +4, more preferably in the range from -1 to +2, most preferably in the range from -0.5 to +1.2. Generally, acidic compositions, in particular having a pH range as defined above, are typically free of cyanide, which is desired for environmental reasons. Thus, also the composition of the present invention is preferably free of cyanide. Furthermore, above mentioned pH ranges lead to an improved quality of the deposited tin silver alloy compared to a composition with a pH significantly higher than 4 or even being alkaline. Furthermore, the stability is increased if the pH is in the above defined pH ranges. In particular undesired plate out is observed if the pH is significantly higher than 4 or even alkaline. In order to prevent plate out in compositions having a pH significantly higher than 4 or even alkaline, typically very strong complexing agents are utilized such as environmentally hazardous cyanides. However, this can be successfully avoided in the composition and method of the present invention. As a result, waste water treatment is simplified and environmental issues are prevented. In the context of the present invention, pH is referenced to a temperature of 20°C.

[0027] The aqueous composition of the present invention is for depositing a tin silver alloy, preferably a tin silver alloy being substantially free of sulfur.

[0028] The aqueous composition of the present invention comprises (a) tin ions and (b) silver ions in order to deposit the tin silver alloy. In the aqueous composition the tin ions are preferably tin (II) ions and the silver ions preferably silver (I) ions.

[0029] Preferred is an aqueous composition of the present invention, wherein in the aqueous composition the tin ions are present in a total concentration in the range from 20 g/L to 200 g/L, based on the total volume of the aqueous composition, preferably in the range from 25 g/L to 150 g/L, more preferably in the range from 30 g/L to 120 g/L, even more preferably in the range from 35 g/L to 100 g/L, most preferably in the range from 40 g/L to 90 g/L. A concentration significantly below 20 g/L often results in an undesired low deposition rate. If the concentration significantly exceeds 200 g/L problems with solubility are frequently observed. An optimal compromise of deposition rate and solubility is obtained in above defined preferred concentration ranges. Best results have been obtained with a concentration in the range from 35 g/L to 100 g/L and from 40 g/L to 90 g/L, respectively.

[0030] The tin ions are from a tin ion source. The tin ion source of said tin ions is preferably at least one tin salt, more preferably at least one inorganic tin salt and/or at least one organic tin salt. Preferred inorganic tin salts are selected from the group consisting of tin oxide, tin sulfate, and tin sulfide. Preferred organic tin salts are selected from the group consisting of tin acetate, tin citrate, tin oxalate, and tin alkyl sulfonates. More preferred is an aqueous composition of the present invention, wherein the tin ions are from at least one organic tin salt, preferably from at least one tin alkyl sulfonate. In the aqueous composition of the present invention most preferred is tin methane sulfonate. Preferably in each tin ion source tin is present as tin (II).

[0031] Preferred is an aqueous composition of the present invention, wherein in the aqueous composition the silver ions are present in a total concentration in the range from 0.1 g/L to 10 g/L, based on the total volume of the aqueous composition, preferably in the range from 0.2 g/L to 8 g/L, more preferably in the range from 0.3 g/L to 6 g/L, even more preferably in the range from 0.4 g/L to 4 g/L, most preferably in the range from 0.5 g/L to 2 g/L. A concentration significantly below 0.1 g/L often results in an insufficient amount of silver in the tin silver alloy leading to undesired mechanical and electrical properties in respective solder caps and solder bumps. If the concentration significantly exceeds 10 g/L the composition may not sufficiently stable at all process conditions and plate out is sometimes observed. In Addition, too much silver is usually incorporated into the tin silver alloy, significantly increasing the melting point of a respective solder cap, which is undesired in subsequent reflow processes. Optimal melting points are obtained in the above defined preferred concentration ranges, most preferably in the ranges from 0.4 g/L to 4 g/L and 0.5 g/L to 2 g/L, respectively.

[0032] The silver ions are from a silver ion source. The silver ion source of said silver ions is preferably at least one silver salt, more preferably at least one inorganic silver salt and/or at least one organic silver salt. Preferred inorganic silver salts are selected from the group consisting of silver oxide, silver sulfate, and silver nitrate. Preferred organic silver salts are selected from the group consisting of silver acetate, silver citrate, silver oxalate, and silver alkyl sulfonates. More preferred is an aqueous composition of the present invention, wherein the silver ions are from at least one organic silver salt, preferably from at least one silver alkyl sulfonate. In the aqueous composition of the present invention most preferred is silver methane sulfonate. Preferably in each silver ion source silver is present as silver (I).

[0033] Most preferred, the silver ion source as well as the tin ion source comprise alkylsulfonates, more preferably are alkylsulfonates. This is in particular preferred if the pH in the aqueous composition of the present invention is (re)adjusted by means of alkylsulfonic acids. In this case only one type of organic acid anion is present in the composition of the present invention.

[0034] Preferred is an aqueous composition of the present invention, wherein the molar ratio of the tin ions to the silver

ions is in the range from 200:1 to 5:1, preferably in the range from 150:1 to 10:1, more preferably in the range from 125:1 to 12:1, most preferably in the range from 100:1 to 15:1. If the molar ratio is significantly exceeding 200:1 usually silver is insufficiently incorporated into the tin silver alloy. If the molar ratio is significantly below 5:1 in some cases the tin silver alloy comprises too much silver. However, if the molar ratio is as defined above, in particular in the range from 125:1 to 12:1 and from 100:1 to 15:1, respectively, an excellent uniform tin silver alloy is obtained and dendrites are very much suppressed in solder caped pillars.

[0035] Very preferred is a composition of the present invention, wherein the composition is substantially free of, preferably does not comprise, halide ions, most preferably chloride ions. First, silver chloride is very insoluble in an aqueous environment. Second, it has been observed in some cases that in particular chloride ions, although present in low amounts and not necessarily leading to immediate precipitation of insoluble chlorides, result in deposition defects in the tin silver alloy. Thus, it is preferred to not utilize tin ion sources and silver ion sources comprising halide anions, most preferably chloride ions.

[0036] In some cases, an aqueous composition of the present invention is preferred, wherein the composition additionally comprises copper (II) ions, preferably in a total concentration from 0.06 g/L to 5 g/L, based on the total volume of the aqueous composition, more preferably in a total concentration from 0.3 g/L to 4 g/L, even more preferably in a total concentration from 0.8 g/L to 3 g/L. Such a composition is for basically depositing a tin silver copper alloy.

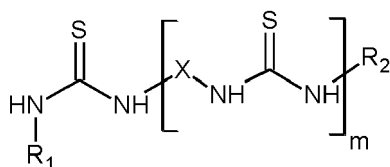
[0037] In some of these cases an aqueous composition of the present invention is preferred, wherein the composition comprises copper (II) ions in a total concentration from 0.06 g/L to 0.6 g/L, based on the total volume of the aqueous composition, preferably from 0.2 g/L to 0.5 g/L, more preferably from 0.3 g/L to 0.4 g/L. In such cases copper is incorporated into the tin silver alloy only to a very limited extent.

[0038] In alternative cases an aqueous composition of the present invention is preferred, wherein the composition comprises copper (II) ions in a total concentration from 0.7 g/L to 5 g/L, based on the total volume of the aqueous composition, preferably from 1 g/L to 4.2 g/L, more preferably from 1.3 g/L to 3.6 g/L, even more preferably from 2.1 g/L to 3.1 g/L. In such cases copper is incorporated into the tin silver alloy to a more significant extent.

[0039] However, in most cases it is in particular desired to not include copper ions in the aqueous composition of the present invention such that the obtained tin silver alloy is substantially free of, preferably does not comprise, copper. Thus, in such cases an aqueous composition of the present invention is preferred, wherein the composition is substantially free of, preferably does not comprise, copper ions, preferably is substantially free of, preferably does not comprise, copper ions and bismuth ions.

[0040] Preferred is an aqueous composition of the present invention being substantially free of, preferably not comprising, nickel ions, zinc ions, iron ions, lead ions, and aluminum ions.

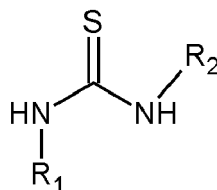
[0041] The aqueous composition of the present invention comprises, besides (a) tin ions and (b) silver ions, (c) at least one (preferably one) complexing agent (as described throughout the present text). The at least one complexing agent (I) is a compound according to the following formula (I):



(I)

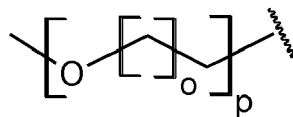
or a salt thereof.

[0042] The basic structure of the complexing agent is a thiourea, wherein either only one unbridged thiourea-unit comprising one C=S-group without the bridging moiety X or once or twice bridged thiourea-units comprising two or three C=S-groups are present. In case of the unbridged, single thiourea-unit an R₁-substituent is attached to one nitrogen and the R₂-substituent is attached to the other nitrogen of the thiourea-unit. A possible structure comprising a single unit, only, may look like:



[0043] In case of bridged thiourea-units the thiourea-units are bridged or connected via the structural unit X. Without being bound by the theory, it is believed that the provision of at least one sulfur-atom, preferably multiple sulfur-atoms combined with ether groups in the complexing agent results in a better and more stable complexation of silver ions in aqueous solutions. Due to the fact that the index m may be 0, 1 or 2, up to three sulfur units can be present in the molecule.

[0044] The end groups of the complexing agent R_1 , R_2 denotes a substituent according to the following formula (II)

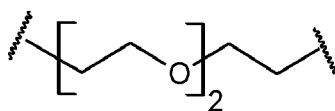


(II),

wherein $o = 1, 2$ and $p = 1 - 12$, preferably $p = 1 - 3$.

[0045] Therefore, the end positions of the complexing agent each represent an ether group. R_1 , R_2 can be selected independently. R_1 and R_2 can each be the same or a different ether substituent. Based on the selection of the end groups the water solubility of the overall molecule can be tailored. Preferably, index p can be selected from the group consisting of 1, 2, 3, 4, 5, 6, 7, 8 and further preferred index p can be selected from the group consisting of 1, 2, 3, 4, 5, 6, preferably p is 1, 2 or 3, more preferably R_1 , R_2 are identical, and p is 1, 2 or 3.

[0046] In case of two or three thiourea units these are connected via a substituent X, wherein X denotes a C2-C4 alkanediyl or a moiety according to the following formula (III)



(III).

[0047] The bridging group X may either be aliphatic in nature, wherein X comprises an aliphatic group consisting of 2, 3 or 4 linked CH_2 -groups, wherein two CH_2 -groups are linked to different thiourea-units. Besides a pure aliphatic bridge, the connecting part can also be formed from the above depicted ether-unit according to formula (III). The dashed lines indicate the covalent linkage to the thiourea-units. It seems also to be possible to influence or alter the solubility behavior and the geometry of the overall molecule by variation of the linker X. This flexibility can be used to tailor the complexing behavior of the compound to silver-ions.

[0048] The compound according to formula (I) serves as complexing agent in the aqueous compositions of the present invention. The complexing agent stabilizes the plating bath even in unfavorable storage conditions and homogeneous plating results with respect to the silver content in the deposited alloy are achievable. Preferred is an aqueous composition of the present invention, wherein compounds of formula (I) are the only complexing agents in the composition. It is in particular preferred that the aqueous composition of the present invention is substantially free of, preferably does not comprise, glycine, cysteine, and glutathione, more preferably is substantially free of, preferably does not comprise, amino acids with at least one sulfhydryl group and peptides with at least one sulfhydryl group, most preferably is substantially free of, preferably does not comprise, amino acids and peptides at all. Own experiments indicate that amino acids and peptides have negative influence on the shelf life of the aqueous composition of the present invention, finally causing stability problems. In some cases it has been observed that the shelf life does not go beyond six month, which is not desired. In contrast, a shelf life exceeding six month is desired, and compounds of formula (I) do not negatively affect the shelf life, preferably resulting in a shelf life of more than six month.

[0049] The aqueous composition of the present invention is preferably for electrolytically depositing a tin silver alloy and is preferably not for electroless deposition.

[0050] Therefore, the integration of a complexing agent according to the formula (I) in a tin silver plating bath results in several unexpected advantages.

[0051] In particular preferred is an aqueous composition of the present invention, wherein X is C2-C4 alkanediyl.

[0052] Even more preferred is an aqueous composition of the present invention, wherein X is C2-C3 alkanediyl and R_1 and R_2 are a substituent according to formula (II). Further preferred, X is C2-C3 alkanediyl and R_1 and R_2 are each independently substituents according to formula (II). This selection of the Markush-groups results in very storage stable compositions, wherein the solubility of the complexing agent is enhanced.

[0053] Preferred is an aqueous composition of the present invention, wherein R_1 and R_2 are a substituent according to

formula (II) and p is selected from the group consisting of 1, 2 or 3. This selection of the Markush-groups results in very storage stable compositions, wherein the solubility of the complexing agent is enhanced.

[0054] In particular preferred is an aqueous composition of the present invention, wherein X denotes C2-C4 alkanediyl and R_1 , R_2 independently denotes a substituent according to formula (II).

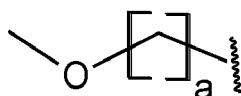
[0055] In particular preferred is an aqueous composition of the present invention, wherein X denotes C2 alkanediyl and R_1 , R_2 independently denotes a substituent according to formula (II).

[0056] In particular preferred is an aqueous composition of the present invention, wherein X denotes C2 alkanediyl and R_1 , R_2 independently denotes a substituent according to formula (II) and $p = 1-12$.

[0057] In particular preferred is an aqueous composition of the present invention, wherein X denotes C2 alkanediyl and R_1 , R_2 independently denotes a substituent according to formula (II) and $p = 1-5$, preferably 1-3.

[0058] In particular preferred is an aqueous composition of the present invention, wherein X denotes C2 alkanediyl and R_1 , R_2 both denotes PEG and $p = 1$.

[0059] In particular preferred is an aqueous composition of the present invention, wherein $m = 0$ and R_1 and R_2 each independently denote a substituent according to the following formula IV



(IV),

wherein $a = 2$ or 3 .

[0060] Preferably, a can be 2 for R_1 and R_2 . Preferably, a can be 3 for R_1 and R_2 . Preferably, a can be 2 for R_1 and 3 for R_2 .

[0061] In particular preferred is an aqueous composition of the present invention, wherein the compound is selected from the group consisting of 12,17-dithioxo-2,5,8,21,24,27-hexaoxa-11,13,16,18-tetraazaooctacosane, 6,12-dithioxo-2,16-dioxa-5,7,11,13-tetraazaheptadecane, 6,11-dithioxo-2,15-dioxa-5,7,10,12-tetraazahexadecane, 1,3-bis(2-methoxyethyl)thiourea, 1,3-bis(2-methoxypropyl)thiourea or mixtures thereof.

[0062] In particular preferred is an aqueous composition of the present invention, wherein the concentration of the complexing agent in the aqueous composition is greater than or equal to 30 mmol/L and less than or equal to 120 mmol/L, preferably greater than or equal to 50 mmol/L and less than or equal to 80 mmol/L. Within these concentration ranges very stable tin silver aqueous solutions can be formulated. If the total concentration is significantly below 30 mmol/L, silver ions are not sufficiently complexed and undesired plate out is frequently observed.

[0063] The aqueous composition of the present invention preferably comprises further compounds.

[0064] Preferred is an aqueous composition of the present invention furthermore comprising

(d) at least one organic acid anion, preferably an alkyl sulfonic acid anion, most preferably methane sulfonic acid anions.

[0065] Said at least one organic acid anion is preferably obtained from the source of tin ions and/or the source of silver ions.

[0066] Also preferably, said at least one organic acid anion is obtained from an organic acid, preferably from at least one alkyl sulfonic acid, most preferably from methane sulfonic acid.

[0067] Most preferably, said at least one organic acid anion is obtained from the source of tin ions, the source of silver ions, and an organic acid. In such a case, the aqueous composition of the present invention preferably contains only one type of organic acid anion, which is very preferred. Therefore, most preferred is an aqueous composition of the present invention, wherein in the composition alkyl sulfonate, preferably methane sulfonate, is the only organic acid anion. This provides a number of advantages because solubility of metal ions is typically high in the presence of alkyl sulfonic acids. Furthermore, undesired oxidation of tin (II) ions to tin (IV) ions is significantly reduced. In addition, it has been observed that the corrosive effect of alkyl sulfonic acids is reduced compared to strong inorganic acids.

[0068] Alkyl sulfonic acids are preferred acids because they serve as optimal pH adjuster and typically result in a very strong acidic pH. If other organic acid anions are utilized, preferably acetate, oxalate, and citrate, either as organic acid or in the source of tin ions and/or silver ions, an additional strong acid is usually needed to obtain the preferred strong acidic pH, for example strong inorganic acids, which include additional inorganic anions. This is less preferred, e.g. for the reasons stated above. Thus, preferred is an aqueous composition of the present invention, wherein the composition is substantially free of, preferably does not comprise, inorganic acids. Instead, strong organic acids are preferred in the composition of the present invention.

[0069] Preferred is an aqueous composition of the present invention, wherein in the aqueous composition the total concentration of all organic acid anions is in the range from 0.5 mol/L to 4.0 mol/L, based on the total volume of the aqueous composition, preferably from 0.6 mol/L to 2.5 mol/L, more preferably from 0.7 mol/L to 2 mol/L, even more preferably from 0.8 mol/L to 1.5 mol/L, most preferably from 0.9 mol/L to 1.3 mol/L. Preferably, the total concentration as defined above is formed by only one type of organic acid anions, more preferably by only alkyl sulfonates, most preferably by only methane

sulfonate. If the total concentration is significantly exceeding 4.0 mol/L the composition is not sufficiently stable anymore. Furthermore, a too high total concentration creates severe issues or even damages on the substrate. If the total concentration is significantly below 0.5 mol/L an insufficient conductivity of the aqueous composition is usually obtained.

[0070] In order to increase the wettability, the aqueous composition of the present invention preferably comprises at least one surfactant. The kind of surfactant is not particularly limited. Thus, preferred is an aqueous composition of the present invention furthermore comprising

(e) at least one surfactant, preferably selected from the group consisting of nonionic surfactants, amphoteric surfactants, cationic surfactants, and anionic surfactants, preferably nonionic surfactants and cationic surfactants, more preferably alkoxyated cationic surfactants and polyether nonionic surfactants, even more preferably alkylene oxide co-polymers and alkoxyated amines, most preferably ethylene oxide/propylene oxide co-polymers and ethoxyated amines.

[0071] Preferred is an aqueous composition of the present invention, wherein the total concentration of all surfactants is in the range from 0.1 g/L to 20 g/L, based on the total volume of the aqueous composition, preferably from 0.4 g/L to 10 g/L, more preferably from 0.6 g/L to 8 g/L, most preferably from 1 g/L to 5 g/L. If the total concentration is significantly below 0.1 g/L in many cases the wettability is insufficient. If the total concentration is significantly exceeding 20 g/L it is often observed that undesired foam is formed.

[0072] In order to avoid or at least to suppress foaming, the aqueous composition of the present invention furthermore preferably comprises, at least in many cases, at least one anti-foam agent.

[0073] The aqueous composition of the present invention preferably comprises tin (II) ions. However, tin (II) ions are susceptible to oxidation, which results in tin (IV) ions. Such an oxidation is not desired because it promotes precipitation of tin (IV) species, such as tin (IV) oxide. To avoid oxidation, an anti-oxidizing agent is preferably utilized. Thus, preferred is an aqueous composition of the present invention furthermore comprising

(f) at least one anti-oxidizing agent, preferably selected from the group consisting of compounds comprising a hydroxylated ring moiety, most preferably selected from the group consisting of catechol, hydroquinone, resorcinol, phenol-sulfonic acids, ascorbic acid, and naphtholsulfonic acids.

[0074] Preferred hydroxylated ring moieties are hydroxylated aromatic compounds, more preferably benzene diols, even more preferably selected from the group consisting of catechol, hydroquinone, and resorcinol, most preferably selected from the group consisting of resorcinol and hydroquinone. Most preferred is an aqueous composition of the present invention, wherein the at least one anti-oxidizing agent is resorcinol, more preferably resorcinol is the only anti-oxidizing agent in the aqueous composition of the present invention. Anti-oxidizing agents as defined above are strong enough to avoid oxidation of tin (II) ions to tin (IV) ions without reducing tin (II) ions to metallic tin.

[0075] Preferred is an aqueous composition of the present invention, wherein the total concentration of all anti-oxidizing agents is in the range from 1.0 mmol/L to 100 mmol/L, based on the total volume of the aqueous composition, preferably from 2.0 mmol/L to 70 mmol/L, more preferably from 4.0 mmol/L to 40 mmol/L, even more preferably from 5.0 mmol/L to 20 mmol/L, most preferably from 6.0 mmol/L to 15 mmol/L. Preferably, the total concentration as defined above is formed by only one type of anti-oxidizing agent, more preferably by only benzene diols, most preferably by only resorcinol. If the total concentration as defined above is significantly exceeding 100 mmol/L in many cases it is observed that the plating performance is insufficient. If the total concentration is significantly below 1.0 mmol/L oxidation of tin (II) ions to insoluble tin (IV) species is not sufficiently prevented and undesired precipitation can be observed in some cases

[0076] If the at least one anti-oxidizing agent is known as a typical anti-oxidizing agent, the amount of such a compound is preferably counted among the above-mentioned total concentration of all anti-oxidizing agents. In particular, if the at least one anti-oxidizing agent is an organic acid and comprises a hydroxylated ring moiety, the amount of said compound is counted among above mentioned total concentration of all anti-oxidizing agents.

[0077] Preferred is an aqueous composition of the present invention, wherein in the aqueous composition the weight of said tin ions and said silver ions in total represents 80 wt.-% to 100 wt.-% of all group 3 to group 15 metal cations in the aqueous composition, based on the total weight of all group 3 to group 15 metal cations in the aqueous composition, preferably at least 90 wt.-%, more preferably at least 95 wt.-%, even more preferably at least 98 wt.-%, most preferably at least 99 wt.-%. Group 3 to 15 refers to the 18 groups in the periodic table of elements. Preferably, said tin ions and said silver ions are the only depositable metal ions in the aqueous composition. This means that these metal ions are the only metal ions that are deposited in the tin silver alloy.

[0078] As mentioned above, the present invention also refers to a method for electrolytically depositing a tin silver alloy onto a substrate, the method comprising the steps

(A) providing the substrate,

(B) providing an aqueous composition according to the present invention, preferably as described above as being preferred,

(C) contacting said substrate with said aqueous composition and supplying an electrical current such that said tin

silver alloy is electrolytically deposited onto the substrate.

[0079] The above mentioned preferred embodiments regarding the aqueous composition of the present invention applies likewise to the method of the present invention.

[0080] In step (A) of the method of the present invention, the substrate is provided, preferably a conductive substrate. In some cases, preferred is a method of the present invention, wherein the substrate is a semiconductor base substrate, preferably comprising a conductive or semi-conductive layer thereon. Such a conductive or semi-conductive layer is also often referred to as seed layer. The kind of seed layer is not particularly restricted. A most preferred seed layer is a copper seed layer.

[0081] The substrate preferably is or comprises at least one metalloid and/or gallium, more preferably is or comprises at least one element selected from the group consisting of silicon, germanium, and gallium, most preferably is or comprises silicon. If the substrate is not in itself sufficiently conductive, it preferably comprises above mentioned conductive or semi-conductive layer.

[0082] Most preferred is a method of the present invention, wherein the substrate is a wafer, preferably a wafer comprising a conductive or semi-conductive layer thereon, most preferably comprising a copper seed layer.

[0083] In other cases, preferred is a method of the present invention, wherein the substrate is a non-conductive substrate, preferably a substrate being or comprising glass or plastic. In such a case, the substrate preferably comprises already at least partly a conductive seed layer, or a conductive seed layer is deposited in a subsequent processing step.

[0084] Preferred is a method of the present invention, wherein the substrate (as defined before) comprises a plurality of individual structural features. Preferred is a method of the present invention, wherein the substrate comprises a plurality of metal features, preferably a plurality of metal pillars and/or areas with at least one metal layer, more preferably a plurality of copper pillars and/or areas with at least one copper layer.

[0085] Preferably, the metal features have an aspect ratio in the range from 1:40 to 15:1 (height:width), preferably in the range from 1:30 to 10:1, more preferably in the range from 1:20 to 7:1. Metal pillars and copper pillars, respectively, have a preferred aspect ratio in the range from 1:1 to 10:1, more preferably in the range from 1:1 to 7:1. Metal bumps and copper bumps, respectively, have a preferred aspect ratio in the range from 1:40 to 1:1, preferably in the range from 1:30 to 1:10. In the context of the present invention, individual structural features and metal features, respectively, include individual geometrical forms such as pillars, spots and areas, which are accessible for tin silver alloy deposition by means of the method of the present invention.

[0086] Preferred is a method of the present invention, wherein said metal pillars and copper pillars, respectively, have a cylindrical shape. Preferably, said metal pillars and copper pillars, respectively, have a height in the range from 3 μm to 100 μm , preferably from 5 μm to 90 μm , more preferably from 9 μm to 80 μm , even more preferably from 15 μm to 70 μm , most preferably from 20 μm to 70 μm . Preferably, said metal pillars and copper pillars, respectively, have a width in the range from 5 μm to 100 μm , preferably from 10 μm to 80 μm , more preferably from 10 μm to 30 μm .

[0087] In the method of the present invention said metal bumps and copper bumps, respectively, can have any shape; preferably a cylindrical, polygonal, and/or rectangular shape.

[0088] Preferably, the metal bumps and copper bumps, respectively, have a height in the range from 0.5 μm to 50 μm , preferably from 1 μm to 30 μm , more preferably from 2 μm to 25 μm , even more preferably from 3 μm to 20 μm , most preferably from 4 μm to 15 μm . Preferably, bumps have a width of at least 50 μm , preferably of at least 80 μm , more preferably of at least 100 μm .

[0089] In step (B) an aqueous composition of the present invention, preferably as described throughout the text as being preferred, is provided, typically in a tank for electrolytic metal deposition.

[0090] In step (C) of the method of the present invention the tin silver alloy is electrolytically deposited onto the substrate. Step (C) requires that the substrate is sufficiently conductive in order to electrolytically deposit the tin silver alloy. Either the substrate provided in step (A) is already sufficiently conductive or the substrate provided in step (A) is processed in subsequent steps such that it is sufficiently conductive prior to step (C). Thus, the substrate in step (C) preferably comprises at least one conductive or semi-conductive layer such that the tin silver alloy is electrolytically deposited thereon. Preferably, the at least one conductive or semi-conductive layer is a conductive metallic, conductive semi-metallic, or conductive non-metallic layer. Most preferably it is a conductive metallic layer, preferably a metallic copper layer, typically a copper seed layer.

[0091] A method of the present invention is preferred, wherein in step (C) the tin silver alloy is deposited as solder caps on pillars and/or as solder bumps.

[0092] In the method of the present invention, the substrate is operated as a cathode in order to deposit the tin silver alloy in step (C).

[0093] Preferred is a method of the present invention, wherein the electrical current is a direct current, preferably with a cathodic current density in the range from 1 A/dm² to 100 A/dm², more preferably with a cathodic current density in the range from 3 A/dm² to 70 A/dm², most preferably with a cathodic current density in the range from 5 A/dm² to 50 A/dm². In some cases it is preferred that the direct current in step (C) is not supplemented by current pulses. This means that

preferably in step (C) the direct current is the only electrical current.

[0094] Own experiments show that in particular at comparatively high current densities the method of the present invention gives excellent results. This means that at such current densities excellent and very uniform tin silver alloys are deposited and, additionally, aqueous compositions kept for longer times do show no or only a very low deviations in the deposition quality compared to freshly prepared compositions. The quality of deposited alloy achieved by an aged composition is also not significantly influenced by the current density. Therefore, particular preferred is a method of the present invention, wherein the electrical current comprises a direct current with a cathodic current density in the range from 10 A/dm² to 40 A/dm², more preferably in the range from 12 A/dm² to 35 A/dm².

[0095] A method of the present invention is preferred, wherein in step (C) the contacting and supplying of electrical current is carried out for 3 seconds to 400 min, preferably for 5 seconds to 200 min, most preferably for 6 seconds to 100 min. If the contacting is carried out for significantly less than 3 seconds typically an incomplete tin silver alloy is deposited and the uniformity of the solder caps is insufficient.

[0096] In step (C) of the method of the present invention, preferably a tin silver alloy layer is deposited, preferably with a layer thickness in the range from 1 μm to 150 μm, more preferably in the range from 4 μm to 100 μm, even more preferably in the range from 7 μm to 90 μm, most preferably in the range from 10 μm to 80 μm.

[0097] Preferred is a method of the present invention, wherein the silver content in the electrolytically deposited tin silver alloy is in the range from 0.1 wt-% to 10 wt-%, based on the total weight of the electrolytically deposited tin silver alloy, preferably is in the range from 0.5 wt-% to 5 wt-%, most preferably is in the range from 1.5 wt-% to 3.5 wt-%. Most preferably the rest of the tin silver alloy is tin. Thus, the major metal in the tin silver alloy is tin. As a result, a method of the present invention is preferred, wherein the tin content in the electrolytically deposited tin silver alloy is at least 60 wt-%, based on the total weight of the electrolytically deposited tin silver alloy, preferably at least 70 wt-%, more preferably at least 80 wt-%, even more preferably at least 90 wt-% or at least 95 wt-%, most preferably at least 96.5 wt-%, and even most preferably at least 98.5 wt-% or at least 99.5 wt-%. A tin silver alloy as described above is very much desired and suitable for solder caps on pillars and as solder bumps because of its excellent solderability.

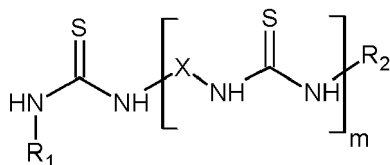
[0098] Only in some cases a method of the present invention is preferred, wherein the tin silver alloy comprises copper.

[0099] In most cases it is very preferred that the tin silver alloy obtained with the method of the present invention is not a ternary alloy, more preferably not a tin silver copper alloy. Preferably, the tin silver alloy is substantially free of, preferably does not comprise, one, more than one or all elements of the group consisting of zinc, nickel, iron, copper, bismuth, aluminum, and lead. In particular, the tin silver alloy obtained with the method of the present invention is substantially free of, preferably does not comprise, lead.

[0100] Preferred is a method of the present invention, wherein in step (C) the aqueous composition has a temperature in the range from 5°C to 90°C, preferably in the range from 15°C to 60°C, more preferably in the range from 20°C to 50°C, most preferably in the range from 22°C to 40°C. If the temperature is significantly below 5°C no adequate deposition speed is obtained. If the temperature is significantly above 90°C undesired evaporation and bath instability occurs.

[0101] The present invention also refers to a use of the aqueous composition of the present invention for electrolytically depositing tin silver alloy solder bumps or tin silver alloy solder caps onto metal pillars, preferably for electrolytically depositing tin silver alloy solder caps onto copper pillars. The aforementioned regarding the aqueous composition of the present invention and the method of the present invention, respectively, applies likewise to the aforementioned use.

[0102] As mentioned above, the present invention also refers to a compound according to the following formula (I)

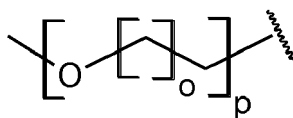


(I)

or a salt thereof;
wherein independently:

$m = 0, 1, 2$, preferably $m = 1, 2$;

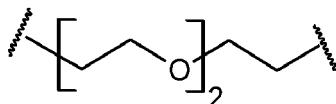
R_1, R_2 denotes a substituent according to the following formula (II)



(II),

wherein $o = 1, 2$; $p = 1 - 12$, preferably $p = 1 - 3$; and

X denotes a C2-C4 alkanediyl or a moiety according to the following formula (III)



(III).

[0103] In particular preferred is a compound of the present invention, wherein X denotes C2-C4 alkanediyl and R_1, R_2 independently denotes methyl or a substituent according to formula (II).

[0104] In particular preferred is a compound of the present invention, wherein X denotes C2-C4 alkanediyl and R_1, R_2 independently denotes a substituent according to formula (II).

[0105] In particular preferred is a compound of the present invention, wherein X denotes C2 alkanediyl and R_1, R_2 independently denotes a substituent according to formula (II).

[0106] In particular preferred is a compound of the present invention, wherein X denotes C2 alkanediyl and R_1, R_2 independently denotes a substituent according to formula (II) and $p = 1-12$.

[0107] In particular preferred is a compound of the present invention, wherein X denotes C2 alkanediyl and R_1, R_2 independently denotes a substituent according to formula (II) and $p = 1-5$.

[0108] In particular preferred is a compound of the present invention, wherein X denotes C2 alkanediyl and R_1, R_2 both denotes PEG and $p = 3$.

[0109] In particular preferred is a compound of the present invention, wherein the compound is 12,17-dithio-2,5,8,21,24,27-hexaoxa-11,13,16,18-tetrazaoctacosane, 6,12-dithio-2,16-dioxa-5,7,11,13-tetrazaheptadecane, 6,11-dithio-2,15-dioxa-5,7,10,12-tetrazahexadecane, 1,3-bis(2-methoxyethyl)thiourea or 1,3-bis(2-methoxypropyl)thiourea.

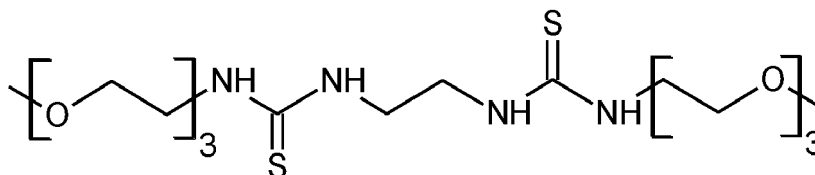
[0110] The present invention is described in more detail by the following non limiting examples.

Examples

1. Synthesis of compounds (I) according to the invention

1.1 Synthesis of 12, 17-dithio-2,5,8,21,24,27-hexaoxa-11, 13, 16, 18-tetrazaoctacosane

[0111]

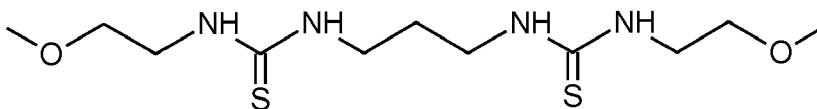


[0112] 1,2-Ethylenediamine (8.2 ml; 7.4 g; 0.12 mol; 1.0 eq) and 1-isothiocyanato-2-(2-(2-methoxyethoxy)ethoxy)ethane (50.011 g; 0.24 mol; 2.0 eq) are reacted in acetonitrile under stirring for 20h. The resulting crude product is dried, dissolved in sulfuric acid and extracted with dichloromethane. The combined organic phases are washed with sulfuric acid and dried.

[0113] Yield: 58.892 g (90 %). NMR: ^1H NMR (400 MHz, Acetone- d_6) δ 7.30 (s, 2H), 7.08 (s, 2H), 3.84 - 3.57 (m, 24H), 3.55 - 3.45 (m, 4H), 3.31 (s, 6H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 184.50, 72.61, 71.10, 70.95, 70.92, 70.26, 58.79, 44.99, 44.34. **MS (ESI):** m/z $\text{C}_{18}\text{H}_{38}\text{N}_4\text{O}_6\text{S}_2$ ($[\text{M}+\text{H}]^+$) 471,2304 (berechnet: 471,2311). **IR (ATR):** 3314 (m), 2923 (m), 2874 (m), 1548 (s), 1456 (m), 1348 (m), 1287 (m), 1217 (m), 1201 (m), 1103 (s), 1029 (m), 933 (m), 849 (m).

1.2 Synthesis of 6,12-dithioxo-2,16-dioxo-5,7,11,13-tetraazaheptadecane

[0114]

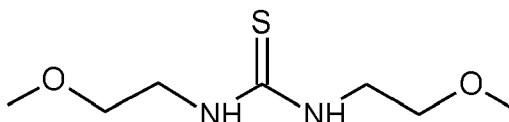


[0115] 1-Isothiocyanato-2-methoxyethane (1.170 g; 10.0 mmol, 2 eq) und 1,3-Diaminopropane (0.42 ml; 0.37 g; 5.0 mmol; 1 eq) are reacted in acetonitrile under stirring for 20h. The resulting crude product is dried, dissolved in sulfuric acid and extracted with dichloromethane. The combined organic phases are washed with sulfuric acid and dried.

[0116] Yield: 1.445 g (94 %). **NMR:** ^1H NMR (400 MHz, Acetone- d_6) δ 7.18 (s, 2H), 6.92 (s, 2H), 3.61 (m, 8H), 3.49 (t, J = 5.4 Hz, 4H), 3.30 (s, 6H), 1.80 (p, J = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 184.25, 71.74, 58.69, 44.60, 42.05, 29.98. **MS (ESI):** m/z $\text{C}_{11}\text{H}_{24}\text{N}_4\text{O}_2\text{S}_2$ ($[\text{M}+\text{H}]^+$) 309, 1426 (calculated: 309.1413). **IR (ATR):** 3274 (m), 3067 (w), 2930 (m), 2890 (m), 2831 (w), 1552 (s), 1458 (m), 1387 (m), 1345 (m), 1288 (m), 1234 (m), 1197 (m), 1116 (s), 1015 (m), 963 (w), 915 (w), 835 (w), 790 (w).

1.3 Synthesis of 1,3-bis(2-methoxyethyl)thiourea

[0117]

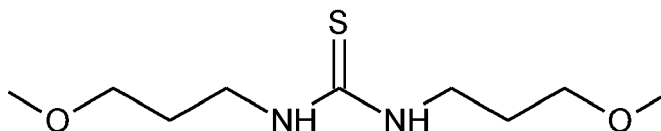


[0118] 2-Methoxyethylamine (3.0 ml; 2.6 g; 34.6 mmol) and carbon disulfide (1.0 ml; 1.3 g; 17.1 mmol) are reacted in acetonitrile. The reaction product was subjected to a cleaning operation with dichloromethane and diluted sulphuric acid solution.

[0119] Yield: 2.427 g (76 %). **NMR:** ^1H NMR (400 MHz, Acetone- d_6) δ 7.07 (s, 2H), 3.65 (s, 4H), 3.48 (t, J = 5.3 Hz, 4H), 3.30 (s, 6H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 184.75, 71.86, 58.66, 44.86. **MS (ESI):** m/z $\text{C}_7\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ ($[\text{M}+\text{H}]^+$) 193.1017 (calculated: 193.1005). **IR (ATR):** 3286 (m), 3065 (w), 2981 (w), 2928 (m), 2890 (m), 2830 (w), 1552 (s), 1458 (m), 1372 (m), 1341 (m), 1289 (m), 1231 (w), 1196 (m), 1117 (s), 1015 (m), 966 (w), 941 (w), 838 (w).

1.4 Synthesis of 1,3-bis(2-methoxypropyl)thiourea

[0120]



[0121] 3-Methoxypropylamine (3.7 ml; 3.2 g; 36.3 mmol; 2.1 eq) and carbon disulfide (1.0 ml; 1.3 g; 17.1 mmol) are reacted in acetonitrile. The reaction product was subjected to a cleaning operation with dichloromethane and diluted sulphuric acid solution.

[0122] Yield: 3.254 g (89 %). **NMR:** ^1H NMR (400 MHz, Acetone- d_6) δ 6.90 (s, 2H), 3.53 (s, 4H), 3.41 (t, J = 6.0 Hz, 4H), 3.27 (s, 6H), 1.80 (p, J = 6.5 Hz, 4H). ^{13}C NMR (101 MHz, Acetone- d_6) δ 183.91, 71.19, 58.60, 42.49, 29.95. **MS (ESI):** m/z $\text{C}_9\text{H}_{20}\text{N}_2\text{O}_2\text{S}$ ($[\text{M}+\text{H}]^+$) 221.1323 (calculated: 221.1318). **IR (ATR):** 3289 (m), 2925 (m), 2874 (m), 2830 (m), 1553 (s), 1480 (m), 1448 (m), 1388 (m), 1346 (m), 1290 (m), 1243 (m), 1215 (m), 1192 (m), 1117 (s), 1044 (m), 970 (w), 895 (m).

2. Aqueous compositions for depositing a tin silver alloy

[0123] In a first step different aqueous compositions are prepared as follows:

2.1 Aqueous composition E-1 (according to the present invention):

[0124] Aqueous composition E-1 according to the present invention comprises 45 g/L tin(II) ions, 1 g/L silver(I) ions, approximately 1 mol/L methane sulfonic acid, 2.5 g/L surfactant, 10 mM antioxidant and 18.8 g/l (0.062 M) of the complexing agent according to the invention 6,11-dithioxo-2,15-dioxo-5,7,10,12-tetraazahexadecane. The pH is approximately 0.

1.2 Comparative aqueous compositions C (not according to the present invention):

[0125] For comparative purposes, comparative aqueous composition C-1 comprises 45 g/L tin(II) ions, 1 g/L silver (I) ions, approximately 1 mol/L methane sulfonic acid (MSA), 20-40mM of the complexing agent 2,2'-dithiodi-aniline and 20-40mM of the complexing agent 2-Dimethyl-aminoethanthiol. The pH is approximately 0.

[0126] For comparative purposes, comparative aqueous composition C-2 comprises 45 g/L tin(II) ions, 1 g/L silver (I) ions, approximately 1 mol/L methane sulfonic acid, 2.5 g/L surfactant, 10 mM antioxidant and 11.4 g/L (0.062 M) complexing agent 3,6-dithiaoctane-1,8-diol. The pH is approximately 0.

[0127] For comparative purposes, comparative aqueous composition C-3 comprises 45 g/L tin(II) ions, 1 g/L silver (I) ions, approximately 1 mol/L methane sulfonic acid, 2.5 g/L surfactant, 10 mM antioxidant and 2.5 g/L (0.0137 M) complexing agent 3,6-dithiaoctane-1,8-diol. The pH is approximately 0.

[0128] The pH is approximately 0.

3. Stability Testing

[0129] The aqueous compositions were subjected to a stability test. 250 ml of the compositions E-1 and C-1 - C-3 were each filled in a 250 ml glass container and stored at room temperature in a hood.

[0130] The initial assessment revealed that all compositions were slightly yellowish and clear.

[0131] After 3-month storage time at room temperature the inventive composition E-1 was still a clear, yellowish liquid. No precipitates were visible in the liquid.

[0132] Comparative composition C-1 was clear, slightly orange and crystal formation was visible at the bottom of the glass container. Comparative compositions C-2 and C-3 were cloudy. Composition C-2 showed white precipitates at the bottom of the glass container, wherein composition C-3 exhibited strong brown precipitates.

[0133] After 5-month storage time at room temperature the inventive composition E-1 was still a clear, yellowish liquid.

[0134] Comparative composition C-1 was clear, slightly orange and at the bottom of the glass container crystal formation was visible. Comparative compositions C-2 and C-3 both were cloudy. Composition C-2 showed white precipitates at the bottom of the glass container, wherein composition C-3 exhibited strong brown precipitates.

[0135] The stability testing revealed that the inventive complexing agent provides better stabilization of plating bath compositions compared to other state of the art complexing agents.

4. Plating results

[0136] In order to assess the ability of the complexing agent according to the invention to preserve the plating efficiency for a long time period, a plating bath composition E-2 was formulated. The plating bath was made from methane sulfonic acid 70% solution (106 ml/L), SnMSA 40% solution (214 ml/L), SnAg (100 ml/L), the inventive complexer 6,11-dithioxo-2,15-dioxo-5,7,10,12-tetraazahexadecan (18.8 g/L) and SnAg solution (75 ml/L equals 1.5 g/L Ag⁺).

[0137] The bath was used in a plating experiment (plating of 5 test coupons) and after plating the bath was stored for 4 months at room temperature. During the storage period no precipitation or color change of the composition appeared. In comparison, current state of the art SnAg fresh plating baths precipitate within a 4 week time period even in air-tight containers. The precipitation in standard baths appear much earlier, i.e. in the course of several days, in case that the bath was used in a plating experiment. This behavior is expected based on the fact that such used solutions are oxygen saturated.

[0138] The used bath was again subjected in the course of a plating experiment. For comparison a fresh bath of the same composition was used. A tin silver alloy was deposited at two different currents, i.e. 5 and 10 amps per square decimeter (ASD). Since the Ag content in the deposit is highly sensitive to its bath concentration, similar Ag contents in deposits are a strong hint, that the silver-ion is well stabilized by the complexing agent in the bath for the 4 months period.

[0139] The plating experiment revealed the following silver contents in weight-%:

	5 ASD	10 ASD
Fresh bath	4.3	2.4

(continued)

	5 ASD	10 ASD
4 months stored at RT	4.0	2.3

[0140] Within the error of the experiment very similar or only slightly worse results are achieved with an "old" plating bath comprising the complexing agent according to the invention as indicated by the silver contents. This finding is a strong indicator that the complexing agent according to the invention is able to preserve the plating abilities of a plating bath composition over much longer time period compared to complexing agent already known in this field.

5. Complexing properties determined by titration experiments

[0141] In order to evaluate the complexing properties of two complexing agents according to the invention for silver ions titrations were carried out. The titrations were performed as follows:

In a first step an aqueous stock solution (concentration of complexing compound: 50 g/L) comprising the respective complexing agent for silver ions was prepared.

In a second step, portions from the stock solution were added stepwise to a titration solution comprising silver methanesulfonate (concentration corresponding to 1 g/L Ag (I) ions) and a silver rotating disk electrode (RDE) (1000 rpm). The change in overpotential upon adding portions from the stock solution was determined in reference to a reference electrode. The temperature of the titration solution was 25°C.

[0142] The results of the titrations are summarized in Figure 1 and Figure 2.

[0143] Figure 1 shows the titration results for the complexing agent according to the invention 12,17-dithioxo-2,5,8,21,24,27-hexaoxa-11,13,16,18-tetraaza-octacosane. It can be deduced from the titration that at already low concentrations of the complexing agent large shifts in the overpotential are achieved. In the range of approximately 70 mmol/L an overall shift ΔE of -657 mV is achieved for the Ag^+ -ion, wherein the potential for the Sn^{2+} -ion remains nearly constant. This change in Ag^+ -potential is a strong indicator that the Ag^+ -ion is selectively complexed by the complexing agent according to the invention. Therefore, this complexing agent is very suitable for stabilizing electroplating silver baths and especially for preventing the precipitation of silver from silver/tin baths.

[0144] Figure 2 shows the titration results for the complexing agent according to the invention 6,12-dithioxo-2,16-dioxa-5,7,11,13-tetraazaheptadecan. It can be deduced from the titration that at already low concentrations of the complexing agent large shifts in the overpotential are achieved. In the range of approximately 70 mmol/L an overall shift ΔE of -664 mV is achieved for the Ag^+ -ion, wherein the potential for the Sn^{2+} -ion remains nearly constant. This change in Ag^+ -potential is a strong indicator that the Ag^+ -ion is selectively complexed by the complexing agent according to the invention. Therefore, this complexing agent is very suitable for stabilizing electroplating silver baths and especially for preventing the precipitation of silver from silver/tin baths.

[0145] Figure 3 shows the titration results for the complexing agent according to the invention 1,3-bis(2-methoxyethyl) thiourea. It can be deduced from the titration that at already low concentrations of the complexing agent large shifts in the overpotential are achieved. In the range of approximately 70 mmol/L an overall shift ΔE of -524 mV is achieved for the Ag^+ -ion, wherein the potential for the Sn^{2+} -ion remains nearly constant. This change in Ag^+ -potential is a strong indicator that the Ag^+ -ion is selectively complexed by the complexing agent according to the invention. Therefore, this complexing agent is very suitable for stabilizing electroplating silver baths and especially for preventing the precipitation of silver from silver/tin baths.

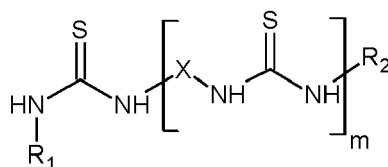
[0146] Figure 4 shows the titration results for the complexing agent according to the invention 1,3-bis(2-methoxypropyl) thiourea. It can be deduced from the titration that at already low concentrations of the complexing agent large shifts in the overpotential are achieved. In the range of approximately 70 mmol/L an overall shift ΔE of -524 mV is achieved for the Ag^+ -ion, wherein the potential for the Sn^{2+} -ion remains nearly constant. This change in Ag^+ -potential is a strong indicator that the Ag^+ -ion is selectively complexed by the complexing agent according to the invention. Therefore, this complexing agent is very suitable for stabilizing electroplating silver baths and especially for preventing the precipitation of silver from silver/tin baths.

[0147] The complexing agents according to the invention show remarkable complexing properties with respect to silver-ions. The complexing agents are able to induce shifts in the overpotential at moderate concentrations in the range of around and even larger than 600 mV. This change in the overpotential is an indicator of a stronger complexation and provides additional stability by hindering oxidation of Sn^{2+} -ions and reduction of Ag^{1+} -ions.

Claims

1. An aqueous composition for depositing a tin silver alloy, the composition comprising

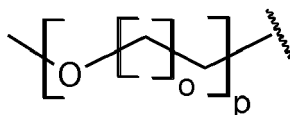
- (a) tin ions,
 (b) silver ions,
 (c) at least a complexing agent according to the following formula (I)



(I)

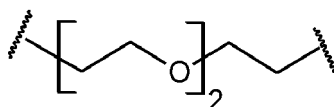
or a salt thereof;
 wherein independently:

- $m = 0, 1, 2$, preferably $m = 1, 2$;
 R_1, R_2 denotes a substituent according to the following formula (II)



(II),

- wherein $o = 1, 2$ and $p = 1 - 12$, preferably $p = 1 - 3$;
 X denotes a C2-C4 alkanediyl or a moiety according to the following formula (III)



(III).

2. The composition of claim 1, wherein X is C2-C4 alkanediyl.

3. The composition of any of the aforementioned claims, wherein at least one of R_1 or R_2 is methyl.

4. The composition of any of the aforementioned claims, wherein at least one of R_1 or R_2 is a substituent according to formula (II).

5. The composition of any of the aforementioned claims, wherein at least one of R_1 or R_2 is a substituent according to formula (II) and p is selected from the group consisting of 1, 2 or 3.

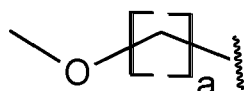
6. The composition of any of the aforementioned claims, wherein the concentration of the complexing agent in the aqueous composition is greater than or equal to 30 mmol/L and less than or equal to 120 mmol/L, preferably greater than or equal to 50 mmol/L and less than or equal to 80 mmol/L.

7. The composition of any of the aforementioned claims, furthermore comprising (d) at least one organic acid anion, preferably an alkyl sulfonic acid anion, most preferably methane sulfonic acid anions.

8. The composition of any of the aforementioned claims, furthermore comprising (e) at least one surfactant, preferably selected from the group consisting of nonionic surfactants, amphoteric surfactants, cationic surfactants, and anionic surfactants, preferably nonionic surfactants and cationic surfactants, more preferably alkoxyated cationic surfactants

and polyether nonionic surfactants, even more preferably alkylene oxide co-polymers and alkoxyated amines, most preferably ethylene oxide/propylene oxide co-polymers and ethoxylated amines.

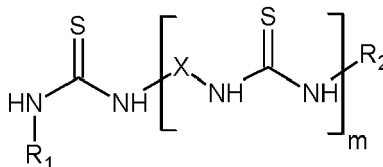
9. The composition of any of the aforementioned claims, furthermore comprising (f) at least one anti-oxidizing agent, preferably selected from the group consisting of compounds comprising a hydroxylated ring moiety, most preferably selected from the group consisting of catechol, hydroquinone, resorcinol, phenolsulfonic acids, ascorbic acid, and naphtholsulfonic acids.
10. The composition of any of the aforementioned claims, wherein $m = 0$ and R_1 and R_2 each independently denote a substituent according to the following formula IV



(IV),

wherein $a = 2$ or 3 .

11. A method for electrolytically depositing a tin silver alloy onto a substrate, the method comprising the steps
- (A) providing the substrate,
 (B) providing an aqueous composition according to any of claims 1 to 10,
 (C) contacting said substrate with said aqueous composition and supplying an electrical current such that said tin silver alloy is electrolytically deposited onto the substrate.
12. The method of claim 11, wherein the silver content in the electrolytically deposited tin silver alloy is in the range from 0.1 wt-% to 10 wt-%, based on the total weight of the electrolytically deposited tin silver alloy, preferably is in the range from 0.5 wt-% to 5 wt-%, most preferably is in the range from 1.5 wt-% to 3.5 wt-%.
13. The method of claim 11 or 12, wherein the substrate comprises a plurality of metal features, preferably a plurality of metal pillars and/or areas with at least one metal layer, more preferably a plurality of copper pillars and/or areas with at least one copper layer.
14. Use of an aqueous composition according to any of claims 1 to 10 for electrolytically depositing tin silver alloy solder bumps or tin silver alloy solder caps onto metal pillars, preferably for electrolytically depositing tin silver alloy solder caps onto copper pillars.
15. A compound according to the following formula (I)

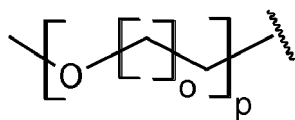


(I)

or a salt thereof;
 wherein independently:

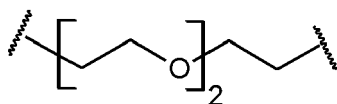
$m = 0, 1, 2$, preferably $m = 1, 2$;

R_1, R_2 denotes a substituent according to the following formula (II)



(II),

wherein $o = 1, 2$; $p = 1 - 12$, preferably $p = 1 - 3$; and
X denotes a C2-C4 alkanediyl or a moiety according to the following formula (III)



(III).

Figure 1

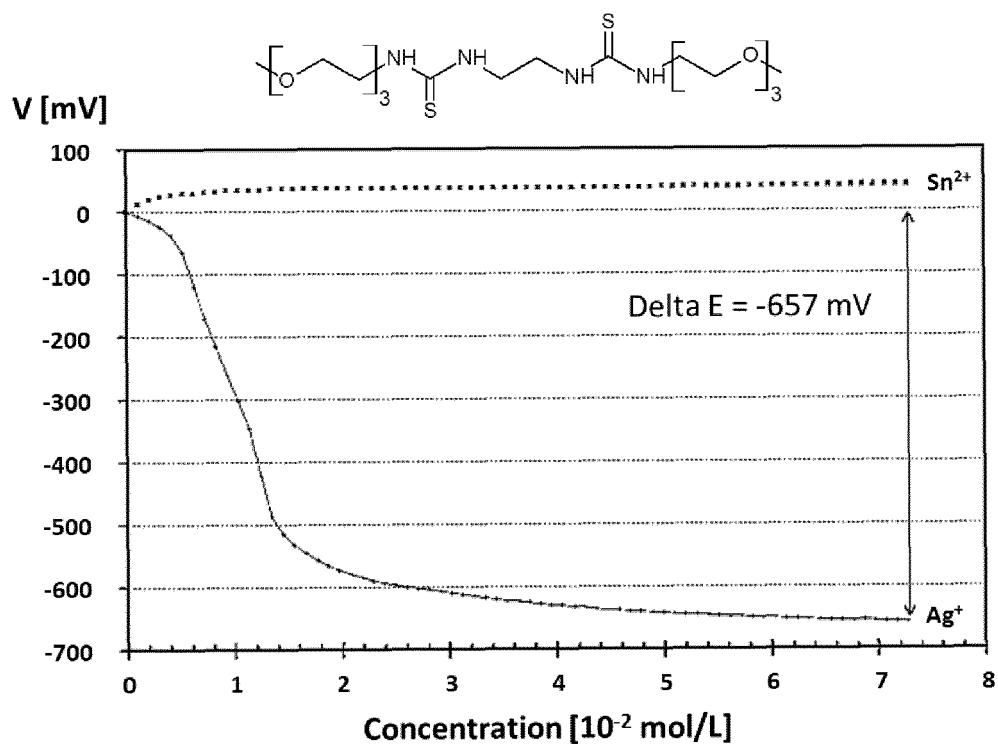


Figure 2

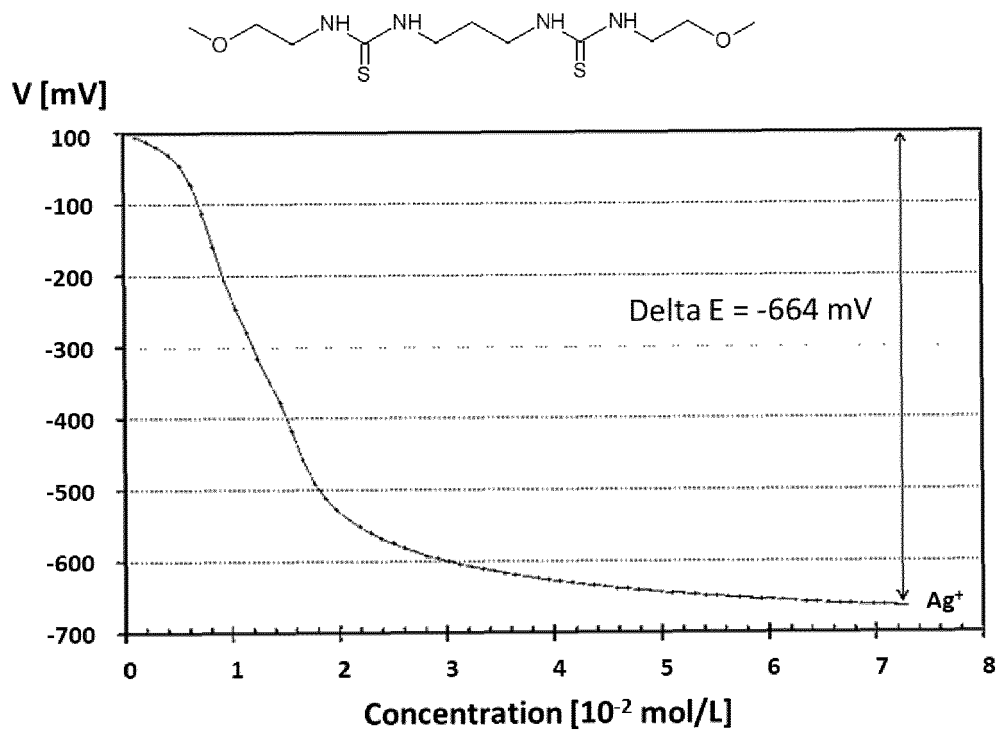


Figure 3

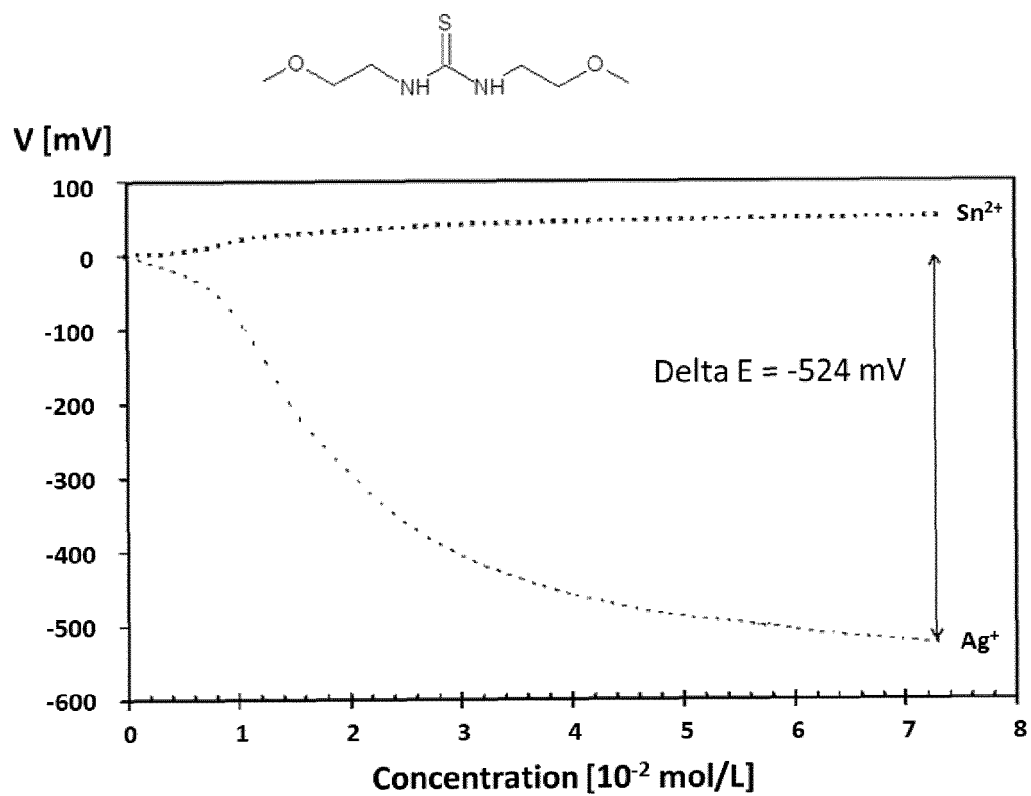
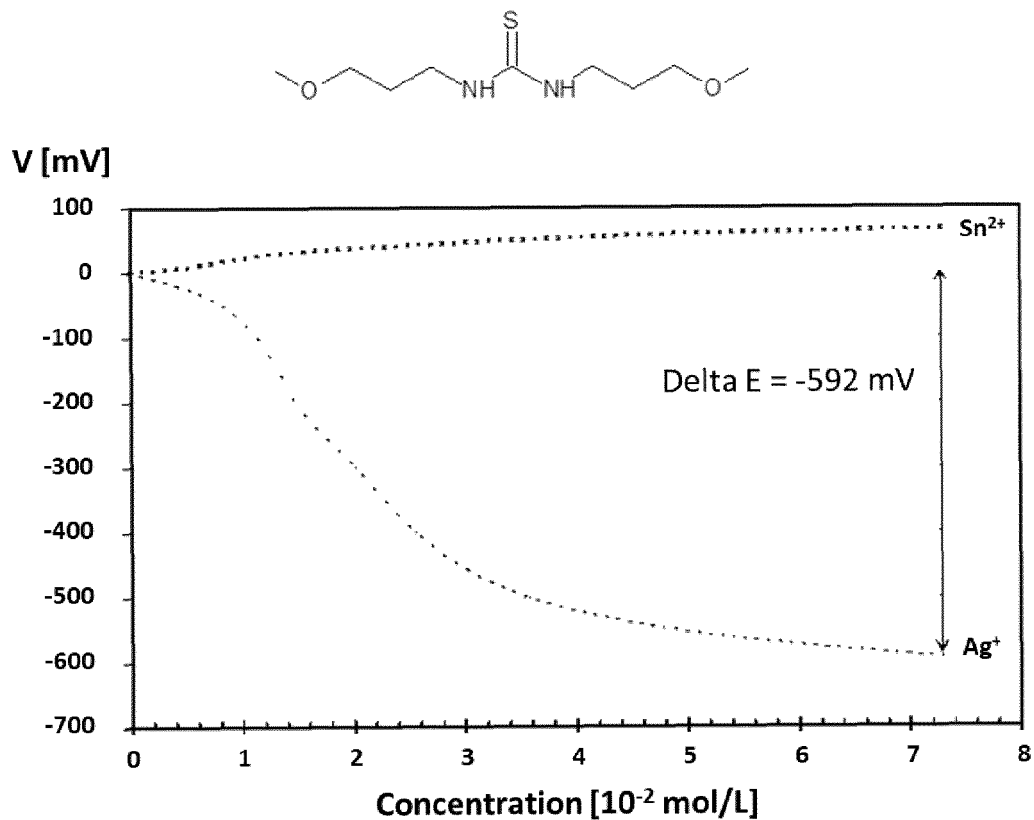


Figure 4





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Place of search The Hague		Date of completion of the search 23 April 2024	Examiner Le Hervet, Morgan
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