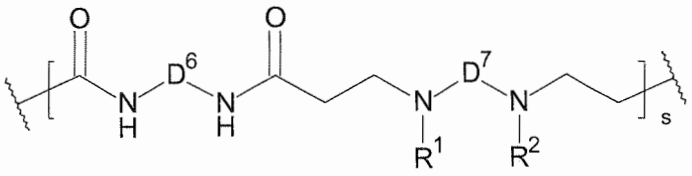
It is a further object of the embodiments disclosed herein to provide a copper electroplating bath cabable of depositing a low impurity metal layer.

Summary

It has been found, that particular polyaminoamides and derivatives thereof as defined herein may be used as additives, in particular leveling agents, in metal, particularly in copper electroplating baths showing an improved performance.

Therefore ~~in a first aspect~~, there is provided a composition comprising a source of metal ions and at least one additive comprising at least one polyaminoamide, said polyaminoamide comprising the structural unit represented by formula I



(I)

or derivatives of the polyaminoamide of formula I obtainable by complete or partial protonation, N-functionalization or N-quaternization with a non-aromatic reactant,

wherein

D^6 is, for each repeating unit 1 to s independently, a divalent group selected from a saturated or unsaturated C_1-C_{20} organic radical,

D^7 is selected from straight chain or branched C_2-C_{20} alkanediyl, which may optionally be interrupted by heteroatoms or divalent groups selected from O, S and NR^{10},

R^1 is, for each repeating unit 1 to s independently, selected from H, C_1-C_{20} alkyl, and C_1-C_{20} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl, or , together with R^2, forms a divalent group D^8, and

R^2 is, for each repeating unit 1 to s independently, selected from H, C_1-C_{20} alkyl, and C_1-C_{20} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl, or , together with R^1, forms a divalent group D^8, and

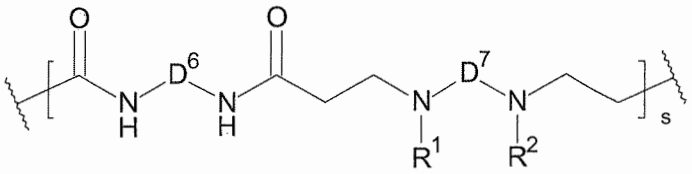
D^8 is selected from straight chain or branched C_1-C_{18} alkanediyl, which may optionally be interrupted by heteroatoms or divalent groups selected from O, S and NR^{10}, and

s is an integer from 1 to 250, and

R^{10} is selected from H, C_1-C_{20} alkyl, and C_1-C_{20} alkenyl, which may optionally be substituted

by hydroxyl, alkoxy or alkoxycarbonyl.

In a first aspect, there is provided the use of an a composition for metal electroplating, wherein the composition comprises a source of metal ions and at least one additive comprising at least one polyaminoamide, said polyaminoamide comprising the structural unit represented by formula I



(I)

or derivatives of the polyaminoamide of formula I obtainable by complete or partial protonation, N-functionalization or N-quaternization with a non-aromatic reactant,

wherein

D^6 is, for each repeating unit 1 to s independently, a divalent group selected from a saturated or unsaturated C_1-C_{20} organic radical,

D^7 is, for each repeating unit 1 to s independently, a divalent group selected from straight chain or branched C_2-C_{20} alkanediyl, which may optionally be interrupted by heteroatoms or divalent groups selected from O, S and NR^{10},

R^1 is, for each repeating unit 1 to s independently, selected from H, C_1-C_{10} alkyl, and C_1-C_{10} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl, and

R^2 is, for each repeating unit 1 to s independently, selected from H, C_1-C_{10} alkyl, and C_1-C_{10} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl, and

s is an integer from 1 to 250.

In a second aspect, there is provided the use of polyaminoamides as described herein in a bath for depositing metal containing layers.

In a third aspect, there is provided a process for depositing a metal layer on a substrate by contacting a plating solution as described herein with the substrate, and applying a current to the substrate to deposit a metal layer onto the substrate. The process is particularly useful for depositing metal, particularly copper layers on substrate comprising micrometer and/or nanometer-sized features.

It has been found that the use of compositions according to the present disclosure for electroplating provides deposited metal layers, particularly copper layers, having reduced overplating, particularly reduced mounding. The metal layers provided by the present disclosure are substantially planar, even on substrates exhibiting apertures of a very wide range of different aperture sizes (scale: below or equal 130 nanometers to 2 micrometers). Furthermore it has been found that the present disclosure provides metal layers substantially without the formation of added defects, such as voids, in the features.

The agents/additives according to the present disclosure can further advantageously be used for electroplating of copper in through silicon vias (TSV). Such vias normally have diameters of several micrometers up to 100 micrometers and large aspect ratios of at least 4, sometimes above 10.

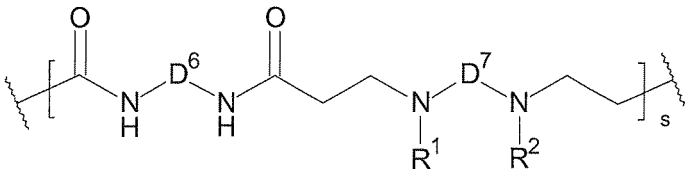
Furthermore the agents/additives according to the present disclosure can advantageously be used in bonding technologies such as the manufacture of copper pillars of typically 50 to 100 micrometers height and diameter for the bumping process, in circuit board technologies like the manufacture of high-density-interconnects on printed circuit boards using microvia plating or plated-through-hole technologies, or in other packaging processes for electronic circuits.

A further significant advantage of this leveling effect is that less material has to be removed in post-deposition operations. For example, chemical mechanical polishing (CMP) is used to reveal the underlying features. The more level deposit of the disclosure corresponds to a reduction in the amount of metal which must be deposited, therefore resulting in less removal later by CMP. There is a reduction in the amount of scrapped metal and, more significantly, a reduction in the time required for the CMP operation. The material removal operation is also less severe which, coupled with the reduced duration, corresponds to a reduction in the tendency of the material removal operation to impart defects.

Detailed description of the Invention

Claims

1. Use of ~~A~~a composition for metal electroplating, wherein the composition comprise~~sing~~s a source of metal ions and at least one additive comprising at least one polyaminoamide, said polyaminoamide comprising the structural unit represented by formula I



(I)

or derivatives of the polyaminoamide of formula I obtainable by complete or partial protonation, N-functionalization or N-quaternization with a non-aromatic reactant,

wherein

D^6 is, for each repeating unit 1 to s independently, a divalent group selected from a saturated or unsaturated C_1-C_{20} organic radical,

D^7 is, for each repeating unit 1 to s independently, a divalent group selected from straight chain or branched C_2-C_{20} alkanediyl, which may optionally be interrupted by heteroatoms or divalent groups selected from O, S and NR^{10},

R^1 is, for each repeating unit 1 to s independently, selected from H, C_1-C_{210} alkyl, and C_1-C_{210} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl~~, or , together with R^2, may form a divalent group D^8~~, and

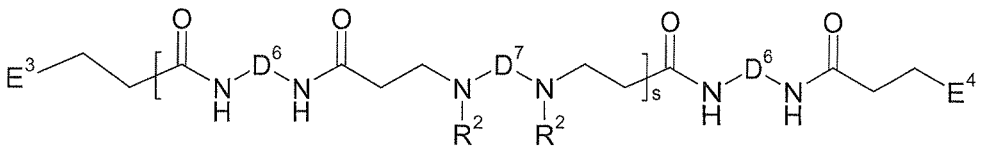
R^2 is, for each repeating unit 1 to s independently, selected from H, C_1-C_{120} alkyl, and C_1-C_{210} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl~~, or , together with R^1, may form a divalent group D^8~~, and

~~D^8 is selected from straight chain or branched C_4-C_{18} alkanediyl, which may optionally be interrupted by heteroatoms or divalent groups selected from O, S and NR^{10},~~

s is an integer from 1 to 250~~.~~

~~R^{10} is selected from H, C_1-C_{20} alkyl, and C_1-C_{20} alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl~~.

2. The ~~composition~~ use according to claim 1, wherein the polyaminoamide is represented by formula IV



(IV)

wherein D^6, D^7, R^1, R^2, and s have the prescribed meanings and

E^3, E^4 are independently selected from

(a) NH-C_1-C_{20}-alkyl or NH-C_1-C_{20}-alkenyl,

(b) N-(C_1-C_{20}-alkyl)$_2$ or N-(C_1-C_{20}-alkenyl)$_2$ or N-(C_1-C_{20}-alkyl)(C_1-C_{20}-alkenyl)

(c) NR^2-D^7-NR^2H, or

(d) NR^2-D^7-NR^2-CH_2-CH_2-CO-NH-(C_1-C_{20}-alkyl) or NR^2-D^7-NR^2-CH_2-CH_2-CO-NH-(C_1-C_{20}-alkenyl).

3. The ~~composition~~ use according to claim 2, wherein E^3 and E^4 are independently selected from NR^1-D^7-NR^2H

4. The ~~composition~~ use according to anyone of the preceding claims, wherein the metal ions comprise copper ion.

5. The use~~composition~~ according to anyone of the preceding claims, wherein D^6 is, for each repeating unit 1 to s independently, selected from $(CH_2)_g$, wherein g is an integer from 1 to 6.

6. The use~~composition~~ according to anyone of the preceding claims, wherein D^7 is selected from straight chain C_2- to C_6-alkanediyl.

7. The use~~composition~~ according to anyone of the preceding claims, wherein s is an integer from 1 to 150, more preferably from 2 to 100, most preferably from 2 to 50.

8. The use~~composition~~ according to anyone of the preceding claims, wherein R^1 is selected from H, C_1-C_{210}-alkyl, C_1-C_{120}-alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl.

9. The use~~composition~~ according to anyone of the preceding claims, wherein R^2 is selected from H, C_1-C_{120}-alkyl, or C_1-C_{120}-alkenyl, which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl.

~~10. The composition according to anyone of claims 1 to 7, wherein R^1 and R^2 together form a divalent group D^8, with D^8 being selected from straight chain or branched C_4-C_{48} alkanediyl, which may optionally be interrupted by heteroatoms or divalent groups selected from O, S and NR^{10}, with R^{10} being selected from H, C_1-C_{20} alkyl, and C_1-C_{20} alkenyl,~~

~~which may optionally be substituted by hydroxyl, alkoxy or alkoxycarbonyl.~~

~~11~~10. The use~~composition~~ according to anyone of the preceding claims, further comprising an accelerating agent.

~~12~~11. The use~~composition~~ according to anyone of the preceding claims, further comprising a suppressing agent.

~~13~~12. Use of a polyaminoamide of formula I as defined in anyone of the preceding claims in a bath for depositing metal containing layers.

~~14~~13. A process for depositing a metal layer on a substrate by

a) contacting a metal plating bath comprising a composition ~~according to~~ as defined in any of claims 1 to 1~~2~~12 with the substrate, and

b) applying a current density to the substrate for a time sufficient to deposit a metal layer onto the substrate.

~~15~~14. The process according to claim 13~~14~~, wherein the substrate comprises micrometer or nanometer sized features and the deposition is performed to fill the micrometer or nanometer sized features.

~~16~~15. The process according to claim ~~15~~14, wherein the nanometer-sized features have a size from 1 to 1000 nm and/or an aspect ratio of 4 or more.