CLAIMS

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

    a) 0.0025 wt.% to 2.5 wt.% of abrasive;

    b) 0.5 to 10.0 total wt.% of dual chelators;

    c) 0.001 wt.% to 0.05 wt.% of organic quaternary ammonium salt; and

    d) water;

    optionally

    e) corrosion inhibitor;

    f) oxidizing agent;

    g) biocide;

    h) pH adjusting agent;

wherein

the dual chelators comprise (1) an organic amine; and (2) an amino acid or an amino acid derivative;

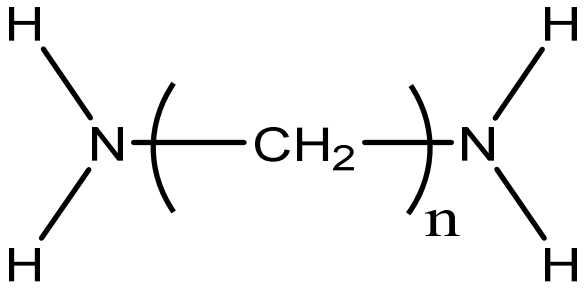
the organic quaternary ammonium salt is selected from the group consisting of choline salt, salt formed between choline and other anionic counter ions, and combinations thereof; and

the pH of the composition is selected from the group consisting of 5.5 to 7.5; and 7.0 to 7.35.

2. The copper chemical mechanical polishing (CMP) composition of Claim 1, wherein

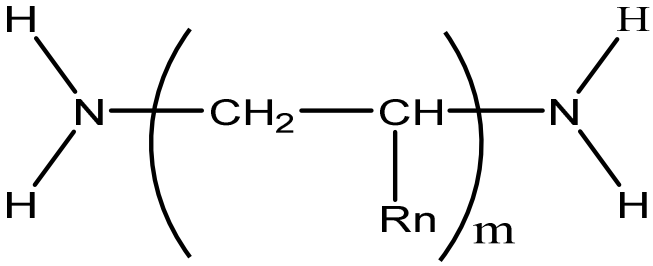
    the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine,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

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



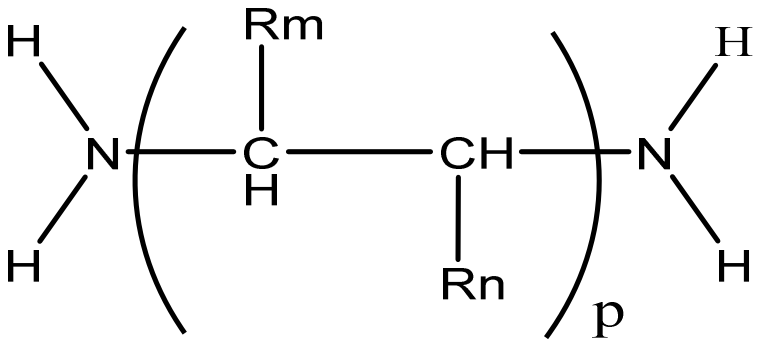
(a)

wherein n is from 2 to 12;



(b)

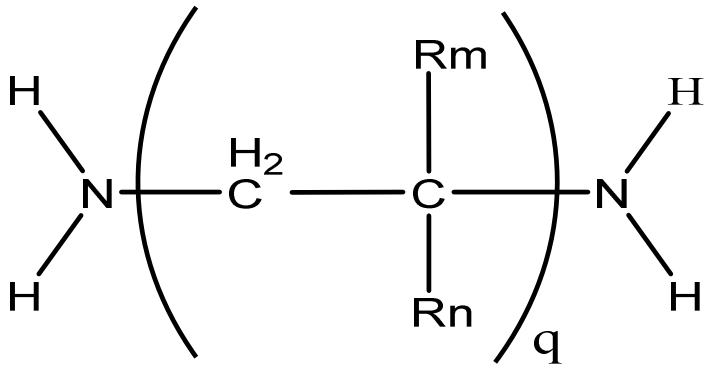
wherein Rn represents an organic alkyl group C_nH_{2n+1}, n is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and m is from 2 to 12;



(c)

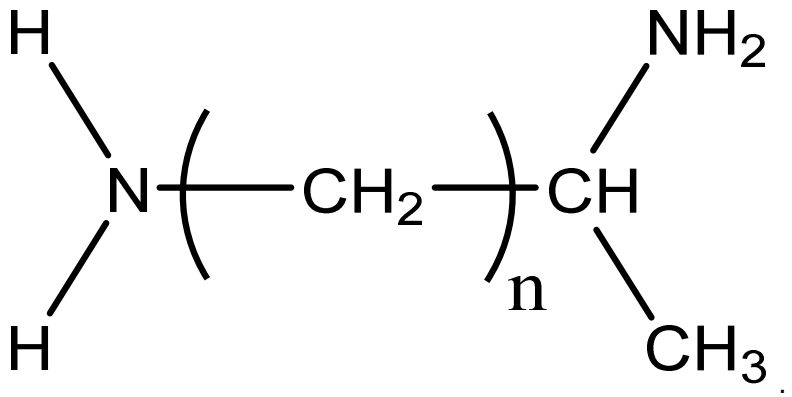
wherein Rn and Rm can be the same or different alkyl groups with n and m numbered independently from 1 to 12;

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and p is from 2 to 12;



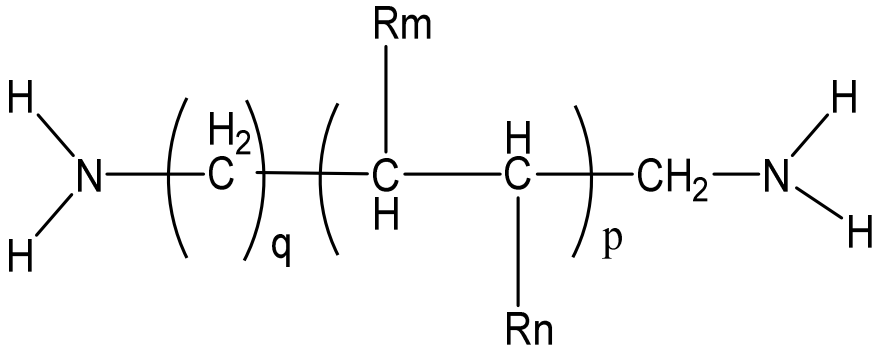
(d)

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and q is from 2 to 12;



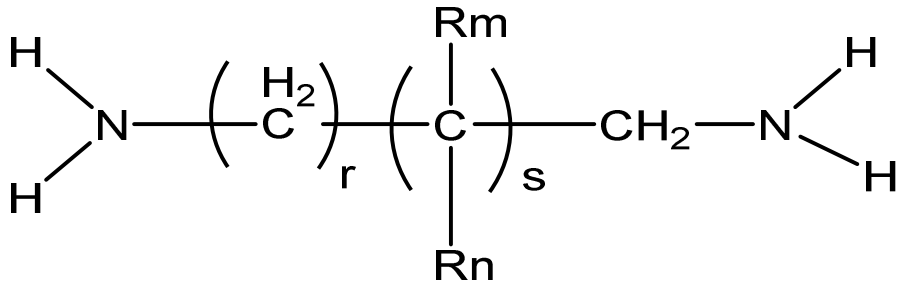
(e)

wherein n is from 1 to 12;



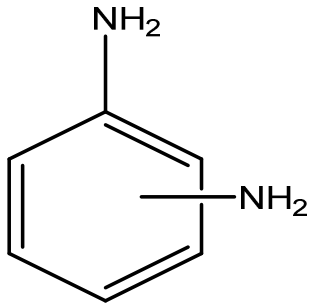
(f)

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; p is selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; and q is selected from the group consisting of 1 to 6, 1 to 4, and 1 to 3;



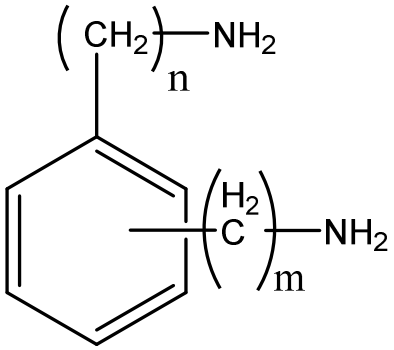
(g)

wherein Rn and Rm are bonded to the same carbon atom and can be the same or different alkyl groups Rn = H or C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; s is selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; and r is selected from the group consisting of 1 to 6, 1 to 4, and 1 to 3;



(h)

and



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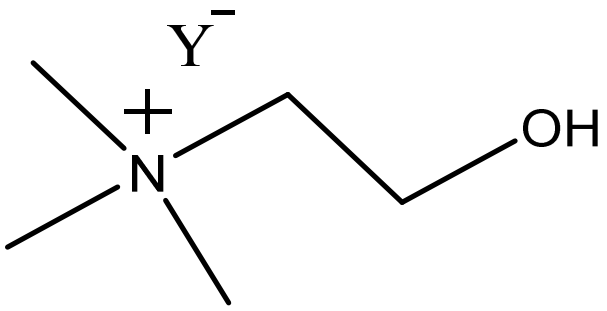
(i)

wherein n and m are numbered independently from 1 to 12.

3. 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, 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.

4. The copper chemical mechanical polishing (CMP) composition of claim 1, wherein the organic amine is selected from the group consisting of ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 2-methyl-propanediamine, 2-methyl-butanediamine, 2,2-dimethyl-1,3-propanediamine, 2,3-dimethyl-2,3-butanediamine, 2,2-dimethyl-

propanediamine and 2,2-dimethyl-butanediamine, 2,3-dimethyl-butane-1,4-diamine, and 2,3-dimethyl-pentane-1,5-diamine, and 2,2-dimethyl-1,4-butanediamine; and
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, and iminodiacetic acid.

5. The copper chemical mechanical polishing (CMP) composition of claim 1, comprises

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

0.5 to 10.0 total wt. % of (1) organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) amino acid 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, and iminodiacetic acid;

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, comprises

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

0.5 to 10.0 total wt. % of (1) organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, and beta-alanine;

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

0.0025 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 10.0 total wt. % of (i) ethylenediamine; and (ii) glycine or alanine;

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

0.5 wt. % to 3.0 wt. % of periodic acid or hydrogen peroxide;

0.001 wt. % to 0.5 wt. % of 3-amino-1,2,4-triazole, 1,2,4-triazole, or benzotriazole and benzotriazole derivatives;

0.0001 wt.% to 0.025 wt.% of the biocide having 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 2.5 wt.% of abrasive;

b) 0.5 to 10.0 total wt.% of dual chelators;

c) 0.001 wt.% to 0.05 wt.% of organic quaternary ammonium salt; and

d) water;

optionally

e) corrosion inhibitor;

f) oxidizing agent;

g) biocide;

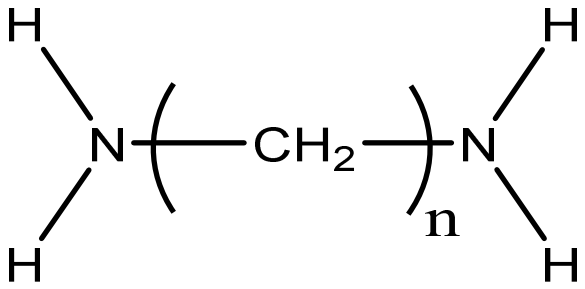
h) pH adjusting agent;

wherein

the dual chelators comprise (1) an organic amine; and (2) an amino acid, or an amino acid derivative;

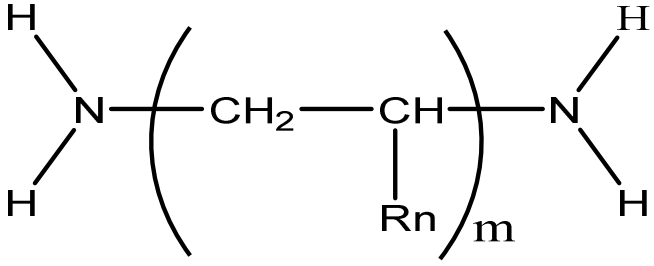
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine,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

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



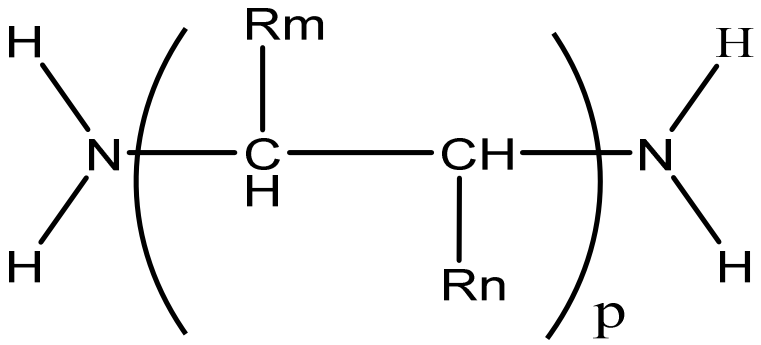
(a)

wherein n is from 2 to 12;



(b)

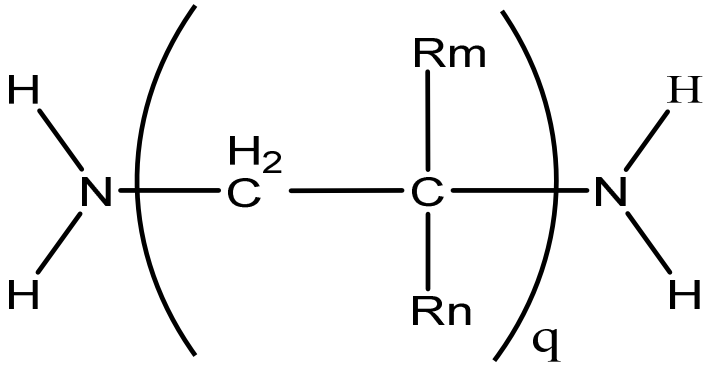
wherein Rn represents an organic alkyl group C_nH_{2n+1}, n is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and m is from 2 to 12;



(c)

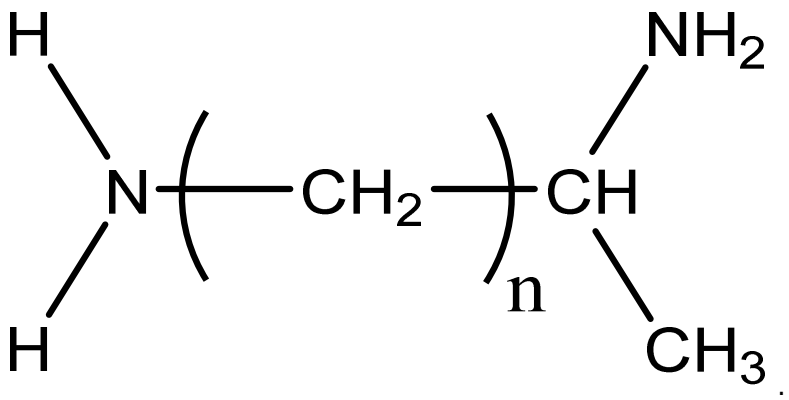
wherein Rn and Rm can be the same or different alkyl groups with n and m numbered independently from 1 to 12;

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and p is from 2 to 12;



(d)

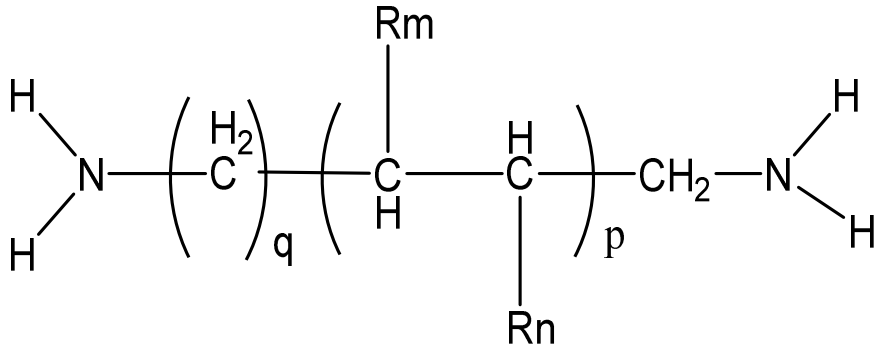
wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and q is from 2 to 12;



(e)

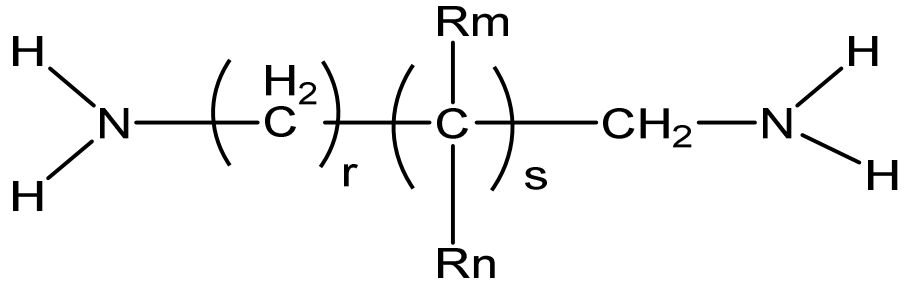
wherein n is from 1 to 12;

wherein n is from 1 to 12;



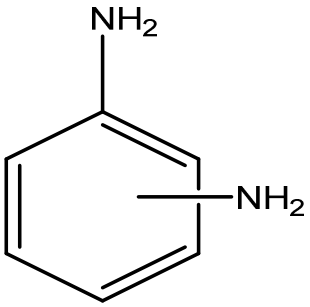
(f)

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; p is selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; and q is selected from the group consisting of 1 to 6, 1 to 4, and 1 to 3;



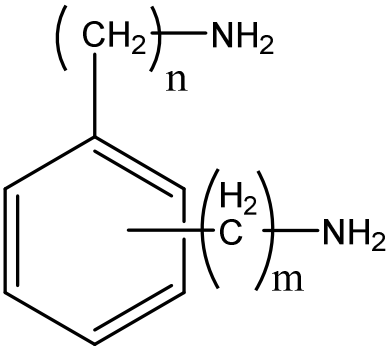
(g)

wherein Rn and Rm are bonded to the same carbon atom and can be the same or different alkyl groups Rn = H or C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; s is selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; and r is selected from the group consisting of 1 to 6, 1 to 4, and 1 to 3;



(h);

and



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(i)

wherein n and m are numbered independently from 1 to 12;

the organic quaternary ammonium salt is selected from the group consisting of choline salt, salt formed between choline and other anionic counter ions, and combinations thereof;

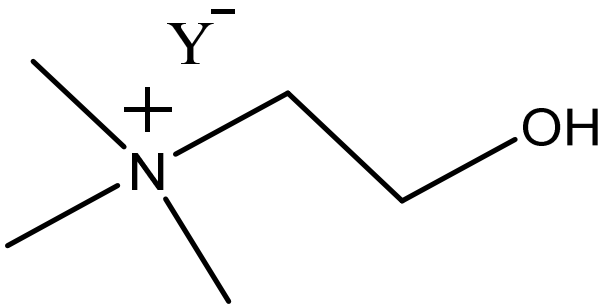
and

the pH of the composition is selected from the group consisting of 5.5 to 7.5; and 7.0 to 7.35;

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.

9. 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, 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.

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

the organic amine is selected from the group consisting of ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 2-methyl-propanediamine, 2-methyl-butanediamine, 2,2-dimethyl-1,3-propanediamine, 2,3-dimethyl-2,3-butanediamine, 2,2-dimethyl-propanediamine and 2,2-dimethyl-butanediamine, 2,3-dimethyl-butane-1,4-diamine, and 2,3-dimethyl-pentane-1,5-diamine, and 2,2-dimethyl-1,4-butanediamine;

and

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, and iminodiacetic acid.

11. 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 10.0 total wt. % of (1) organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) amino acid 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, and iminodiacetic acid;

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

the composition has a pH from 5.5 to 7.5.

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;

0.5 to 10.0 total wt. % of (1) organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, and beta-alanine;

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

0.5 to 10.0 total wt. % of (i) ethylenediamine; and (ii) glycine or alanine;

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

0.5 wt. % to 3.0 wt. % of periodic acid or hydrogen peroxide;

0.001 wt. % to 0.5 wt. % of 3-amino-1,2,4-triazole, 1,2,4-triazole, or benzotriazole and benzotriazole derivatives;

0.0001 wt.% to 0.025 wt.% of the biocide having 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.

14. 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.

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; comprising:

1) the semiconductor substrate;

2) a polish pad;

3) a Cu chemical mechanical polishing composition comprising:

   a) 0.0025 wt.% to 2.5 wt.% of abrasive;

   b) 0.5 to 10.0 total wt.% of dual chelators;

   c) 0.001 wt.% to 0.05 wt.% of organic quaternary ammonium salt; and

   d) water;

      optionally

   e) corrosion inhibitor;

   f) oxidizing agent;

   g) biocide;

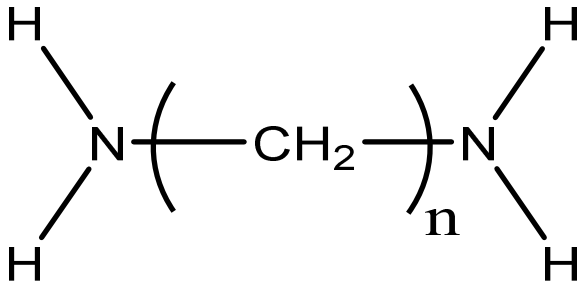
   h) pH adjusting agent;

wherein

the dual chelators comprise (1) an organic amine; and (2) an amino acid, or an amino acid derivative;

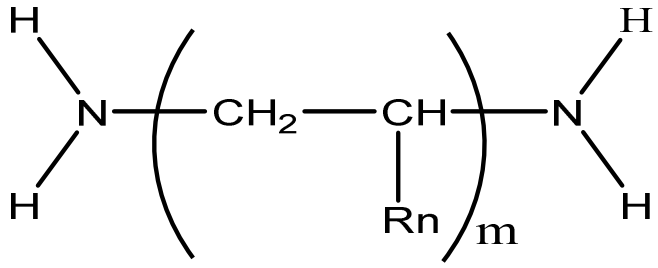
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isoleucine, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparagine, glutamic acid, aspartic acid, tryptophan, histidine, arginine,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

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



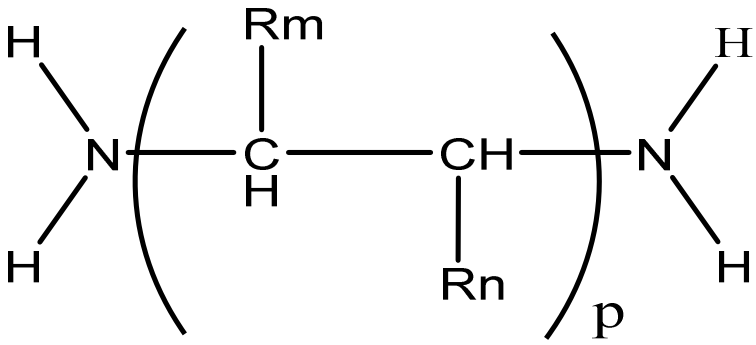
(a)

wherein n is from 2 to 12;



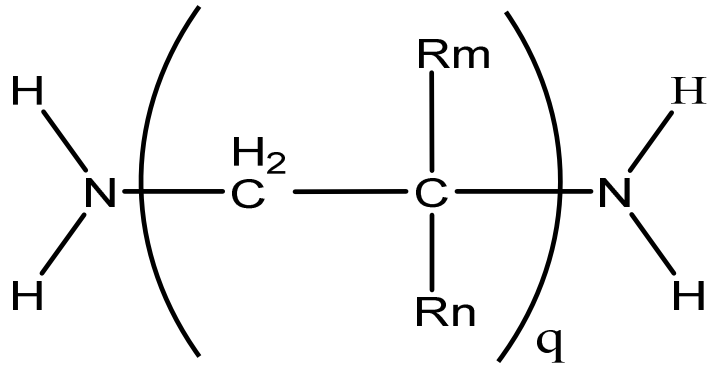
(b)

wherein Rn represents an organic alkyl group C_nH_{2n+1}, n is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and m is from 2 to 12;



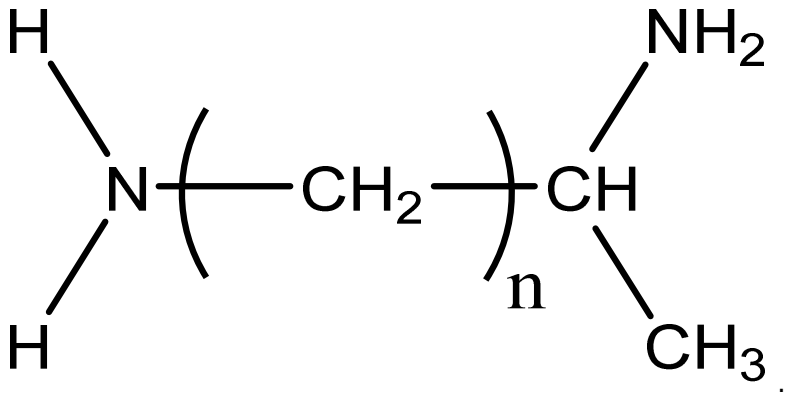
(c)

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and p is from 2 to 12;



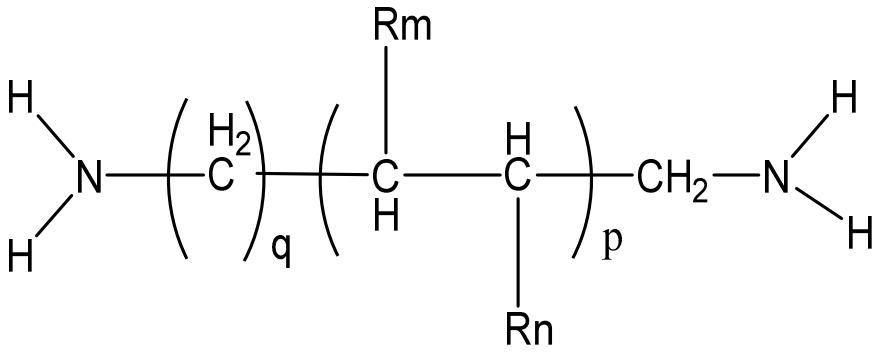
(d)

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and q is from 2 to 12;



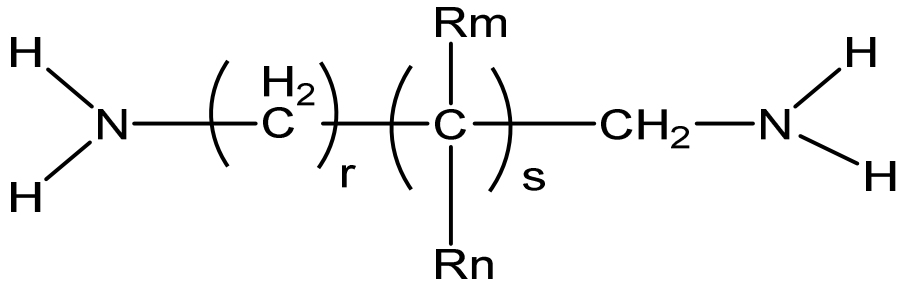
(e)

wherein n is from 1 to 12;



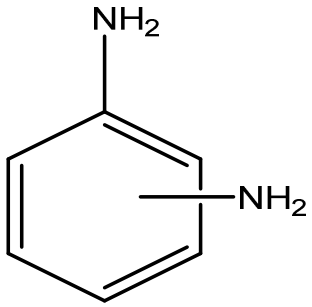
(f)

wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; p is selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; and q is selected from the group consisting of 1 to 6, 1 to 4, and 1 to 3;



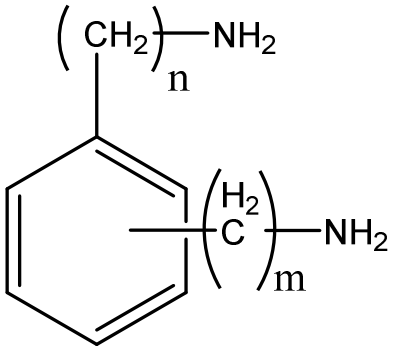
(g)

wherein Rn and Rm are bonded to the same carbon atom and can be the same or different alkyl groups Rn = H or C_nH_{2n+1} and Rm = C_mH_{2m+1}, n and m are independently selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; s is selected from the group consisting of 1 to 12, 1 to 6, and 1 to 3; and r is selected from the group consisting of 1 to 6, 1 to 4, and 1 to 3;



(h);

and



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(i)

wherein n and m are numbered independently from 1 to 12;

the organic quaternary ammonium salt is selected from the group consisting of choline salt, salt formed between choline and other anionic counter ions, and combinations thereof;

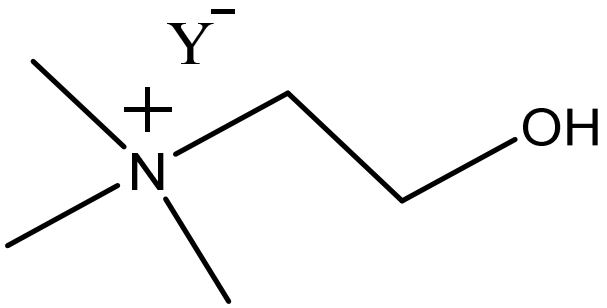
and

the pH of the composition is selected from the group consisting of 5.5 to 7.5; and 7.0 to 7.35;

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 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, 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.

17. The system of claim 15, wherein

the organic amine is selected from the group consisting of ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 2-methyl-propanediamine, 2-methyl-butanediamine, 2,2-dimethyl-1,3-propanediamine, 2,3-dimethyl-2,3-butanediamine, 2,2-dimethyl-propanediamine and 2,2-dimethyl-butanediamine, 2,3-dimethyl-butane-1,4-diamine, and 2,3-dimethyl-pentane-1,5-diamine, and 2,2-dimethyl-1,4-butanediamine; and

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, and iminodiacetic acid.

18. The system 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 10.0 total wt. % of (1) organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) amino acid 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, and iminodiacetic acid;

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 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 10.0 total wt. % of (1) organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, and beta-alanine;

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 of claim 15, wherein the Cu chemical mechanical polishing composition comprises

0.0025 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 10.0 total wt. % of (i) ethylenediamine; and (ii) glycine or alanine;

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

0.5 wt. % to 3.0 wt. % of periodic acid or hydrogen peroxide;

0.001 wt. % to 0.5 wt. % of 3-amino-1,2,4-triazole, 1,2,4-triazole, or benzotriazole and benzotriazole derivatives;

0.0001 wt.% to 0.025 wt.% of the biocide having 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.

21. The system of claim 15, 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.