may result from migration of copper into the solder phase, it has been necessary to provide a nickel cap on the distal end of the bump or pillar as a barrier between the copper phase and the solder phase, thus adding to the expense and complication of the manufacturing process.

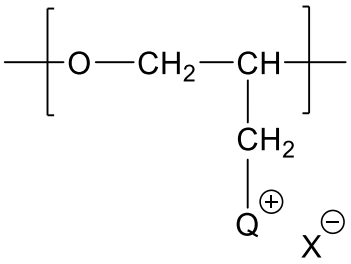
SUMMARY OF THE INVENTION

[0011] Described herein are improved compositions and processes for electrodeposition of wafer level packaging (WLP) features. Particularly effective for this purpose is a process in which a feature such as a bump, pillar, or megabump is deposited from a plating solution that comprises a source of copper ions, an acid, a leveler, a suppressor, and an accelerator.

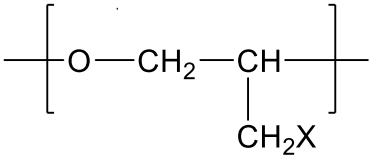
[0012] The process described herein is effective for forming WLP features on semiconductor substrates for interconnection of an electronic circuit of a semiconductor device with a circuit external to the device. This includes, for example, features having diameters as small as about 1 μm or as large as about 240 μm, and heights as small as about 2 μm and as large as about 300 μm; with aspect ratios between about 1:1 and about 2:1, and up to about 10:1 or even up to about 20:1. In one embodiment, current is supplied to an electrolytic solution in contact with a cathode comprising a WLP structure such as an under bump structure on a semiconductor assembly, wherein the electrolytic solution comprises a source of copper ions, an acid, a leveler, and a suppressor, thereby electrodepositing a copper bump or pillar on the under bump structure.

[0012a] In one aspect of the disclosure, there is provided an electrodeposition composition comprising a) a source of copper ions; b) an acid; c) a suppressor; d) a leveler, wherein the leveler comprises

i) a quaternized dipyridyl compound, wherein the quaternized dipyridyl compound comprises a compound having a structure of a reaction product of N,N'-tetraalkylthiourea with an intermediate produced by a reaction of a dipyridyl with a difunctional alkylating agent; or a ii) quaternized poly(epihalohydrin) wherein the quaternized poly(epihalohydrin) compound comprises n repeating units corresponding to structure 1N and p repeating units corresponding to structure 1P



(1N)



(1P)

wherein Q has a structure corresponding to that which may be obtained by reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine selected from the group consisting of: (i) $NR^aR^bR^c$ wherein each of R^a, R^b and R^c is independently selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, aryl and heterocyclic; (ii) an N-substituted and optionally further substituted heteroalicyclic amine wherein the N-substituent is selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, aryl, and heterocyclic; and (iii) a substituted or unsubstituted nitrogen-containing heteroaryl compound;and wherein n is an integer between 3 and 35, p is an integer between 0 and 25; X is a halo substituent; and X^- is a monovalent anion; and e)an accelerator.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0013] In various preferred embodiments of the invention, as described herein, a copper bump or pillar having a suitable distal configuration is deposited at a relatively high rate of vertical growth. By "suitable distal configuration" what is meant is that the copper bump or pillar is not unduly domed, unduly dished, or irregular in shape. The rate of growth of bumps and pillars having suitable distal configurations compares favorably with the rate that is achieved using electrodeposition baths that do not involve the composition and process described herein.
The electrolytic plating bath generally comprises:

a) a source of copper ions;
b) an acid component;
c) a suppressor;

WHAT IS CLAIMED IS:

1. An electrodeposition composition comprising:

(a) a source of copper ions;

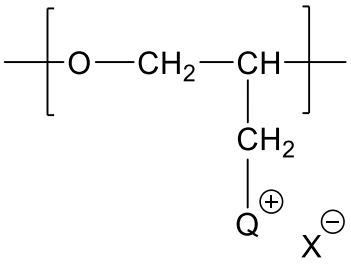
(b) an acid;

(c) a suppressor;

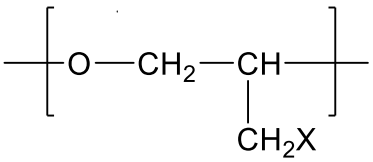
(d) a leveler, wherein the leveler comprises

i) a quaternized dipyridyl compound, wherein the quaternized dipyridyl compound comprises a structure of a reaction product of N,N'-tetraalkylthiourea with an intermediate produced by a reaction of a dipyridyl with a difunctional alkylating agent; or

ii) a quaternized poly(epihalohydrin) wherein the quaternized poly(epihalohydrin) compound comprises n repeating units corresponding to structure 1N and p repeating units corresponding to structure 1P



(1N)



(1P)

wherein Q has a structure corresponding to that which may be obtained by reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine selected from the group consisting of: (i) $NR^aR^bR^c$ wherein each of R^a, R^b and R^c is independently selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, aryl and heterocyclic; (ii) an N-substituted and optionally further substituted heteroalicyclic amine wherein the N-substituent is selected from the group consisting of substituted or unsubstituted alkyl, alicyclic, aralkyl, aryl, and heterocyclic; and (iii) a substituted or unsubstituted nitrogen-containing heteroaryl compound;and wherein n is an integer between 3

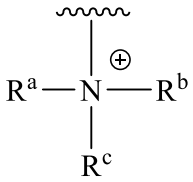
and 35, p is an integer between 0 and 25; X is a halo substituent; and X^- is a monovalent anion; and

e) an accelerator.

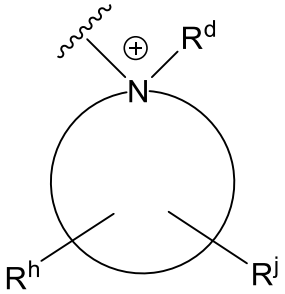
2. The composition of claim 1, wherein the difunctional alkylating agent is selected from the group consisting of 1-chloro-2-(2-chloroethoxy)ethane, 1,2-bis(2-chloroethoxy)ethane, 1,3-dichloropropan-2-one, 1,3-dichloropropan-2-ol, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,7-dichloroheptane, 1,8-dichlorooctane, 1,2-di(2-chloroethyl)ether.

3. The composition of claim 1, wherein the value of n is between 10 and 15.

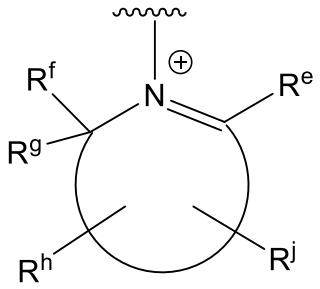
4. The composition as set forth in claim 1, wherein Q is selected from the group consisting of:



(2A)



(2B) or



(**2C)**

wherein: (i) structure IIB is an N-substituted heterocyclic moiety; (ii) structure IIC is a heterocyclic moiety; (iii) each of R^a, R^b, R^c and R^d is independently selected from the group consisting of substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aralkyl, substituted or unsubstituted alicyclic, substituted or unsubstituted aryl, and substituted or unsubstituted heterocyclic; and (iv) each of R^e, R^f, R^g, R^h and R^j is independently selected from the group consisting of hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aralkyl, substituted or unsubstituted alicyclic, and substituted or unsubstituted aryl, and substituted or unsubstituted heterocyclic.

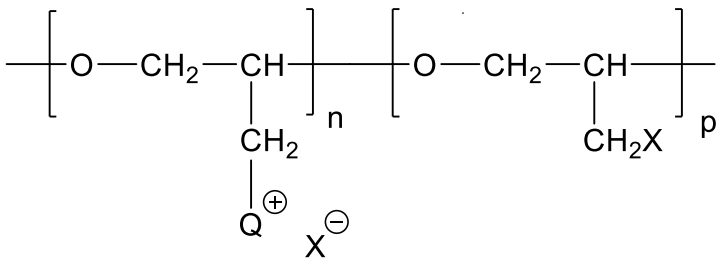
5. The composition as set forth in claim 1, wherein the quaternized poly(epihalohydrin) comprises additional repeating units comprising residues of at least one alkylene oxide, or

wherein the quaternized poly(epihalohydrin) comprises repeating units that are residues of ethylene oxide, or

wherein the quaternized poly(epihalohydrin) comprises repeating units that are residues of propylene oxide.

6. The composition as set forth in claim 5, wherein the total of alkylene oxide repeating units in said quaternized poly(epihalohydrin) is q, and the ratio of q/n+p+q is not greater than about 0.05, or is between about 0.05 and about 0.50.

7. The composition as set forth in claim 1, wherein repeating units of said poly(epihalohydrin) consist essentially of residues of epihalohydrin and residues of quaternized epihalohydrin



(I)

8. The composition as set forth in claim 1, wherein the quaternized poly(epihalohydrin) repeating units and non-quaternized epihalohydrin repeating units in said quaternized poly(epihalohydrin) are arranged in a block, alternating or random configuration.

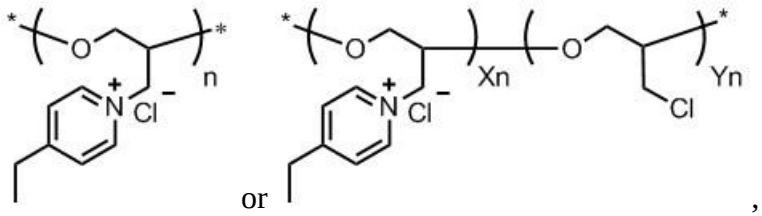
9. The composition as set forth in claim 1, wherein Q corresponds to the structure that may be obtained in reacting a pendent methylene halide group of poly(epihalohydrin) with a tertiary amine that comprises $NR^aR^bR^c$; wherein one of R^a, R^b and R^c is selected from the group consisting of unsubstituted alkyl having at least three carbon atoms, hydroxyalkyl, dihydroxyalkyl, phenyl, hydroxyphenyl, dihydroxyphenyl, benzyl, hydroxyphenylmethyl and dihydroxyphenylmethyl, and each of the others of R^a, R^b and R^c is independently selected from lower alkyl having between 1 and 3 carbon atoms.

10. The composition as set forth in claim 1, wherein Q has the structure which may be obtained from reacting a pendent methylene chloride group of poly(epihalohydrin) with:

a) a quaternizing agent selected from the group consisting of 3-hydroxypropyldimethylamine, n-butyldimethylamine, di(3-hydroxypropyl)methylamine, 2,3-dihydroxypropyldimethylamine, 3-hydroxypropyldiethylamine, 2-hydroxypropyldimethylamine, 4-hydroxybutyldimethylamine, 2-hydroxyethyldimethylamine, n-propyldimethylamine, 2-hydroxyethoxyethyldimethylamine, di(2-hydroxyethyl)methylamine, benzyldimethylamine and 4-hydroxybenzyldimethylamine; or

b) a pendent methylene halide group with a tertiary amine selected from the group consisting of 3-hydroxypropyldimethylamine, n-butyldimethylamine, di(3-hydroxypropyl)methylamine, 2,3-dihydroxypropyldimethylamine, 3-hydroxypropyldiethylamine, 2-hydroxypropyldimethylamine, 4-hydroxybutyldimethylamine, 2-hydroxyethyldimethylamine, n-propyldimethylamine, 2-hydroxyethoxyethyldimethylamine, di(2-hydroxyethyl)methylamine, benzyldimethylamine, and 4-hydroxybenzyldimethyleamine, 2-methylpyridine, 3-methylpyridine, 4-methylpyridine, 2-ethylpyridine, 3-ethylpyridine, 4-ethylpyridine, 2-propylpyridine, 3-propylpyridine, 4-propylpyridine, 4-tertbutylpyridine, 4-cyanopyridine, 4-isopropylpyridine, 4-methoxypyridine, 3,4-lutidine, 3-methoxypyridine, 3-pyridinemethanol, and 4-pyridinemethanol.

11. The composition as set forth in claim 1, wherein the quaternized poly(epihalohydrin) comprises:

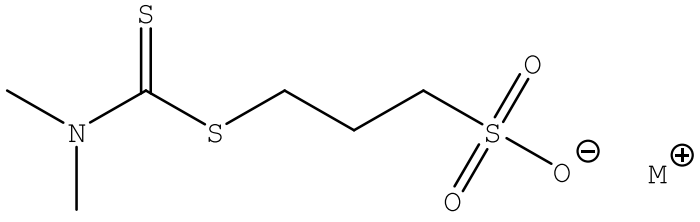


or ,

wherein X is between 0.3 and 0.7.

12. The composition as set forth in claim 1, wherein the aqueous electrodeposition composition further comprises an accelerator

13. The composition as set forth in claim 12, wherein the accelerator comprises an organic sulfur compound, having the following general structure (5):



Structure (5) ,

wherein M is selected from the group consisting of alkali metal ions and charge balancing cations.

14. The composition as set forth in claim 1, wherein the suppressor comprises a compound selected from the group consisting of:

a) an alkoxylated amine;

b) a polyether compound comprising a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1 and bonded to a nitrogen-containing species; and

c) a polyalkylene glycol having a terminal sulfonic acid moiety and a terminal aromatic moiety formed by condensing a substituted phenol with a terminal hydroxyl of said polyalkylene glycol.

15. The composition as set forth in claim 13, wherein the suppressor is a polyether compound and the PO repeat units and EO repeat units are present in a PO:EO ratio between 2:3 and 2:1.

16. The composition as set forth in claim 13, wherein the suppressor is an alkoxylated amine, and the alkoxylated amine is selected from the group consisting of a tetraalkoxylated alkylene diamine, an alkoxylated diethylene triamine, a tetraalkoxylated triethylene tetraamine, and combinations of one or more of the foregoing.

17. The composition as set forth in claim 1, wherein the ratio of n/n+p is at least 0.4 and less than 1.0.

18. The composition as set forth in claim 17, wherein the ratio of n/n+p is between 0.40 and 0.60 or between 0.70 and 0.95.