

CLAIMS

1. A copper chemical mechanical polishing (CMP) composition comprising:

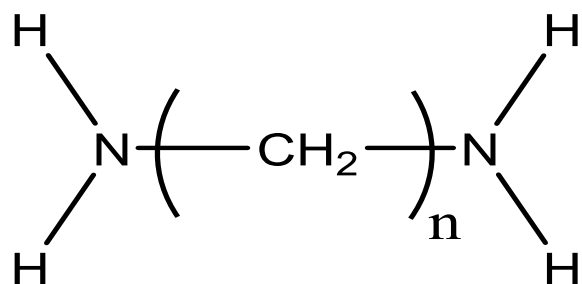
- a) 0.0025 wt.% to 25 wt.% abrasive selected from the group consisting of colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; colloidal aluminum oxide including alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide; colloidal cerium oxide; nano-sized inorganic metal oxide particles; nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasive; surface-coated or modified abrasive; composite particles; and combinations thereof;
- b) 0.1 wt. % to 18.0 wt. % three chelators selected from the group consisting of amino acid, amino acid derivative, organic amine, and combinations thereof; wherein at least one chelator is an amino acid or an amino acid derivative;
- c) 0.005 wt.% to 0.5 wt.% corrosion inhibitor;
- d) 0.0005 wt.% to 0.25 wt.% organic quaternary ammonium salt which is a choline salt formed between choline and other anionic counter ions;
- e) 0.1 wt.% to 10 wt.% oxidizing agent;
- f) 0.0001 wt.% to 0.05 wt.% biocide;
- g) 0 wt.% to 1 wt.% pH adjusting agent; and
- h) water;

the composition has a pH from 3.0 to 12.0;

wherein

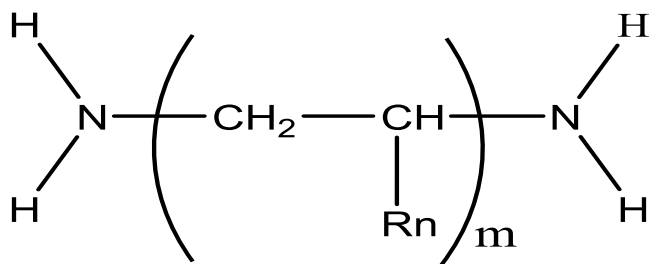
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof; and

the organic amine has a general molecular structure selected from the group consisting of:



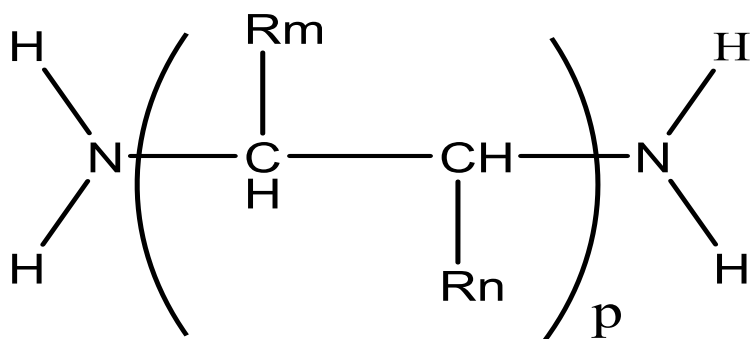
(a)

wherein n is from 2 to 12;



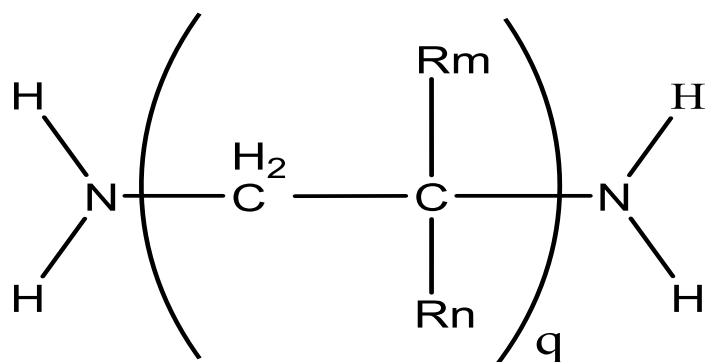
(b)

wherein R_n represents an organic alkyl group with n carbon atoms, n is from 1 to 12 and m is from 2 to 12;



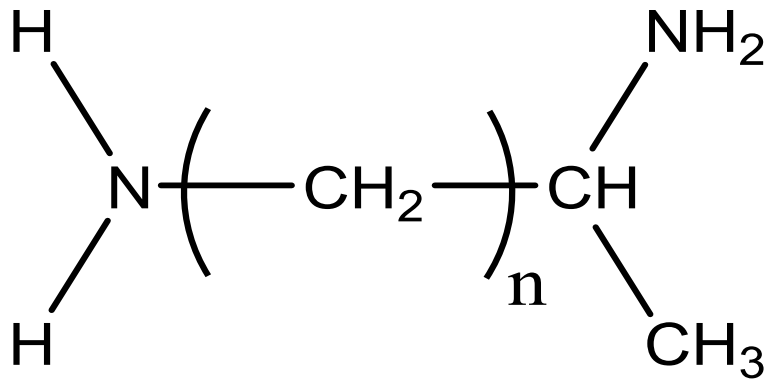
(c)

wherein R_n and R_m can be the same or different alkyl groups with n carbon atoms and m carbon atoms respectively, n and m are numbered independently from 1 to 12, and p is from 2 to 12;



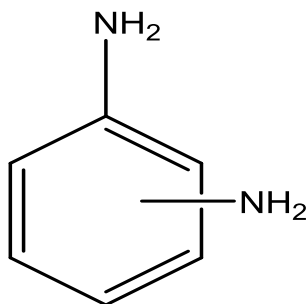
(d)

wherein R_n and R_m can be the same or different alkyl groups with n carbon atoms and m carbon atoms respectively, n and m are numbered independently from 1 to 12, and q is from 2 to 12;

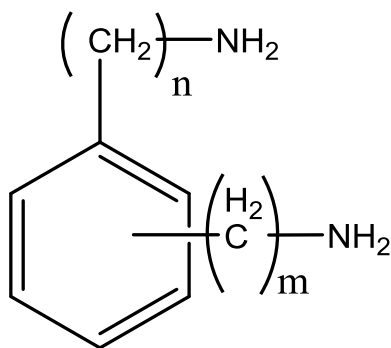


(e)

wherein n is from 1 to 12;



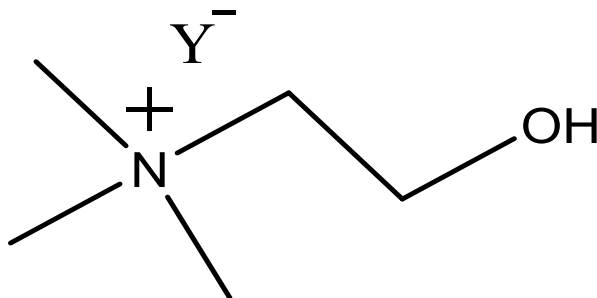
(f);



(g)

wherein n and m is numbered independently from 1 to 12;
and combinations thereof.

2. The copper chemical mechanical polishing (CMP) composition of claim 1, wherein the choline salt has a general molecular structure shown below:



wherein anion Y⁻ can be bicarbonate, hydroxide, p-toluene-sulfonate, or bitartate; the corrosion inhibitor is selected from the group consisting of 1,2,4-triazole, benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, tetrazole and tetrazole derivatives, and combinations thereof;

the oxidizing agent is selected from the group consisting of periodic acid, hydrogen peroxide, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and combinations thereof;

the biocide has an active ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof; and

the pH adjusting agent is either (1) selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, and combinations thereof for adjusting pH toward acidic; or (2) selected from the group consisting of sodium hydride, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic amine, and combinations thereof for adjusting pH toward alkaline.

3. The copper chemical mechanical polishing (CMP) composition of claim 1, wherein the organic amine is selected from the group consisting of ethylenediamine, propylenediamine, butylenediamine, and the combinations thereof.
4. The copper chemical mechanical polishing (CMP) composition of claim 1, wherein the three chelators are selected from (1) one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) two of different amino acids, two of different amino acid derivatives, or combinations of one amino acid with one amino derivative.
5. The copper chemical mechanical polishing (CMP) composition of claim 1, comprising
0.0025 wt.% to 2.5 wt.% of colloidal silica or high purity colloidal silica;
0.5 wt. % to 10.0 total wt. % of (1) one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) two of the amino acids, two of the amino acid derivatives, or combinations of one of the amino acid with one of the amino derivative; wherein the two amino acids are different and the two of the amino acid derivatives are different;
0.001 wt. % to 0.05 wt. % of choline bicarbonate salt; and
the composition has a pH from 5.5 to 7.5.
6. The copper chemical mechanical polishing (CMP) composition of claim 1, comprising
0.0025 wt.% to 2.5 wt.% of colloidal silica or high purity colloidal silica;
1.0 to 2.5 total wt. % of (1) one organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) two different amino acids selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, and other amino acids and their derivatives;
0.001 wt. % to 0.05 wt. % of choline bicarbonate salt; and
the composition has a pH from 5.5 to 7.5.

7. The copper chemical mechanical polishing (CMP) composition of claim 1, comprising
- 0.005 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;
 - 0.5 to 1.5 total wt. % of ethylenediamine; glycine and DL-alanine;
 - 0.002 wt. % to 0.01 wt. % of choline bicarbonate salt;
 - 0.5 wt. % to 2.0 wt. % of periodic acid or hydrogen peroxide;
 - 0.025 wt. % to 0.05 wt. % of 1,2,4-triazole or benzotriazole and benzotriazole derivatives;
 - 0.002 wt. % to 0.010 wt. % of the biocide has an active ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof; and
 - the composition has a pH from 7.0 to 7.35.
8. A method of chemical mechanical polishing a semiconductor substrate having at least one surface comprising copper (Cu) or copper-containing material and at least one second material; comprising steps of:
- 1) providing the semiconductor substrate;
 - 2) providing a polish pad;
 - 3) providing a Cu chemical mechanical polishing composition comprising
 - a) 0.0025 wt.% to 25 wt.% abrasive selected from the group consisting of colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; colloidal aluminum oxide including alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide; colloidal cerium oxide; nano-sized inorganic metal oxide particles; nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasive; surface-coated or modified abrasive; composite particles; and combinations thereof;

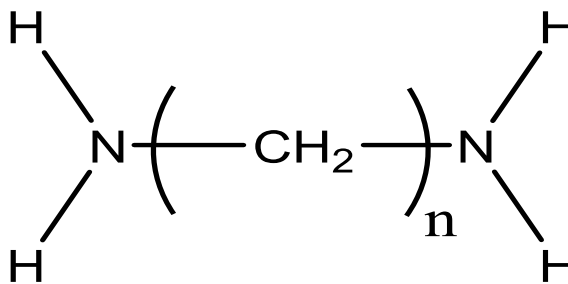
- b) 0.1 wt. % to 18.0 wt. % three chelators selected from the group consisting of amino acid, amino acid derivative, organic amine, and combinations thereof; wherein at least one chelator is an amino acid or an amino acid derivative;
- c) 0.005 wt.% to 0.5 wt.% corrosion inhibitor;
- d) 0.0005 wt.% to 0.25 wt.% organic quaternary ammonium salt which is a choline salt formed between choline and other anionic counter ions;
- e) 0.1 wt.% to 10 wt.% oxidizing agent;
- f) 0.0001 wt.% to 0.05 wt.% biocide;
- g) 0 wt.% to 1 wt.% pH adjusting agent; and
- h) water;

the composition has a pH from 3.0 to 12.0;

wherein

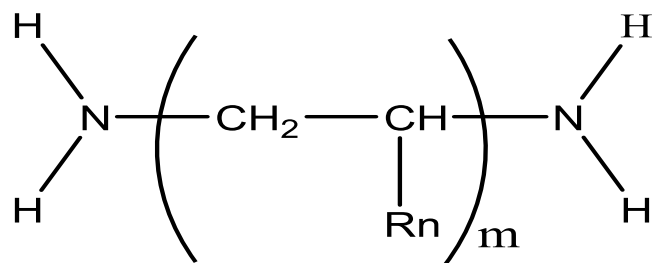
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof; and

the organic amine has a general molecular structure selected from the group consisting of:



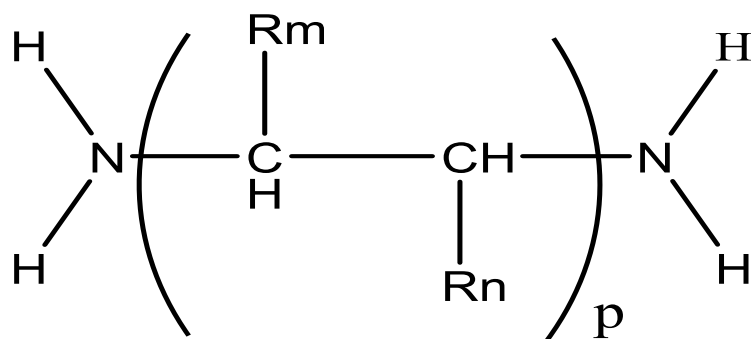
(a)

wherein n is from 2 to 12;



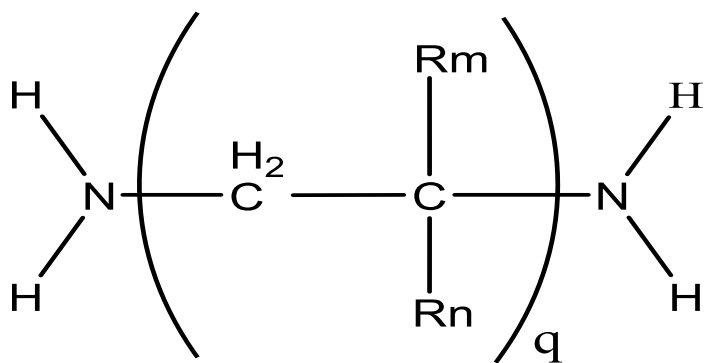
(b)

wherein R_n represents an organic alkyl group with n carbon atoms, n is from 1 to 12 and m is from 2 to 12;



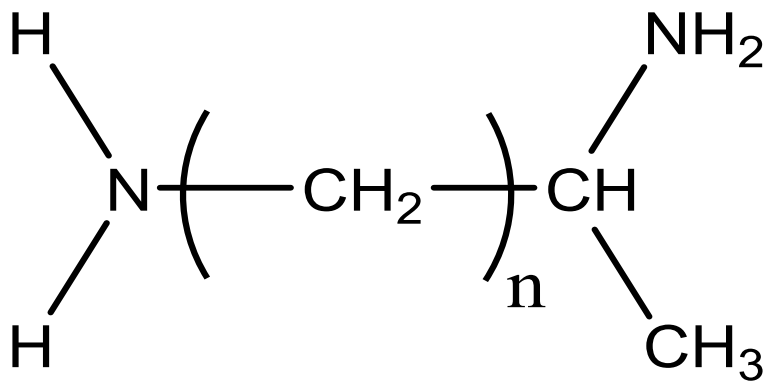
(c)

wherein R_n and R_m can be the same or different alkyl groups with n carbon atoms and m carbon atoms respectively, n and m are numbered independently from 1 to 12, and p is from 2 to 12;



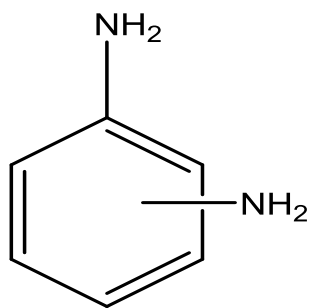
(d)

wherein R_n and R_m can be the same or different alkyl groups with n carbon atoms and m carbon atoms respectively, n and m are numbered independently from 1 to 12, and q is from 2 to 12;

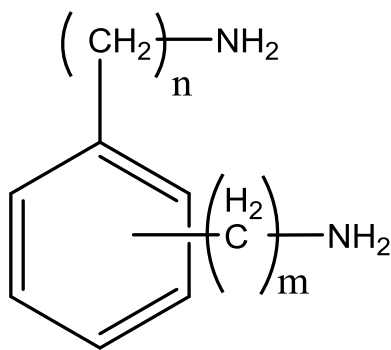


(e)

wherein n is from 1 to 12;



(f);



(g)

wherein n and m is numbered independently from 1 to 12;
and combinations thereof;

- 4) contacting the at least one surface with the polish pad and the Cu chemical mechanical polishing composition; and
- 5) polishing the at least one surface to remove copper or copper-containing material;

wherein at least a portion of the at least one surface comprising copper (Cu) or copper-containing material and at least one second material is in contact with both the polishing pad and the Cu chemical mechanical polishing composition.

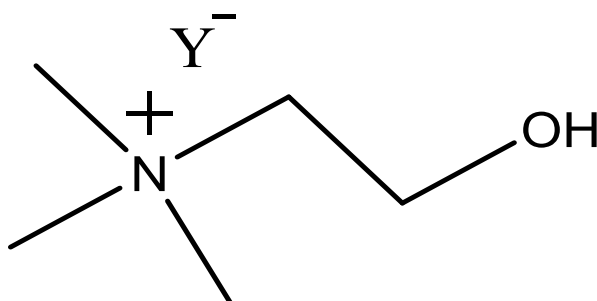
9. The method for chemical mechanical polishing of Claim 8, wherein

the second material is selected from the group consisting of barrier layer selected from the group consisting of Ta, TaN, Ti, and TiN film; dielectric layer selected from the group consisting of TEOS, low-k; and ultra low-k film; and

removal rate of Cu vs removal rate of the second material is equal or greater than 500:1.

10. The method for chemical mechanical polishing of Claim 8, wherein

the choline salt has a general molecular structure shown below:



wherein anion Y⁻ can be bicarbonate, hydroxide, p-toluene-sulfonate, or bitartate; the corrosion inhibitor is selected from the group consisting of 1,2,4-triazole, benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, tetrazole and tetrazole derivatives, and combinations thereof;

the oxidizing agent is selected from the group consisting of periodic acid, hydrogen peroxide, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and combinations thereof;

the biocide has an active ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof; and

the pH adjusting agent is either (1) selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, and combinations thereof for adjusting pH toward acidic; or (2) selected from the group consisting of sodium hydride, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic amine, and combinations thereof for adjusting pH toward alkaline.

11. The method for chemical mechanical polishing of Claim 8, wherein

the three chelators are selected from (1) one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) two of different amino acids, two of different amino acid derivatives, or combinations of one amino acid with one amino derivative.

12. The method for chemical mechanical polishing of Claim 8, wherein the Cu chemical mechanical polishing composition comprises

0.0025 wt.% to 2.5 wt.% of colloidal silica or high purity colloidal silica;

0.1 to 18.0 total wt. % of (1) one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) two of the amino acids, two of the amino acid derivatives, or combinations of one of the amino acid with one of the amino derivative; wherein the two amino acids are different and the two of the amino acid derivatives are different;

0.001 wt. % to 0.05 wt. % of choline bicarbonate salt; and

the composition has a pH from 5.5 to 7.5.

13. The method for chemical mechanical polishing of Claim 8, wherein the Cu chemical mechanical polishing composition comprises

0.0025 wt.% to 2.5 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 1.5 total wt. % of (1) one organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) two different amino acids selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, and other amino acids and their derivatives;

0.001 wt. % to 0.05 wt. % of choline bicarbonate salt; and

the composition has a pH from 5.5 to 7.5.

14. The method for chemical mechanical polishing of Claim 8, wherein the Cu chemical mechanical polishing composition comprises

0.005 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 1.5 total wt. % of ethylenediamine; glycine and DL-alanine;

0.002 wt. % to 0.01 wt. % of choline bicarbonate salt;

0.5 wt. % to 2.0 wt. % of periodic acid or hydrogen peroxide;

0.025 wt. % to 0.05 wt. % of 1,2,4-triazole or benzotriazole and benzotriazole derivatives;

0.002 wt. % to 0.010 wt. % of the biocide has an active ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof; and

the composition has a pH from 7.0 to 7.35.

15. A system for chemical mechanical polishing a semiconductor substrate having at least one surface comprising copper (Cu) or copper-containing material and at least one second material, the system comprising:

1) a polish pad; and

2) a Cu chemical mechanical polishing composition comprising

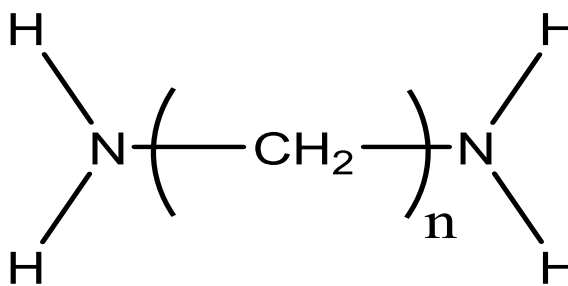
- a) 0.0025 wt.% to 25 wt.% abrasive selected from the group consisting of colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; colloidal aluminum oxide including alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide; colloidal cerium oxide; nano-sized inorganic metal oxide particles; nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasive; surface-coated or modified abrasive; composite particles; and combinations thereof;
- b) 0.1 wt. % to 18.0 wt. % three chelators selected from the group consisting of amino acid, amino acid derivative, organic amine, and combinations thereof; wherein at least one chelator is an amino acid or an amino acid derivative;
- c) 0.005 wt.% to 0.5 wt.% corrosion inhibitor;
- d) 0.0005 wt.% to 0.25 wt.% organic quaternary ammonium salt which is a choline salt formed between choline and other anionic counter ions;
- e) 0.1 wt.% to 10 wt.% oxidizing agent;
- f) 0.0001 wt.% to 0.05 wt.% biocide;
- g) 0 wt.% to 1 wt.% pH adjusting agent; and
- h) water;

the composition has a pH from 3.0 to 12.0;

wherein

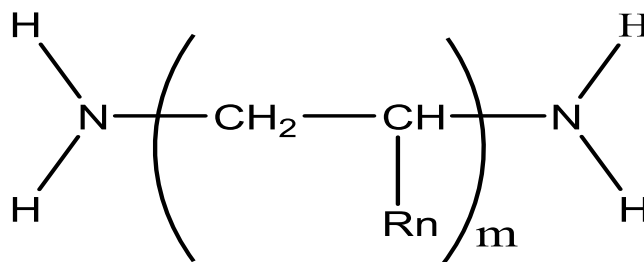
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof; and

the organic amine has a general molecular structure selected from the group consisting of:



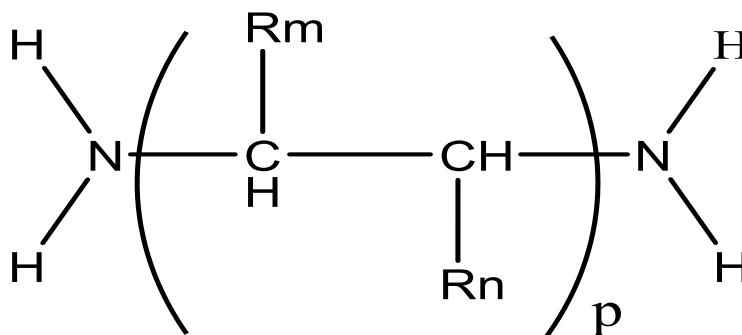
(a)

wherein n is from 2 to 12;



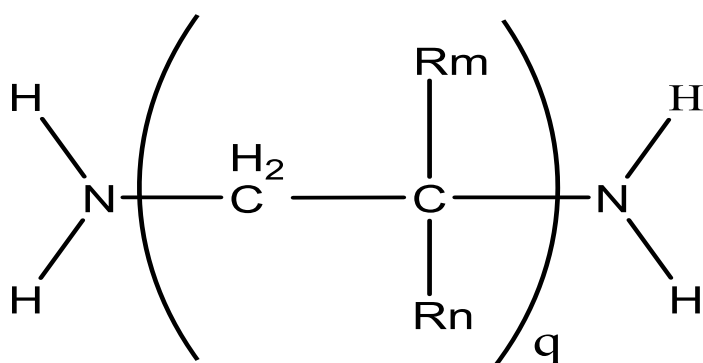
(b)

wherein R_n represents an organic alkyl group with n carbon atoms, n is from 1 to 12 and m is from 2 to 12;



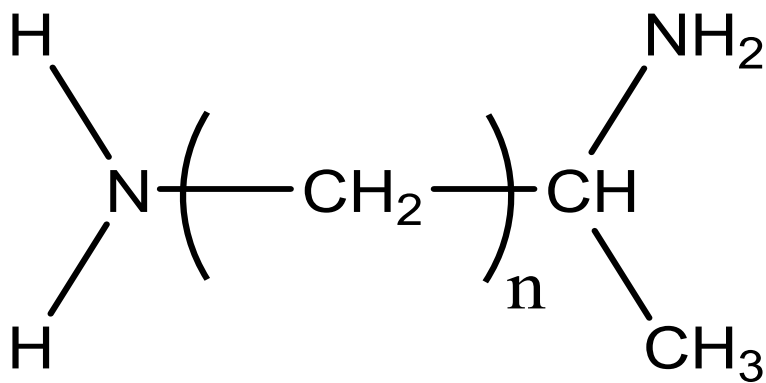
(c)

wherein R_n and R_m can be the same or different alkyl groups with n carbon atoms and m carbon atoms respectively, n and m are numbered independently from 1 to 12, and p is from 2 to 12;



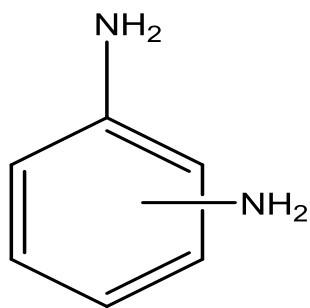
(d)

wherein R_n and R_m can be the same or different alkyl groups with n carbon atoms and m carbon atoms respectively, n and m are numbered independently from 1 to 12, and q is from 2 to 12;

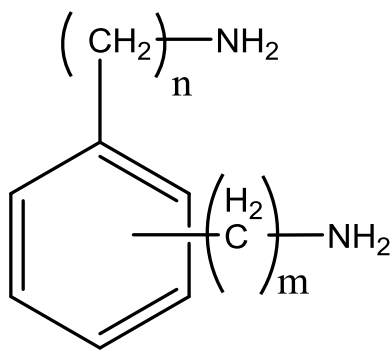


(e)

wherein n is from 1 to 12;



(f);



(g)

wherein n and m is numbered independently from 1 to 12;
and combinations thereof;

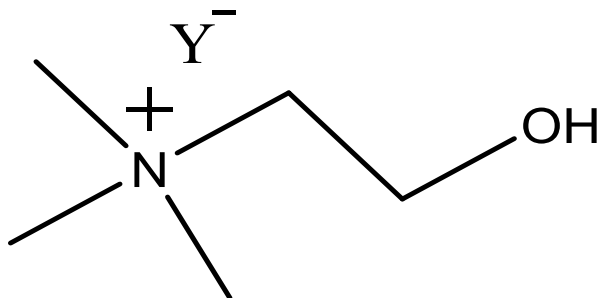
wherein at least a portion of the at least one surface comprising copper (Cu) or copper-containing material and at least one second material is in contact with both the polishing pad and the Cu chemical mechanical polishing composition.

16. The system for chemical mechanical polishing of Claim 15, wherein

the three chelators are selected from (1) one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) two of different amino acids, two of different amino acid derivatives, or combinations of one amino acid with one amino derivative.

17. The system for chemical mechanical polishing of Claim 15, wherein

the choline salt has a general molecular structure shown below:



wherein anion Y^- can be bicarbonate, hydroxide, p-toluene-sulfonate, or bitartate; the corrosion inhibitor is selected from the group consisting of 1,2,4-triazole, benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, tetrazole and tetrazole derivatives, and combinations thereof;

the oxidizing agent is selected from the group consisting of periodic acid, hydrogen peroxide, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and combinations thereof;

the biocide has an active ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof; and

the pH adjusting agent is either (1) selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, and combinations thereof for adjusting pH toward acidic; or (2) selected from the group consisting of sodium hydride, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic amine, and combinations thereof for adjusting pH toward alkaline.

18. The system for chemical mechanical polishing of Claim 15, wherein the Cu chemical mechanical polishing composition comprises

0.0025 wt.% to 2.5 wt.% of colloidal silica or high purity colloidal silica;

0.1 to 18.0 total wt. % of (1) one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) two of the amino acids, two of the amino acid derivatives, or combinations of one of the amino acid with one of the amino derivative; wherein the two amino acids are different and the two of the amino acid derivatives are different;

0.001 wt. % to 0.05 wt. % of choline bicarbonate salt; and

the composition has a pH from 5.5 to 7.5.

19. The system for chemical mechanical polishing of Claim 15, wherein the Cu chemical mechanical polishing composition comprises

0.0025 wt.% to 2.5 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 1.5 total wt. % of (1) one organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) two different amino acids selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, and other amino acids and their derivatives;

0.001 wt. % to 0.05 wt. % of choline bicarbonate salt; and

the composition has a pH from 5.5 to 7.5.

20. The system for chemical mechanical polishing of Claim 15, wherein the Cu chemical mechanical polishing composition comprises

0.005 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 1.5 total wt. % of ethylenediamine; glycine and DL-alanine;

0.002 wt. % to 0.01 wt. % of choline bicarbonate salt;

0.5 wt. % to 2.0 wt. % of periodic acid or hydrogen peroxide;

0.025 wt. % to 0.05 wt. % of 1,2,4-triazole or benzotriazole and benzotriazole derivatives;

0.002 wt. % to 0.010 wt. % of the biocide has an active ingredient selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and combinations thereof; and

the composition has a pH from 7.0 to 7.35.