TITLE OF THE INVENTION:

CHEMICAL MECHANICAL POLISHING FOR COPPER AND THROUGH SILICA VIA APPLICATIONS

CROSS REFERENCE TO RELATED PATENT APPLICATIONS

[0001] The application claims the benefit of U.S. Application No. 62/811,874 filed on February 28th, 2019. The disclosure of Application No. 62/798,638 is hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] This invention relates generally to the chemical-mechanical planarization or chemical-mechanical polishing (CMP) of semiconductor wafers. More specifically, present invention relates to high and tunable Cu film removal rates for the broad or advanced node copper or Through Silica Via (TSV) CMP applications. CMP polishing formulations, CMP polishing compositions or CMP polishing slurries are interchangeable in present invention.

[0003] Copper is the current material of choice for interconnect metal used in the fabrication of integrated electronic devices due to its low resistivity, high reliability, and scalability. Copper chemical mechanical planarization processes are necessary to remove copper overburden from inlaid trench structures while achieving global planarization with low metal loss.

[0004] With advancing technology nodes the need to reduce metal loss becomes increasingly important. Any new polishing formulations must also maintain high removal rates, high selectivity to the barrier material and low defectivity.

[0005] Copper CMP have been done in the art, for example, US9,3065,806; US20160314989; US20130092651; US 20130078811; US 8,679,980; US 8,791,019; US 8,435,421; US 7,955,520; US 20130280910; US 20100221918; US 8,236,695; TW I385226; US 20120094490; US 7,955,520; US US20040175942; US6773476; US8236695; 20090053896; US8,586,481; US20100221918; US20170271172; US2017035139; US20110070736; US20080254628; and US20100015807.

[0006] However, the disclosed formulations were unable to meet the performance requirements of high Cu removal rates which become more and more challenging for advanced technology nodes.

[0007] This invention discloses bulk copper CMP polishing formulations developed to meet challenging requirements of high Cu removal rates for the advanced technology node Cu CMP applications.

Summary of The Invention

[0008] Described herein are CMP polishing compositions, methods and systems for the copper and Through Silica Via (TSV) CMP applications.

[0009] In one aspect, the invention herein provides chemical mechanical polishing (CMP) composition for a copper bulk and Through Silica Via (TSV) comprises:

a) abrasive;

b) at least two chelators; and

c) oxidizing agent;

d) water;

optionally

e) corrosion inhibitor;

f) organic quaternary ammonium salt;

g) biocide; and

h) pH adjusting agent;

wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative; and

the pH of the composition is from 3.0 to 12.0; preferably from 5.5 to 7.5; and more preferably from 7.0 to 7.35.

[0010] In another aspect, the invention provides a method of chemical mechanical polishing a semiconductor substrate containing at least one copper or copper-containing surface, comprising steps of:

i. providing the semiconductor substrate;

ii. providing a polish pad;

iii. providing a chemical mechanical polishing composition comprising

a) abrasive;

b) oxidizing agent;

c) at least two chelators; and

d) water;

a. optionally

e) corrosion inhibitor;

f) organic quaternary ammonium salt;

g) biocide; and

h) pH adjusting agent;

wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative; and

the pH of the composition is from 3.0 to 12.0; preferably from 5.5 to 7.5; and more preferably from 7.0 to 7.35;

iv. contacting the semiconductor substrate with the polish pad and the chemical mechanical polishing composition; and

v. polishing the semiconductor substrate;

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

[0011] In yet another aspect, the invention provides a method of a selective chemical mechanical polishing comprising steps of:

a) providing a semiconductor substrate having at least one surface containing a first material and at least one second material;

b) providing a polishing pad;

c) providing a chemical mechanical polishing or Through Silica Via (TSV) composition comprising

i. abrasive;

ii. oxidizing agent;

iii. at least two chelators; and

iv. water;

optionally

v. corrosion inhibitor;

vi. organic quaternary ammonium salt;

vii. biocide; and

viii. pH adjusting agent;

wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative;

the pH of the composition is from 3.0 to 12.0; preferably from 5.5 to 7.5; and more preferably from 7.0 to 7.35;

d) polishing the semiconductor substrate to selectively remove the first material;

wherein removal rate of the first material to removal rate of the second material is equal or greater than 500:1; preferably 1000:1; and more preferably 3000:1; and

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

[0012] In yet another aspect, the invention provides a system of chemical mechanical polishing a semiconductor substrate containing at least one copper or copper-containing surface, comprising

1) the semiconductor substrate;
2) a polish pad; and
3) a chemical mechanical polishing composition comprising
   a) abrasive;
   b) oxidizing agent;
   c) at least two chelators; and
   d) water;

   optionally

   e) corrosion inhibitor;
   f) organic quaternary ammonium salt;
   g) biocide; and
   h) pH adjusting agent;

   wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative; and

the pH of the composition is from 3.0 to 12.0; preferably from 5.5 to 7.5; and more preferably from 7.0 to 7.35;

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

[0013] The abrasive particles used include, but are not limited to, colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica, such as alumina doped silica particles; 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, such as alumina, titania, zirconia, ceria etc.; nano-sized diamond particles, nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasives, surface-coated or modified abrasives, or other composite particles, and mixtures thereof.

[0014] The corrosion inhibitors include but are not limited to family of hetero aromatic compounds containing nitrogen atom(s) in their aromatic rings, such as 1,2,4-triazole, 3-amino-1,2,4-triazole, benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, and tetrazole and tetrazole derivatives.

[0015] The biocide includes but is not limited to Kathon™, Kathon™ CG/ICP II, from Dow Chemical Co. They have active ingredients of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

[0016] The oxidizing agent includes, but is not limited to, periodic acid, hydrogen peroxide, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and mixtures thereof.

[0017] The at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative.

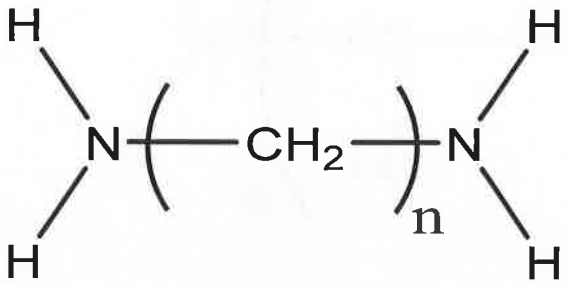
[0018] The at least two chelators can be combinations of at least two amino acids, combinations of at least two amino acid derivatives, combinations of at least one amino acid with at least one amino acid derivative, combinations of at least one amino acid with at least one organic amine, combinations of at least one amino acid derivative with at least one organic amine, combinations of at least one amino acid with at least one amino derivative and at least one organic amine. As an example, the two chelators can be glycine, and ethylenediamine.

[0019] The amino acids and amino acid derivatives include, but not limited to, glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline,

serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof.

[0020] The organic amines chelators have general molecular structures, as depicted below.

[0021] The organic amine with structure (a) has two primary amine functional groups as terminal groups on both ends of the molecule.

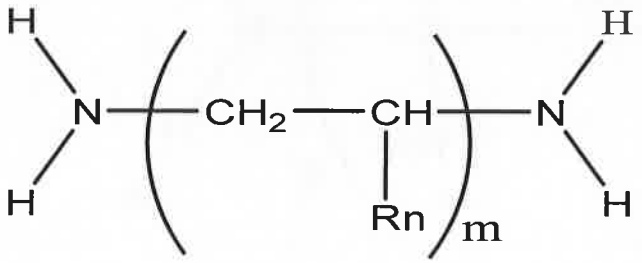


(a).

[0022] n is numbered from 2 to 12.

[0023] For examples, the organic amine is ethylenediamine, 1,3-propanediamine or 1,4-butanediamine as n=2, 3 or 4.

[0024] The organic amine with structure (b) also has two primary amine functional groups as terminal groups on both ends of the molecule.



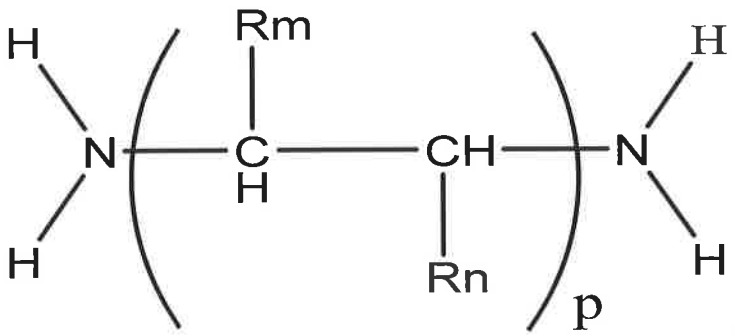
(b).

[0025] An alkyl group links the two terminal primary amine functional groups. The alkyl group Rn = C_nH_{2n+1}, n is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0026] m can be numbered from 2 to 12.

[0027] The linking alkyl group Rn between two terminal primary amine functional groups can also be a branched alkyl group.

[0028] The organic amine with structure (c) is shown below.

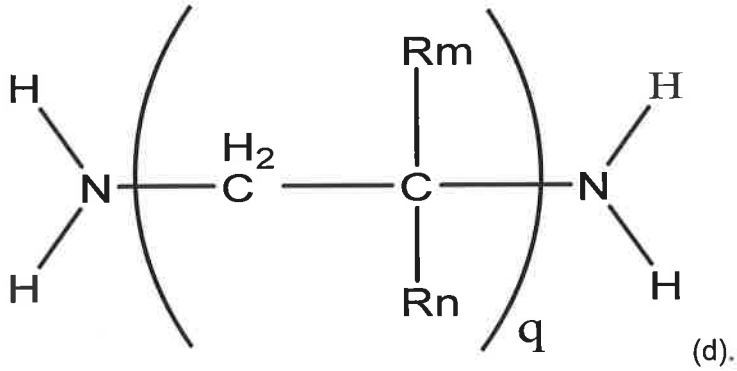


(c).

[0029] Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0030] p is from is from 2 to 12, preferably 2 to 6, and more preferably 2 to 3.

[0031] The organic amine with structure (d) is shown below.



(d).

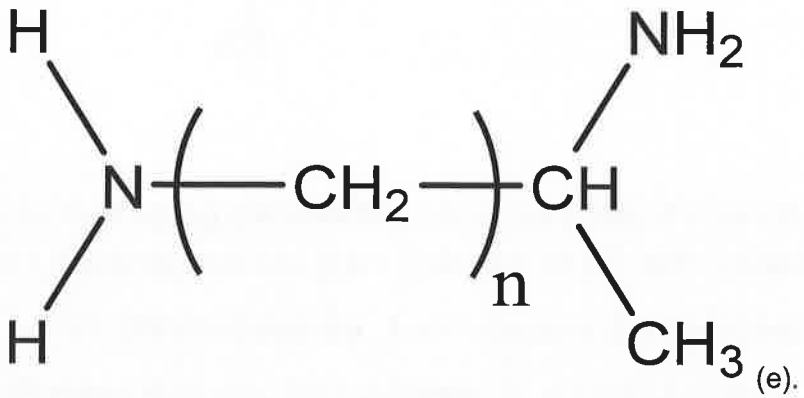
[0032] Rn and Rm groups are bonded to the same carbon atom. Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0033] q is from 2 to 12, preferably 2 to 6, and more preferably 2 to 3.

[0034] The organic diamine compounds with two primary amine moieties can be described as the binary chelating agents.

[0035] The organic diamine molecules with other molecular structures can be also used as a chelating agent in the CMP slurries.

[0036] The organic diamine molecules with structure (e) is shown below.



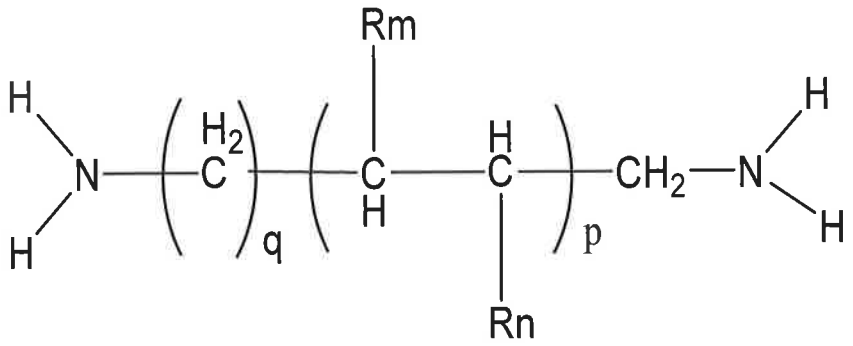
(e).

[0037] The organic diamines have one terminal primary amine functional group at one end and another primary organic amine attached to the beta carbon atoms on the other end of the molecules.

[0038] There can be a secondary primary amine functional groups bonded to the other carbon atoms at other positions, such as gamma etc. and the first primary amine function group still maintains as the terminal primary amine functional group in the same molecules.

[0039] n is numbered from 2 to 12.

[0040] The organic amine with structure (f) is shown below.



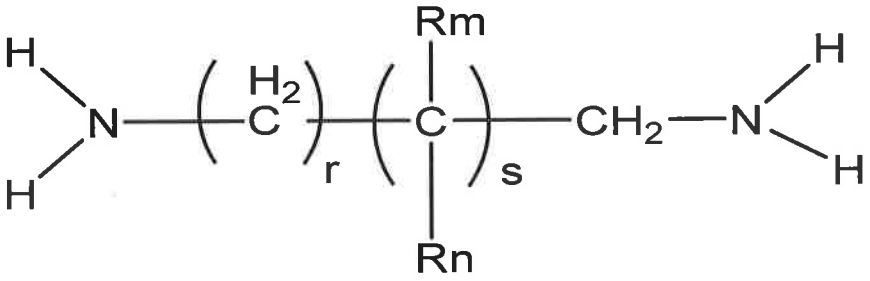
(f).

[0041] Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0042] q is from 1 to 6, preferably 1 to 4, and more preferably 1 to 3.

[0043] p is from is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0044] The organic amine with structure (g) is shown below.



(g).

[0045] Rn and Rm groups are bonded to the same carbon atom. Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

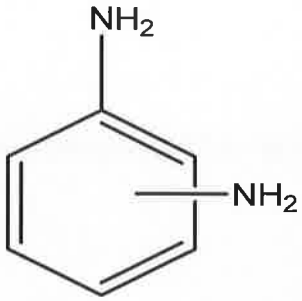
[0046] r is from 1 to 6, preferably 1 to 4, and more preferably 1 to 3.

[0047] s is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0048] Examples include but are not limited to 2-methyl-propanediamine, 2-methyl-butanediamine, 2,2-dimethyl-1,3-propanediamine, and 2,3-dimethyl-2,3-butanediamine, 2-dimethyl-propanediamine, 2,2-dimethyl-butanediamine, 2,3-dimethyl-butane-1,4-diamine, 2,3-dimethyl-pentane-1,5-diamine, and 2,2-dimethyl-1,4-butanediamine.

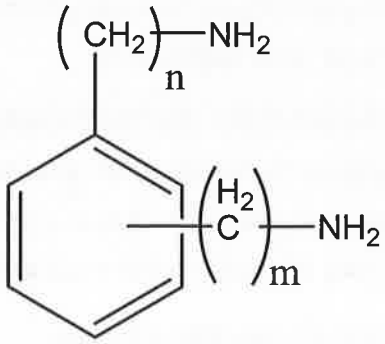
[0049] Any aromatic organic molecules with two primary amine functional groups can be used as one of the chelating agents in the invented Cu CMP slurries.

[0050] For example, aromatic organic amines have the general molecular structures as depicted in (h) and (i) as shown below:



(h);

and

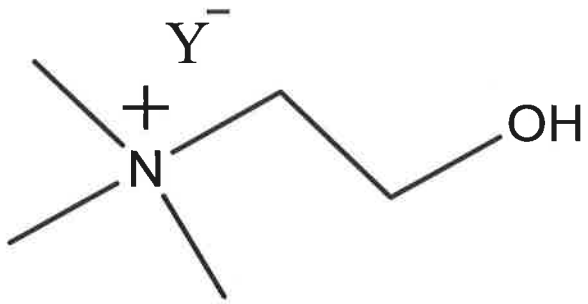


(i).

[0051] In structure (i), n and m can be the same or different and can be from 1 to 12.

[0052] The organic quaternary ammonium salt, includes but is not limited to choline salt, such as choline bicarbonate salt, or all other salts formed between choline and other anionic counter ions.

[0053] The choline salts can have the general molecular structures shown below:



wherein anion Y^- can be bicarbonate, hydroxide, p-toluene-sulfonate, bitartate, and other suitable anionic counter ions.

DETAILED DESCRIPTION OF THE INVENTION

[0054] As industry standards trend toward smaller device features, there is a continuously developing need for new Cu bulk metal polishing slurries that afford high and tunable Cu removal rates for the broad and advanced node applications.

[0055] The copper bulk CMP or Through Silica Via (TSV) polishing compositions described herein satisfy the need for high and tunable Cu film removal rates, for high selectivity between copper and dielectric films, for high selectivity between copper and barrier films, and for better Cu film corrosion protection through using the suitable corrosion inhibitors.

[0056] The CMP polishing compositions comprise abrasive;

a) oxidizing agent;

b) at least two chelators; and

c) water;

optionally

d) corrosion inhibitor;

e) organic quaternary ammonium salt;

f) biocide; and

g) pH adjusting agent;

wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative; and

the pH of the composition is from 3.0 to 12.0; preferably from 5.5 to 7.5; and more preferably from 7.0 to 7.35;

[0057] The Cu CMP polishing compositions provide high and tunable Cu removal rates, and low barrier film and dielectric film removal rates which provide very high and desirable selectivity of Cu film vs. other barrier films, such as Ta, TaN, Ti, and TiN, and/or dielectric films, such as TEOS, low-k, and ultra low-k films.

[0058] The chemical mechanical polishing compositions also provide no pad stain Cu CMP performances which allow the extended polish pad life and also allow more stable end-point detections.

[0059] The abrasive particles used for the disclosed herein Cu bulk CMP polishing compositions include, but are not limited to, colloidal silica or high purity colloidal silica; the colloidal silica particles doped by other metal oxide within lattice of the colloidal silica, such as alumina doped silica particles; 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, such as alumina, titania, zirconia, ceria etc.; nano-sized diamond particles, nano-sized silicon nitride particles; mono-modal, bi-modal, multi-modal colloidal abrasive particles; organic polymer-based soft abrasives, surface-coated or modified abrasives, or other composite particles, and mixtures thereof.

[0060] The colloidal silica can be made from silicate salts, the high purity colloidal silica can be made from TEOS or TMOS. The colloidal silica or high purity colloidal silica can have narrow or broad particle size distributions with mono-model or multi-models, various sizes and various shapes including spherical shape, cocoon shape, aggregate shape and other shapes,

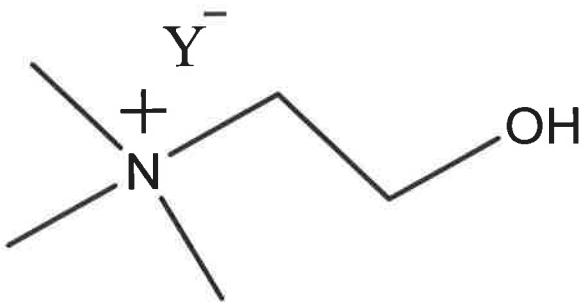
[0061] The nano-sized particles also can have different shapes, such as spherical, cocoon, aggregate, and others.

[0062] The particle size of the abrasives used in the Cu CMP slurries is ranged from 5nm to 500nm, preferred size is ranged from 10nm to 250nm, the more preferred size is ranged from 25nm to 100nm.

[0063] The Cu bulk CMP polishing compositions of this invention preferably contain 0.0025 wt.% to 25 wt.% abrasives; the preferred concentration of abrasives ranges from 0.0025 wt.% to 2.5 wt.%. The most preferred concentration of abrasives ranges from 0.005 wt.% to 0.15 wt.%.

[0064] The organic quaternary ammonium salt, includes but is not limited to choline salt, such as choline bicarbonate salt, or all other salts formed between choline and other anionic counter ions.

[0065] The choline salts can have the general molecular structures shown below:



wherein anion Y^- can be bicarbonate, hydroxide, p-toluene-sulfonate, bitartate, and other suitable anionic counter ions.

[0066] The CMP slurry contains 0.005 wt.% to 0.25 wt.% quaternary ammonium salt; the preferred concentration ranges from 0.001 wt.% to 0.05 wt.%; and the most preferred concentration ranges from 0.002 wt.% to 0.01 wt.%

[0067] Various per-oxy inorganic or organic oxidizing agents or other types of oxidizing agents can be used to oxidize the metallic copper film to the mixture of copper oxides to allow

their quick reactions with chelating agents and corrosion inhibitors. The oxidizing agent includes, but is not limited to, periodic acid, hydrogen peroxide, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and mixtures thereof. The preferred oxidizer is hydrogen peroxide.

[0068] The CMP slurry contains 0.1 wt.% to 10 wt.% oxidizing agents; the preferred concentration ranges from 0.25wt.% to 3wt.%; and the most preferred concentration ranges from 0.5wt.% to 2.0wt.%.

[0069] The corrosion inhibitors used for the disclosed copper bulk CMP slurry can be those prior arts reported corrosion inhibitors. The corrosion inhibitors include, but are not limited to family of hetero aromatic compounds containing nitrogen atom(s) in their aromatic rings, such as 1,2,4-triazole, amitrole (or 3-amino-1,2,4-triazole), benzotriazole and benzotriazole derivatives, tetrazole and tetrazole derivatives, imidazole and imidazole derivatives, benzimidazole and benzimidazole derivatives, pyrazole and pyrazole derivatives, and tetrazole and tetrazole derivatives.

[0070] The CMP slurry contains 0.005 wt.% to 1.0 wt.% corrosion inhibitor; the preferred concentration ranges from 0.01 wt.% to 0.5 wt.%; and the most preferred concentration ranges from 0.025 wt.% to 0.25 wt.%.

[0071] A biocide having active ingredients for providing more stable shelf time of the invented Cu chemical mechanical polishing compositions can be used.

[0072] The biocide includes but is not limited to Kathon™, Kathon™ CG/ICP II, from Dow Chemical Co. They have active ingredients of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

[0073] The CMP slurry contains 0.0001 wt.% to 0.05 wt.% biocide; the preferred concentration ranges from 0.0001 wt.% to 0.025 wt.%; and the most preferred concentration ranges from 0.0001 wt.% to 0.01 wt.%.

[0074] Optionally, acidic or basic compounds or pH adjusting agents can be used to allow pH of Cu bulk CMP polishing compositions being adjusted to the optimized pH value,

[0075] The pH adjusting agents include, but are not limited to, the following: nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, other inorganic or organic acids, and mixtures thereof. pH adjusting agents also include the basic pH adjusting agents, such as sodium

hydride, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic amines, and other chemical reagents that are able to be used to adjust pH towards the more alkaline direction.

[0076] The CMP slurry contains 0 wt.% to 1 wt.% pH adjusting agent; the preferred concentration ranges from 0.01 wt.% to 0.5 wt.%; and the most preferred concentration ranges from 0.1 wt.% to 0.25 wt.%.

[0077] pH of the Cu polishing compositions is from about 3.0 to about 12.0; preferred pH range is from 5.5 to 7.5; and the most preferred pH range is from 7.0 to 7.35.

[0078] The CMP slurry contains 0.1 wt.% to 18 wt.% of at least two chelators; the preferred concentration ranges for the sum of at least two used chelators are from 0.5 wt.% to 15 wt.%; and the most preferred concentration ranges for the sum of at least two used chelators are from 2.0 wt.% to 10.0 wt.%.

[0079] The at least two chelators are selected independently from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations thereof, wherein the at least one chelator is an amino acid or an amino acid derivative.

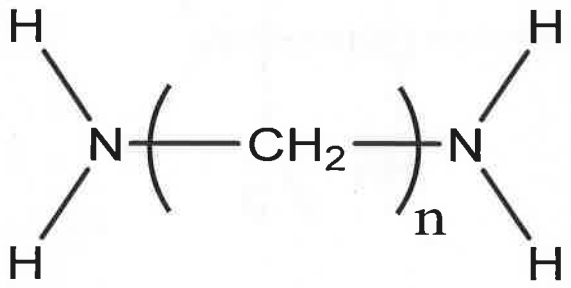
[0080] The at least two chelators can be combinations of at least two amino acids, combinations of at least two amino acid derivatives, combinations of at least one amino acid with at least one amino acid derivative, combinations of at least one amino acid with at least one organic amine, combinations of at least one amino acid derivative with at least one organic amine, combinations of at least one amino acid with at least one amino derivative and at least one organic amine. As an example, the two chelators can be glycine, and ethylenediamine.

[0081] The at least two chelators used as complexing agents to maximize their reactions with the oxidized Cu film surfaces to form softer Cu-chelator layers to be quickly removed during Cu CMP process thus achieving high and tunable Cu removal rates for the broad or advanced node copper or TSV (Through Silica Via) CMP applications.

[0082] The amino acids and amino acid derivatives included, but not limited to, glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, etc.

[0083] The organic amines chelators have general molecular structures, as depicted below.

[0084] The organic amine with structure (a) has two primary amine functional groups as terminal groups on both ends of the molecule.

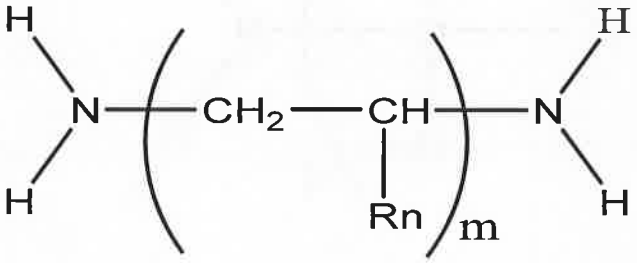


(a).

[0085] n is numbered from 2 to 12.

[0086] For examples, the organic amine is ethylenediamine, 1,3-propanediamine or 1,4-butanediamine as n=2, 3 or 4.

[0087] The organic amine with structure (b) also has two primary amine functional groups as terminal groups on both ends of the molecule.



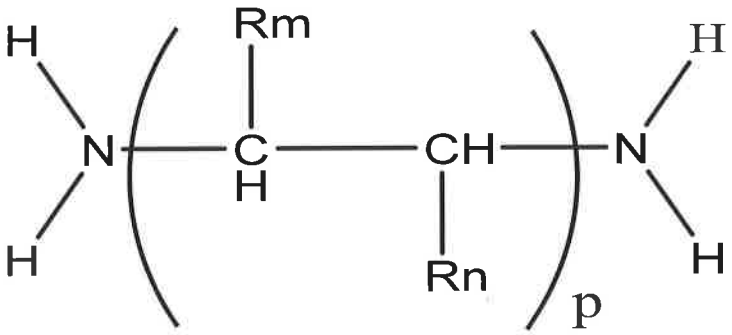
(b).

[0088] An alkyl group links the two terminal primary amine functional groups. The alkyl group Rn = C_nH_{2n+1}, n is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0089] m can be numbered from 2 to 12.

[0090] The linking alkyl group Rn between two terminal primary amine functional groups can also be a branched alkyl group.

[0091] The organic amine with structure (c) is shown below.

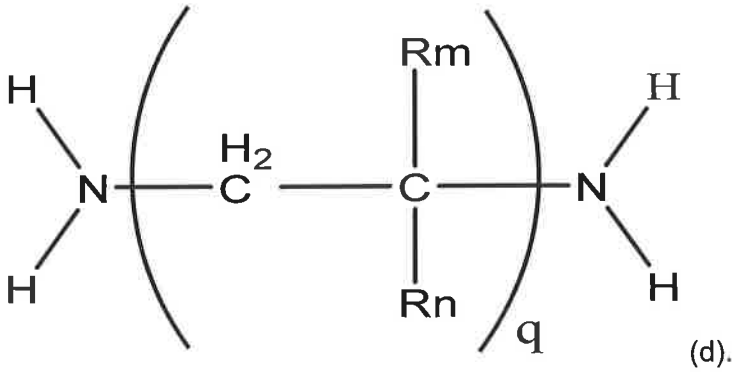


(c).

[0092] Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0093] p is from is from 2 to 12, preferably 2 to 6, and more preferably 2 to 3.

[0094] The organic amine with structure (d) is shown below.



(d).

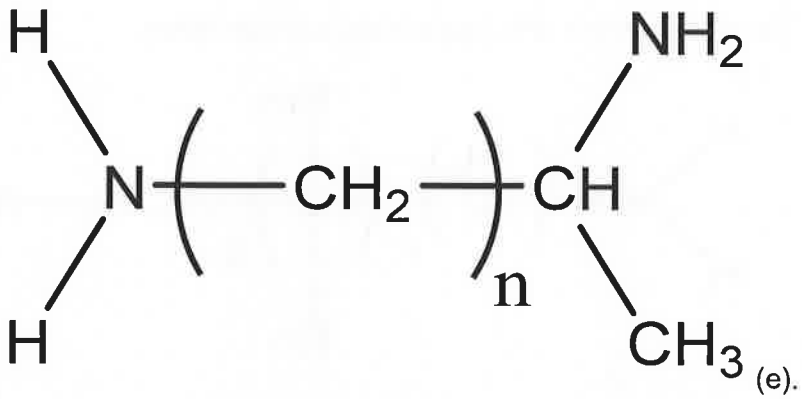
[0095] Rn and Rm groups are bonded to the same carbon atom. Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[0096] q is from 2 to 12, preferably 2 to 6, and more preferably 2 to 3.

[0097] The organic diamine compounds with two primary amine moieties can be described as the binary chelating agents.

[0098] The organic diamine molecules with other molecular structures can be also used as a chelating agent in the CMP slurries.

[0099] The organic diamine molecules with structure (e) is shown below.



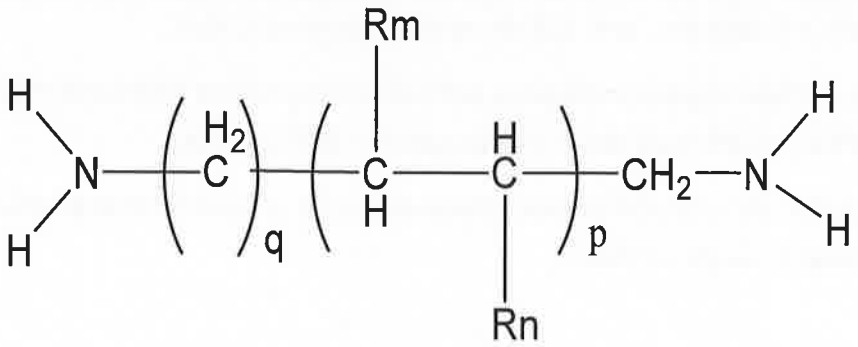
(e).

[00100] The organic diamines have one terminal primary amine functional group at one end and another primary organic amine attached to the beta carbon atoms on the other end of the molecules.

[00101] There can be a secondary primary amine functional groups bonded to the other carbon atoms at other positions, such as gamma etc. and the first primary amine function group still maintains as the terminal primary amine functional group in the same molecules.

[00102] n is numbered from 2 to 12.

[00103] The organic amine with structure (f) is shown below.



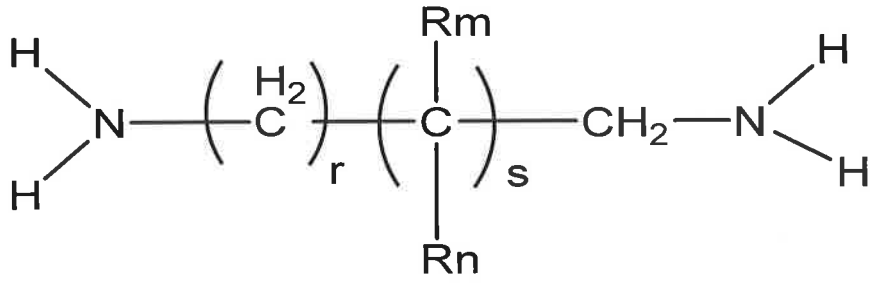
(f).

[00104] Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[00105] q is from 1 to 6, preferably 1 to 4, and more preferably 1 to 3.

[00106] p is from is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[00107] The organic amine with structure (g) is shown below.



(g).

[00108] Rn and Rm groups are bonded to the same carbon atom. Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

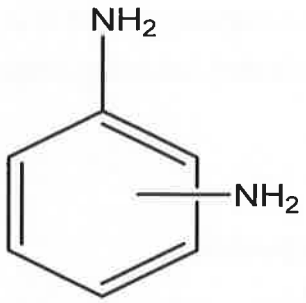
[00109] r is from 1 to 6, preferably 1 to 4, and more preferably 1 to 3.

[00110] s is from 1 to 12, preferably 1 to 6, and more preferably 1 to 3.

[00111] Examples include but are not limited to 2-methyl-propanediamine, 2-methyl-butanediamine, 2,2-dimethyl-1,3-propanediamine, and 2,3-dimethyl-2,3-butanediamine, 2-dimethyl-propanediamine, 2,2-dimethyl-butanediamine, 2,3-dimethyl-butane-1,4-diamine, 2,3-dimethyl-pentane-1,5-diamine, and 2,2-dimethyl-1,4-butanediamine.

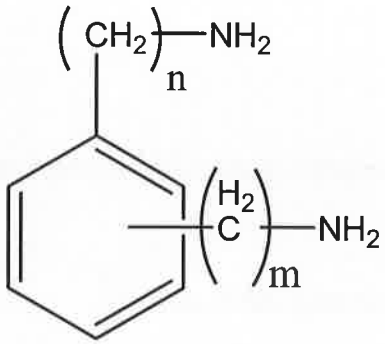
[00112] Any aromatic organic molecules with two primary amine functional groups can be used as one of the chelating agents in the invented Cu CMP slurries.

[00113] For example, aromatic organic amines have the general molecular structures as depicted in (h) and (i) as shown below:



(h);

and



(i).

[00114] In structure (i), n and m can be the same or different and can be from 1 to 12.

[00115] The associated methods and systems described herein entail use of the aforementioned compositions for chemical mechanical planarization of substrates comprised of copper.

[00116] In the methods, a substrate (e.g., a wafer or substrate with Cu or Cu containing surface or Cu plug) is placed face-down on a polishing pad which is fixedly attached to a rotatable platen of a CMP polisher. In this manner, the substrate to be polished and planarized is placed in direct contact with the polishing pad. A wafer carrier system or polishing head is used to hold the substrate in place and to apply a downward pressure against the backside of the substrate during CMP processing while the platen and the substrate are rotated. The polishing composition (slurry) is applied (usually continuously) on the pad during CMP processing to effect the removal of material to planarize the substrate.

[00117] The polishing composition and associated methods as well as systems described herein are effective for CMP of a wide variety of substrates, including most of substrates having copper surfaces, or copper substrates.

Experimental Section

Polishing Pad	Polishing pad, IC1010 pad or Other polishing pad was used during Cu CMP, supplied by Dow Chemicals Company.

PARAMETERS:

Å: angstrom(s) – a unit of length

BP: back pressure, in psi units

CMP: chemical mechanical planarization = chemical mechanical polishing

CS: carrier speed

DF: Down force: pressure applied during CMP, units psi

min: minute(s)

ml: milliliter(s)

mV: millivolt(s)

psi: pounds per square inch

PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)

SF: polishing composition flow, ml/min

Removal Rates

Cu RR 1.0 psi	Measured Copper removal rate at 1.0 psi down pressure of the CMP tool
Cu RR 2.0 psi	Measured Copper removal rate at 2.0 psi down pressure of the CMP tool
Cu RR 3.0 psi	Measured Copper removal rate at 1.0 psi down pressure of the CMP tool
Cu RR 4.0 psi	Measured Copper removal rate at 2.0 psi down pressure of the CMP tool

General Experimental Procedure

[00118] All percentages in the compositions are weight percentages unless otherwise indicated.

[00119] In the examples presented below, CMP experiments were run using the procedures and experimental conditions given below. The CMP tool that was used in the examples is a 200mm Mirra® polisher, manufactured by Applied Materials, 3050 Boweres Avenue, Santa Clara, California, 95054. An IC1010 pad or other type of polishing pad, supplied by Dow Chemicals Company was used on the platen for the blanket wafer polishing studies. Pads were broken-in by polishing twenty-five dummy oxide (deposited by plasma enhanced CVD from a TEOS precursor, PETEOS) wafers. In order to qualify the tool settings and the pad break-in, two PETEOS monitors were polished with Syton® OX-K colloidal silica, supplied by Planarization Platform of Air Products Chemicals Inc. at baseline conditions. Polishing experiments were conducted using blanket Cu wafers with 80K Angstroms in thickness, Ta and TEOS blanket wafers. These blanket wafers were purchased from Silicon Valley Microelectronics, 1150 Campbell Ave, CA, 95126.

Working Example

[00120] In this working example, Reference 1 slurry contained 3.78 wt.% (as 1X) single chelator glycine, 0.18915 wt.% (as 1X) of amitrole (or 3-amino-1,2,4-triazole), 0.00963 wt.% (as 1X) of choline bicarbonate (CBC), 0.037575 wt.% (as 1X) of high purity colloidal silica, and 0.0001 wt.% of biocide, and with pH being adjusted to 7.2.

[00121] Reference# 2 slurry contained 0.004 wt.% single chelator ethylenediamine (EDA), 0.18915 wt.% of amitrole, 0.00963 wt.% of choline bicarbonate, 0.037575 wt.% of high purity colloidal silica, and 0.0001 wt.% of biocide, and with pH being adjusted to 7.2.

[00122] Working composition 1 contained 3.78 wt.% glycine, 0.004 wt.% ethylenediamine, 0.18915 wt.% of amitrole, 0.00963 wt.% of choline bicarbonate, 0.037575 wt.% of high purity colloidal silica, and 0.0001 wt.% of biocide, and with pH being adjusted to 7.2.

[00123] All three slurries used 1.5 wt.% of H_2O_2 as oxidizing agent at point of use, respectively. The CMP polishing slurries had a pH at 7.2.

[00124] Reference 1 also described as used 1X Glycine, 1X Amitrole, 1X CBC, 1X Silica; Reference 2 described as used 1X EDA, 1X Amitrole, 1X CBC, 1X Silica; and the Working composition described as used 1X Glycine, 1X EDA, 1X Amitrole, 1X CBC, 1X Silica; as shown in the following tables.

Example 1

[00125] The polish results of using the Cu bulk CMP polishing slurries were listed in Table 1 and depicted in Figure 1.

Table 1. Cu Removal Rate Comparison in High Cu RR Bulk Slurries

Compositions	Cu RR (Å/min.) at 2.0psi DF	Cu RR (Å/min.) at 3.0psi DF	Cu RR (Å/min.) at 4.0psi DF
1X Glycine + 1X Amitrole + 1X CBC + 1X Silica	16497	22316	27832
1X EDA + 1X Amitrole + 1X CBC + 1X Silica	2455	2535	2550
1X Glycine + 1X EDA + 1X Amitrole + 1X CBC + 1X Silica	17313	23759	31154

[00126] As the results shown in Table 1, Cu CMP polishing composition (Working composition 1) afforded higher Cu film removal rates at different down forces when using two chelators while comparting the Cu removal rates obtained only using a single chelator.

[00127] Cu removal rates were increased from 2550Å/min. for only using ethylenediamine as the single chelator or 27832Å/min. for only using glycine as a single chelator to 31154Å/min. while using ethylenediamine and glycine as dual chelator at 4.0psi down force.

Example 2

[00128] In this working example, reference 3 slurry contained 3.78 wt.% single chelator alanine, 0.18915 wt.% of amitrole, 0.00963 wt.% of choline bicarbonate, 0.037575 wt.% of high purity colloidal silica, and 0.0001 wt.% of biocide, and with pH being adjusted to 7.2.

[00129] Working composition 2 contained 3.78 wt.% alanine, 0.004 wt.% ethylenediamine, 0.18915 wt.% of amitrole, 0.00963 wt.% of choline bicarbonate, 0.037575 wt.% of high purity colloidal silica, and 0.0001 wt.% of biocide, and with pH being adjusted to 7.2.

[00130] All three slurries used 1.5 wt.% of H_2O_2 as oxidizing agent at point of use, respectively. The CMP polishing slurries had a pH at 7.2.

Table 2. Cu Removal Rate Comparison in High Cu RR Bulk Slurries

Compositions	Cu RR (Å/min.) at 2.0psi DF	Cu RR (Å/min.) at 3.0psi DF	Cu RR (Å/min.) at 4.0psi DF
1X Alanine + 1X Amitrole + 1X CBC + 1X Silica	5364	7672	10312
1X EDA + 1X Amitrole + 1X CBC + 1X Silica	2455	2535	2550
1X Alanine + 1X EDA + 1X Amitrole + 1X CBC + 1X Silica	5946	8114	10768

[00131] As the results shown in Table 2, Cu CMP polishing compositions afforded relative higher Cu film removal rates at different down forces when using two chelators while comparting the Cu removal rates obtained only using a single chelator.

Example 3

[00132] In example 3, both Cu CMP polishing compositions contained two chelators, glycine and ethylenediamine (EDA) at the same wt.% concentrations of 3.78 wt. % and 0.004 wt.% respectively; 0.00963 wt. % of Choline Bicarbonate; 0.0001 wt. % of Biocide; 0.037575 wt. % of high purity colloidal silica. Amitrole was used in Working Composition 3 but not in Working Composition 4. Both polishing compositions have the pH values at about 7.2.

[00133] The effects of amitrole in polishing compositions on Cu removal rates were tested and listed in Table 3.

[00134] As the results shown in Table 3, at 2.0psi down force, Cu removal rates were increased from 19044Å/min. with amitrole to 25809Å/min. without amitrole used in the CMP polishing composition.

Table 3. Effects of Amitrole on Cu Removal Rates

Compositions	Cu RR (Å/min.) at 2.0psi DF	Cu RR (Å/min.) at 3.0psi DF
Working Composition 3	19044	37851
Working Composition 4	25809	51892

[00135] As the results further shown in Table 3, at 3.0psi down force, Cu removal rates were increased from 37581Å/min. with amitrole to 51892Å/min. without amitrole used in the CMP polishing composition.

[00136] The results shown in Table 3 clearly indicated that with/or without amitrole can be used to tune the desirable high Cu removal rates.

Example 4

[00137] Base composition contained : two chelators, glycine and ethylenediamine (EDA) at the same wt.% concentrations of 3.78 wt. % and 0.004 wt.% respectively; 0.00963 wt. % of Choline Bicarbonate; 0.0001 wt. % of Biocide; 0.037575 wt. % of high purity colloidal silica, and 0.18915 wt.% of amitrole (without H2O2). Different concentrations of hydrogen peroxide (H_2O_2) were added to the base composition to form different compositions as listed in Table 4. Cu removal rates at 2.0psi down force were measured using the compositions.

[00138] The Cu removal rate results at 2.0psi DF were listed in Table 4.

As the results shown in Table 4, the high Cu removal rates were obtained within the tested range of H_2O_2 from 1.0 wt. % to 3.0 wt. %.

[00139] Furthermore, the high Cu removal rate was tunable by using difference concentration of H_2O_2. For example, by changing the H_2O_2 to 1.5% at the point of use, higher Cu removal rate at 2.0psi DF was achieved with 37706Å/min.

Table 4. Effects of H_2O_2 wt.% on Cu Removal Rates with Two Chelators Based Cu Slurry

Compositions	Cu RR (Å/min.) at 2.0psi DF
Base + 1.0% H_2O_2	29247
Base + 1.5% H_2O_2	37706
Base + 2.0% H_2O_2	35205
Base + 2.5% H_2O_2	27047
Base + 3.0% H_2O_2	21090

Example 5

[0104] In Example 5, the working copper CMP polishing compositions as listed in Table 5 were tuned and modified in order to achieve very high Cu film polishing removal rates.

[0105] The Cu polishing compositions and the corresponding Cu removal rates obtained at different applied down forces were listed in Table 5.

Table 5. Cu Removal Rate Comparison in High Cu RR Bulk Slurries

Compositions	Cu RR (Å/min.) at 1.0psi DF	Cu RR (Å/min.) at 2.0psi DF	Cu RR (Å/min.) at 3.0psi DF	Cu RR (Å/min.) at 4.0psi DF
1X Glycine + 1X EDA + 1X Amitrole + 1X CBC + Silica	17537	26464	36588	45839
1X Glycine + 1X EDA + 0.5X Amitrole + 1X CBC + Silica	25301	34545	43603	47270
2X Glycine + 1X EDA + + 1X CBC + Silica	34564	47718	63683	74055

[0106] As the results shown in Table 5, the high Cu removal rates were achievable and tunable by changing the concentrations of chelator glycine and corrosion inhibitor amitrole, or by removing amitrole from the polishing compositions.

[0107] Further, after removing the amitrole and increasing the first chelator glycine concentration in the polishing compositions, the very high Cu removal rate of 74055Å/min. was achieved at 4.0psi down force.

Example 6

[0108] In Example 6, a working CMP polishing composition using glycine and ethylenediamine as dual chelators (as shown in Table 6) was used for obtaining Cu: Ta and Cu: TEOS selectivity at 2.0psi DF condition.

[0109] The polishing results and Cu:Ta and Cu:TEOS selectivity were all listed in Table 6.

Table 6: Cu:Ta and Cu: TEOS Selectivity at 2.0psi DF

Compositions	Cu RR (Å/min.) at 2.0psi DF	Ta RR (Å/min.) at 2.0psi DF	TEOS RR (Å/min.) at 2.0psi DF	Cu : Ta Selectivity at 2.0psi DF	Cu : TEOS Selectivity at 2.0psi DF
1X Glycine + 1X EDA + 1X Amitrole + 1X CBC + Silica	26464	0	0	Very High	Very High

[0110] As the results shown in Table 6, at 2.0psi down force conditions, the removal rates for both Ta and TEOS film were at 0 Å/min.. Therefore, the Cu: Ta and Cu: TEOS selectivity were very high.

[0111] While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, departures may be made from such details without departing from the spirit or scope of the general inventive concept.

CLAIMS

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

    a) abrasive;

    b) at least two chelators;

    c) oxidizing agent; and

    d) water;

    optionally

    e) corrosion inhibitor;

    f) organic quaternary ammonium salt;

    g) biocide;

    h) pH adjusting agent;

    wherein

    the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative and at least one chelator is organic amine;

    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

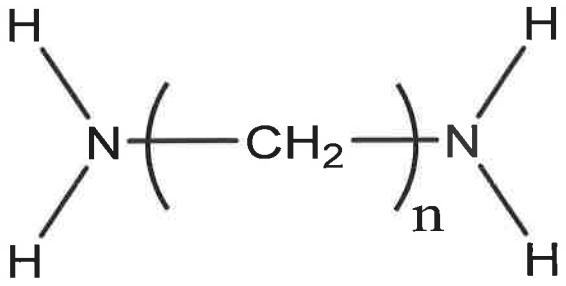
    the pH of the composition is selected from the group consisting of 5.5 to 7.5; and 7.0 to 7.35.

2. The copper chemical mechanical polishing (CMP) composition of Claim 1, wherein the at least two chelators comprise (1)at least one organic amine; and (2) one selected from the group consisting of at least one amino acid, at least one derivative, and combinations of at least one amino acid with at least one amino derivative.

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

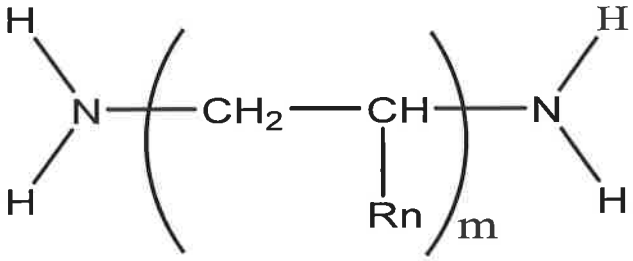
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine,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

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



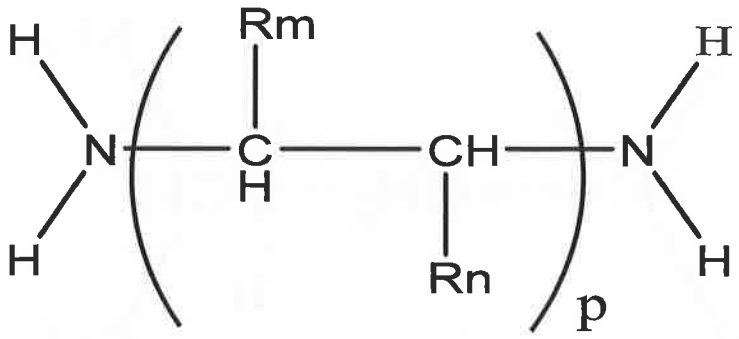
(a)

wherein n is from 2 to 12;



(b)

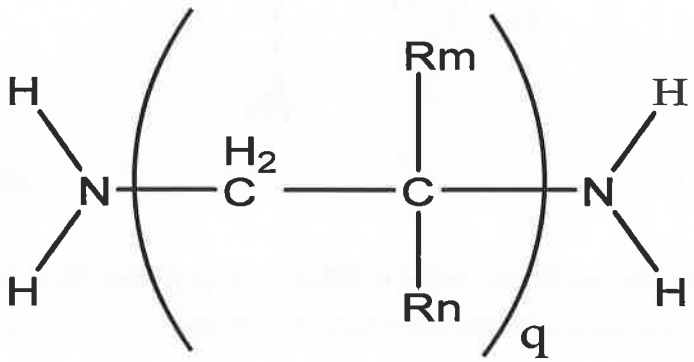
wherein Rn represents an organic alkyl group C_nH_{2n+1}, n is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and m is from 2 to 12;



(c)

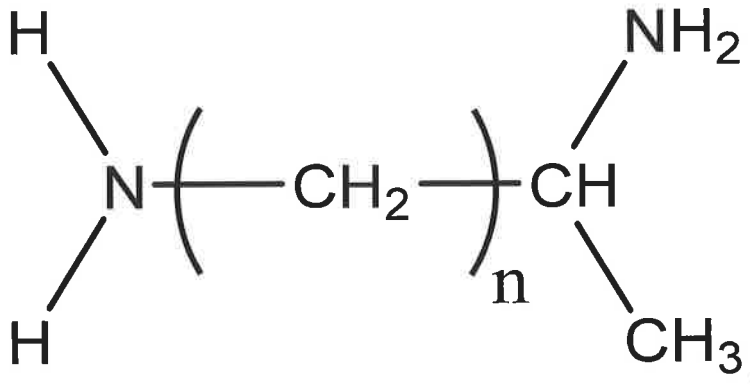
wherein Rn and Rm can be the same or different alkyl groups with n and m numbered independently from 1 to 12;

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



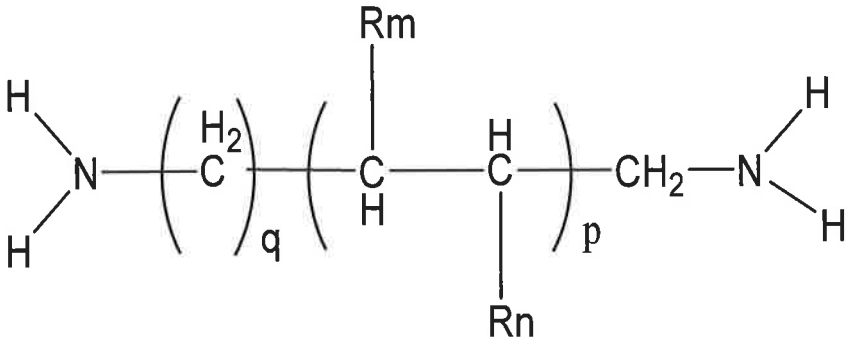
(d)

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



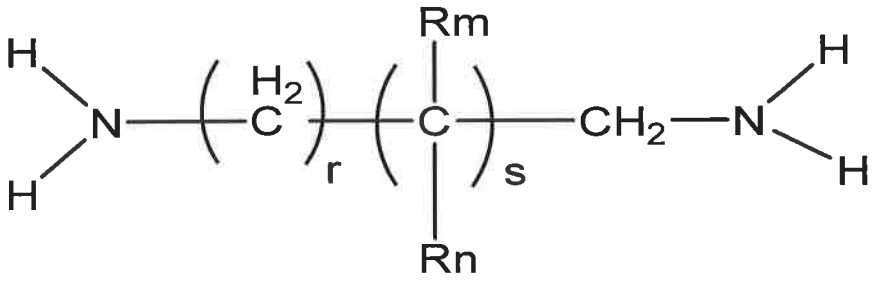
(e)

wherein n is from 1 to 12;



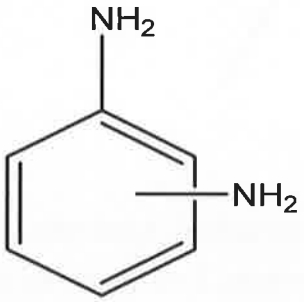
(f)

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



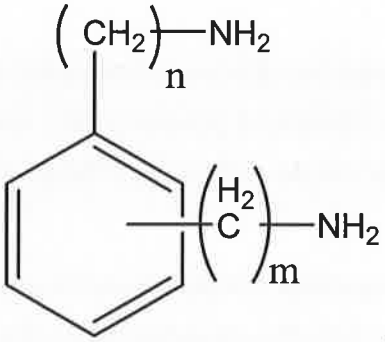
(g)

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



(h)

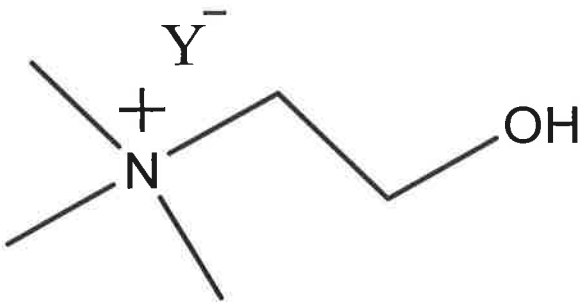
and



(i)

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

4. 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.

5. 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 combinations thereof; 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, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof;

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;

   0.001 to 18.0 total wt. % of (1) at least one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) at least one of amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof;

   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, 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) at least one organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) at least amino acid selected from the

group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, and combination thereof;

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

the composition has a pH from 5.5 to 7.5.

8. The copper chemical mechanical polishing (CMP) composition of claim 1, comprising

0.0005 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 10.0 total wt. % of ethylenediamine; 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.

9. 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) abrasive;
    b) at least two chelators;
    c) oxidizing agent; and

d) water;

optionally

e) corrosion inhibitor;

f) organic quaternary ammonium salt;

g) biocide;

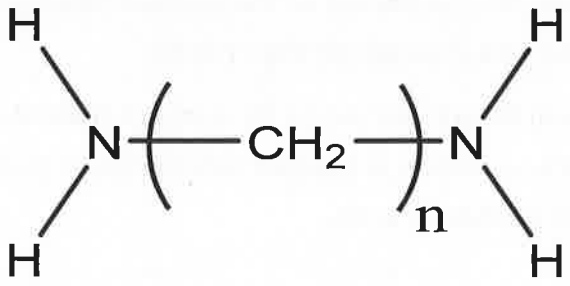
h) pH adjusting agent;

wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative and at least one chelator is organic amine;

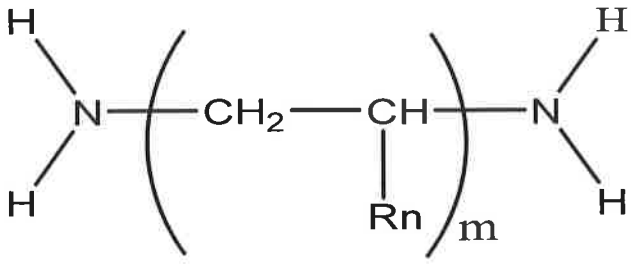
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine,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

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



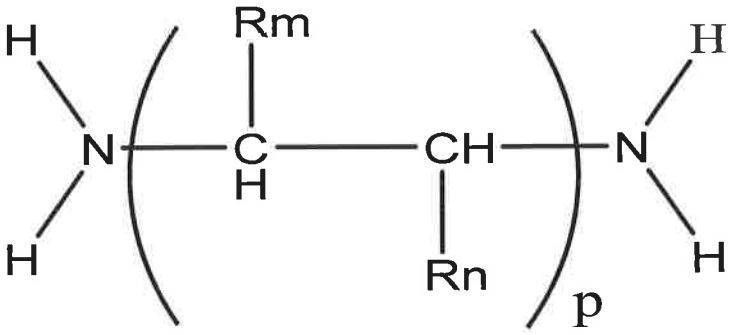
(a)

wherein n is from 2 to 12;



(b)

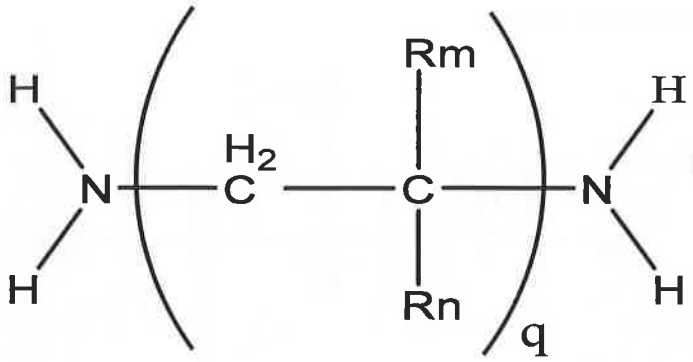
wherein Rn represents an organic alkyl group C_nH_{2n+1}, n is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and m is from 2 to 12;



(c)

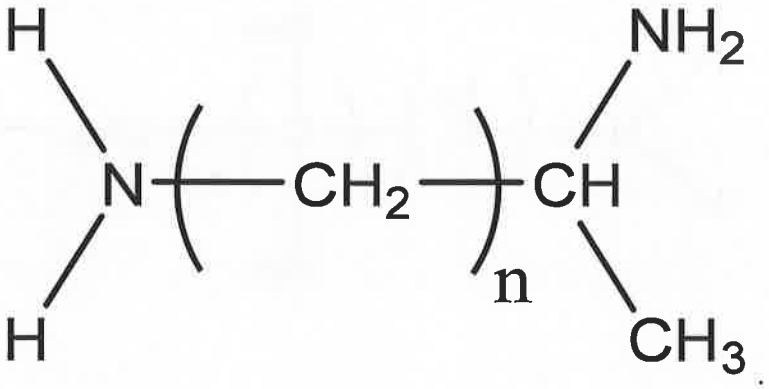
wherein Rn and Rm can be the same or different alkyl groups with n and m numbered independently from 1 to 12;

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



(d)

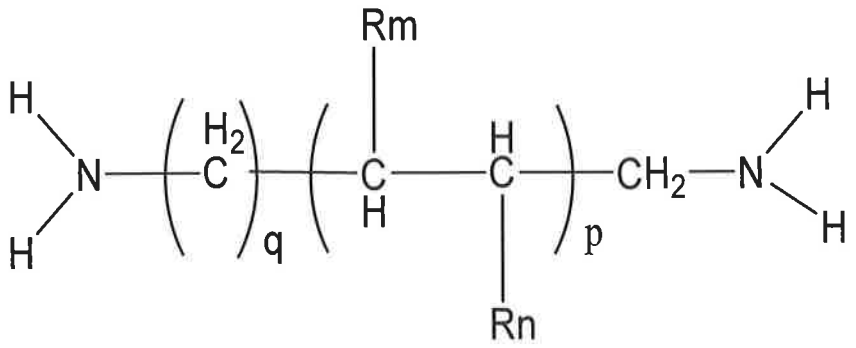
wherein Rn and Rm can be the same or different alkyl groups Rn = C_nH_{2n+1} and Rm = C_mH_{2m+1}, n or m is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and q is from 2 to 12;



(e)

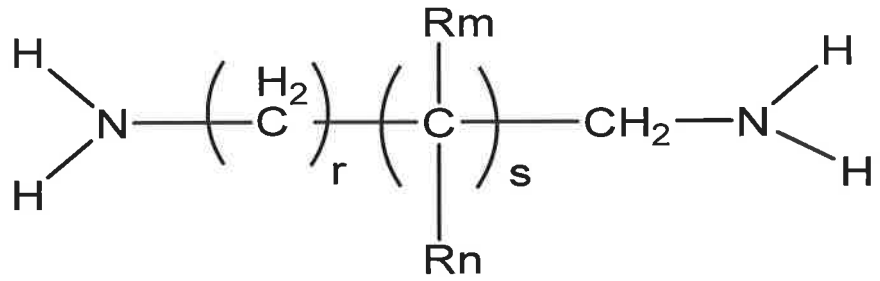
wherein n is from 1 to 12;

wherein n is from 1 to 12;



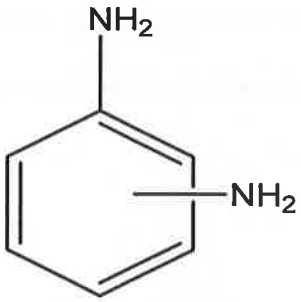
(f)

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



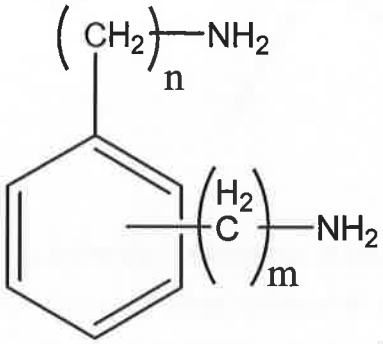
(g)

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



(h);

and



(i)

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

and combinations thereof;

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;

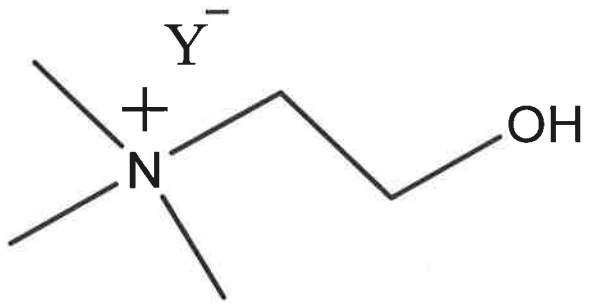
and

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.

10. The method for chemical mechanical polishing of Claim 9, 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 9, 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 combinations thereof;

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, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof;

12. The method for chemical mechanical polishing of Claim 9, wherein the Cu chemical mechanical polishing composition comprises

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

0.001 to 18.0 total wt. % of (1) at least one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) at least one of amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof;

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 9, 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) at least one organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) at least amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, and combination thereof;

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 9, wherein the Cu chemical mechanical polishing composition comprises

0.0005 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 10.0 total wt. % of ethylenediamine; 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.

15. The method for chemical mechanical polishing of Claim 9, 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.

16. 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 steps of:

1) providing the semiconductor substrate;

2) providing a polish pad;

3) providing a Cu chemical mechanical polishing composition comprising:

a) abrasive;

b) at least two chelators;

c) oxidizing agent; and

d) water;

optionally

e) corrosion inhibitor;

f) organic quaternary ammonium salt;

g) biocide;

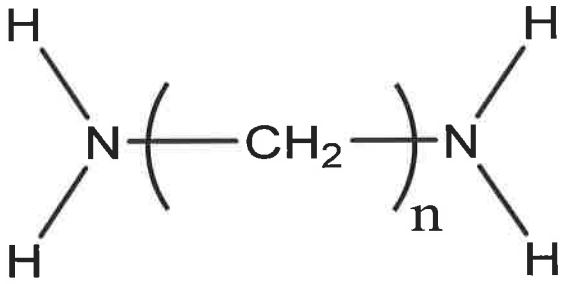
h) pH adjusting agent;

wherein

the at least two chelators are independently selected from the group consisting of amino acids, amino acid derivatives, organic amine, and combinations therefor; wherein at least one chelator is an amino acid or an amino acid derivative and at least one chelator is organic amine;

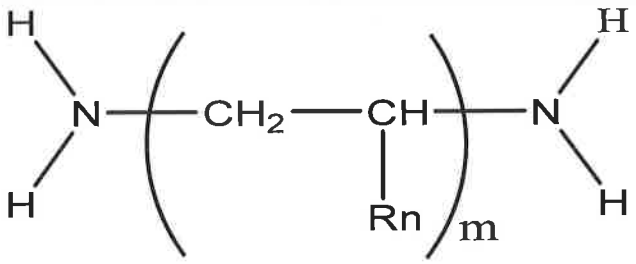
the amino acid or the amino acid derivative is selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine,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

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



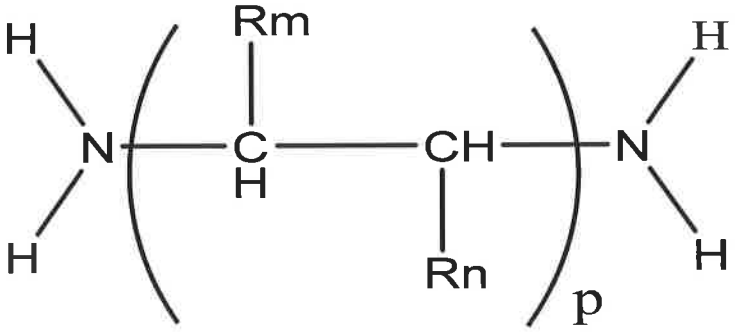
(a)

wherein n is from 2 to 12;



(b)

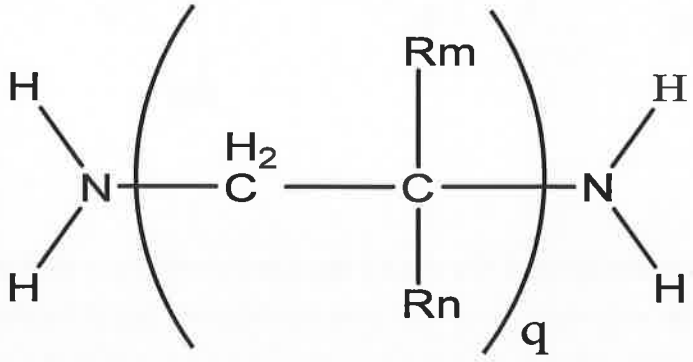
wherein Rn represents an organic alkyl group C_nH_{2n+1}, n is selected from the group consisting of 2 to 12, 1 to 6, and 1 to 3; and m is from 2 to 12;



(c)

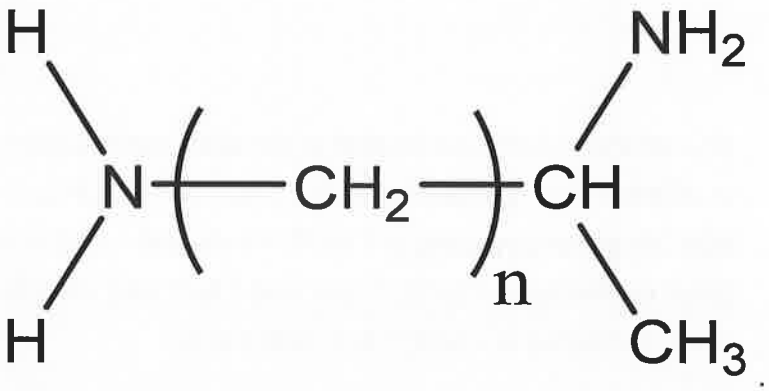
wherein Rn and Rm can be the same or different alkyl groups with n and m numbered independently from 1 to 12;

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



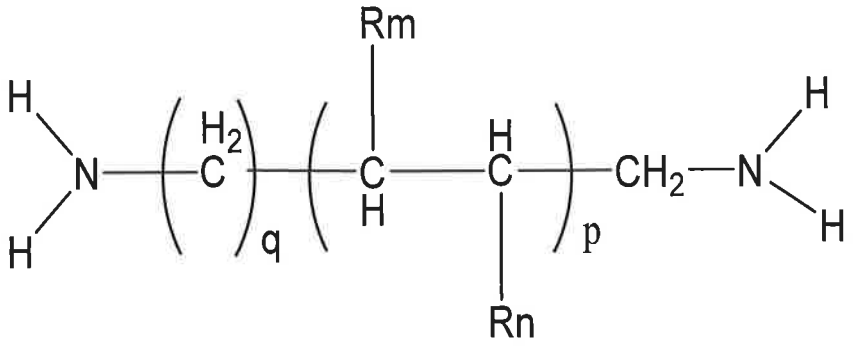
(d)

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



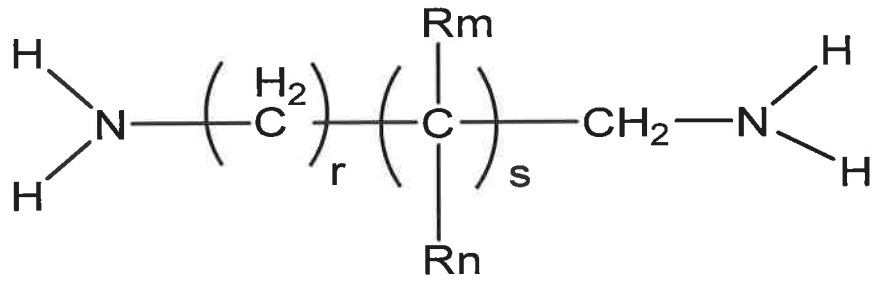
(e)

wherein n is from 1 to 12;



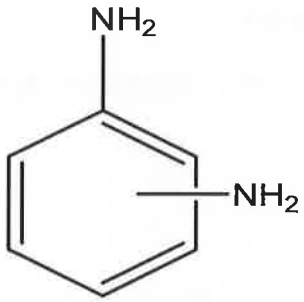
(f)

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



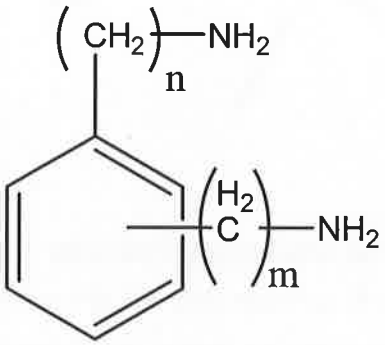
(g)

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



(h);

and



(i)

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

and combinations thereof;

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;

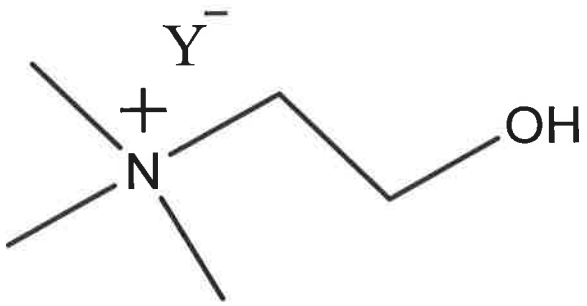
and

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.

17. The system of claim 16, 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 of claim 16, 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 combinations thereof; 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, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof;

19. The system of claim 16, wherein the Cu chemical mechanical polishing composition comprises

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

0.001 to 18.0 total wt. % of (1) at least one of the organic amine selected from the group consisting of ethylenediamine, propylenediamine, and butylenediamine; and (2) at least one of amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, valine, leucine, isolueciene, phenylamine, proline, serine, threonine, tyrosine, glutamine, asparanine, glutamic acid, aspartic acid, tryptophan, histidine, arginine, lysine, methionine, cysteine, iminodiacetic acid, and combinations thereof;

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 16, 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) at least one organic amine selected from ethylenediamine propylenediamine, and butylenediamine; and (2) at least amino acid selected from the group consisting of glycine, D-alanine, L-alanine, DL-alanine, beta-alanine, and combination thereof;

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

the composition has a pH from 5.5 to 7.5.

21. The system of claim 16, wherein the Cu chemical mechanical polishing composition comprises

0.0005 wt.% to 0.15 wt.% of colloidal silica or high purity colloidal silica;

0.5 to 10.0 total wt. % of ethylenediamine; 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.

22. The system of claim 16, 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.