Claims

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

abrasives,

micron-size polyurethane (PU) beads ranging from 2 to 100 μm or 20 to 70 μm;

silicone-containing dispersing agent;

at least one chelating agent;

corrosion inhibitor;

and optionally

organic quaternary ammonium salt;

a biocide;

pH adjuster;

an oxidizer added at the point of use;

liquid carrier such as water; and

the pH of the composition is from 3.0 to 12.0; or 5.5 to 8;

wherein the chelating agent is selected from the group consisting of amino acid, amino acid derivative, organic amine, and combinations thereof.

2. The CMP composition of Claim 1, wherein the abrasives are selected from the group consisting of colloidal silica; colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; colloidal aluminum oxide selected from the group consisting of alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide; colloidal cerium oxide; zirconium oxide, nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, or multi-modal colloidal abrasive particles; organic polymer-based soft abrasives; surface-coated or modified abrasives; and combinations thereof. ; and the abrasives range from 0.0025 wt.% to 25 wt.% or 0.0025 wt.% to 2.5 wt.%; and the micron-size polyurethane (PU) beads range from 0.01 wt.% to 2.0 wt.%, or 0.025 wt.% to 1.0 wt.%.

3. The CMP composition of Claim 1, wherein the silicone-containing dispersing agent comprises a silicone polyether containing both a water-insoluble silicone backbone and a number of water-soluble polyether pendant groups including repeating units of ethylene oxide (EO) and propylene oxide (PO) (EO-PO) functional groups; and the silicone-containing dispersing agent ranges from 0.01 wt.% to 2.0 wt.%, or 0.001 wt.% to 2.0 wt.%.

4. The CMP composition of Claim 1, wherein the at least one chelating agent 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, 2,2-dimethyl-1,3-propanediamine and 2,2-dimethyl-1,4-butanediamine, ethylenediamine, 1,3-diaminepropane, 1,4-diaminebutane, and combinations thereof; and the at least one chelating agent ranges from 0.1 wt.% to 18 wt.%; or 0.5 wt.% to 15 wt.%.

5. The CMP composition of Claim 1, wherein the corrosion inhibitor is selected from the group consisting of 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.; and the corrosion inhibitor ranges from 0.001 wt.% to 1.0 wt.%; or 0.005 wt.% to 0.5 wt.%.

6. The CMP composition of Claim 1, wherein 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 biocide ranges from 0.0001 wt.% to 0.05 wt.%; or 0.0001 wt.% to 0.025 wt.%.

7. The CMP composition of Claim 1, wherein 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 mixtures thereof.; and the oxidizing agent ranges from 0.1 wt.% to 10 wt.%; or 0.25wt.% to 7 wt.%.

8. The CMP composition of Claim 1, wherein the organic quaternary ammonium salt is selected from the group consisting of choline salt having different counter ions selected from the group consisting of choline bicarbonate, choline hydroxide, choline dihydrogen citrate salt, choline ethanolamine, choline bitartrate, and combinations thereof.; and the organic quaternary ammonium salt ranges from 0.005 wt.% to 0.5 wt.%, or 0.001 wt.% to 0.25 wt.%.

9. The CMP composition of Claim 1, wherein the pH adjusting agent is selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, other inorganic or organic acids, and other chemical reagents that are able to be used to adjust pH towards acidic direction; or is selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic amines, and other chemical reagents that are able to be used to adjust pH towards alkaline direction.

10. The CMP composition of Claim 1, wherein the CMP composition comprises at least one of chelating agent selected from the group consisting of glycine, glycine, D-alanine, L-alanine, DL-alanine, ethylenediamine, 1,3-diaminepropane, 1,4-diaminebutane, and combinations; the corrosion inhibitor is selected from the group consisting of 3-amino-1,2,4-triazole, 1,2,4-triazole, imidazole and imidazole derivatives, and combinations; choline bicarbonate or choline hydroxide; biocide; and colloidal silica particles; silicone-containing dispersing agent, and 30 to 50 μm polyurethane (PU) beads.

11. The CMP composition of Claim 1, wherein the CMP composition comprises glycine and alanine, 3-amino-1,2,4-triazole, ethylenediamine, choline bicarbonate, biocide, and colloidal silica particles, silicone-containing dispersing agent, and 30 μm to 50 μm polyurethane (PU) beads.

12. A method of chemical mechanical polishing a semiconductor substrate, comprising steps of:
providing the semiconductor substrate having a surface containing Copper or Through Silicon Via (TSV) Copper;
providing a non-porous solid polishing pad;
providing a chemical mechanical polishing (CMP) composition comprising:
abrasives,
micron-size polyurethane (PU) beads ranging from 2 to 100 μm or 20 to 70 μm;
silicone-containing dispersing agent;
at least one chelating agent;
corrosion inhibitor;
and optionally
organic quaternary ammonium salt;

a biocide;
pH adjuster;
an oxidizer added at the point of use;
liquid carrier such as water; and
the pH of the composition is from 3.0 to 12.0; or 5.5 to 8;
wherein the chelating agent is selected from the group consisting of amino acid, amino acid derivative, organic amine, and combinations thereof;

contacting the surface of the semiconductor substrate with the polishing pad and the chemical mechanical polishing composition; and

polishing the surface of the semiconductor;

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

13. The method of claim 12, wherein the abrasives in the CMP composition are selected from the group consisting of colloidal silica; colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; colloidal aluminum oxide selected from the group consisting of alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide, colloidal cerium oxide; zirconium oxide, nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, or multi-modal colloidal abrasive particles; organic polymer-based soft abrasives; surface-coated or modified abrasives; and mixtures thereof; and the abrasives range from .0025 wt.% to 25 wt.% or 0.0025 wt.% to 2.5 wt.%;
the micron-size polyurethane (PU) beads in the CMP composition range from 0.01 wt.% to 2.0 wt.% or 0.025 wt.% to 1.0 wt.%;
the silicone-containing dispersing agent in the CMP composition comprises a silicone polyether containing both a water-insoluble silicone backbone and water-soluble polyether pendant groups including repeating units of ethylene oxide (EO) and propylene oxide (PO) (EO-PO) functional groups; and the silicone-containing dispersing agent ranges from 0.01 wt.% to 2.0 wt.% or 0.001 wt.% to 2.0 wt.%; and the at least one chelating agent in the CMP composition 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, 2,2-dimethyl-1,3-propanediamine and 2,2-dimethyl-1,4-butanediamine, ethylenediamine, 1,3-diaminepropane, 1,4-diaminebutane, and combinations thereof; and the at least one chelating agent ranges from 0.1 wt.% to 18 wt.% or 0.5 wt.% to 15 wt.%.

14. The method of claim 12, wherein the corrosion inhibitor in the CMP composition is selected from the group consisting of 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; and the corrosion inhibitor ranges from 0.001 wt.% to 1.0 wt.% or 0.005 wt.% to 0.5 wt.%;

the biocide in the CMP composition 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 biocide ranges from 0.0001 wt.% to 0.05 wt.% or 0.0001 wt.% to 0.025 wt.%;

the oxidizing agent in the CMP composition 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 mixtures thereof; and the oxidizing agent ranges from 0.1 wt.% to 10 wt.% or 0.25 wt.% to 7 wt.%;

the organic quaternary ammonium salt in the CMP composition is selected from the group consisting of choline salt having different counter ions selected from the group consisting of choline bicarbonate, choline hydroxide, choline dihydrogen citrate salt, choline ethanolamine, choline bitartrate, and combinations thereof; and the organic quaternary ammonium salt ranges from 0.005 wt.% to 0.5 wt.% or 0.001 wt.% to 0.25 wt.%; and

the pH adjusting agent in the CMP composition is selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, other inorganic or organic acids, and other chemical reagents that are able to be used to adjust pH towards acidic direction; or is selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium

hydroxide, organic amines, and other chemical reagents that are able to be used to adjust pH towards alkaline direction.

15. The method of claim 12, wherein the CMP composition comprises at least one of chelating agent selected from the group consisting of glycine, glycine, D-alanine, L-alanine, DL-alanine, ethylenediamine, 1,3-diaminepropane, 1,4-diaminebutane, and combinations; the corrosion inhibitor is selected from the group consisting of 3-amino-1,2,4-triazole, 1,2,4-triazole, imidazole and imidazole derivatives, and combinations; choline bicarbonate or choline hydroxide; biocide; and colloidal silica particles; silicone-containing dispersing agent, and 30 to 50 μm polyurethane (PU) beads.

16. The method of claim 12, wherein the CMP composition comprises glycine and alanine, 3-amino-1,2,4-triazole, ethylenediamine, choline bicarbonate, biocide, and colloidal silica particles, silicone-containing dispersing agent, and 30 μm to 50 μm polyurethane (PU) beads.

17. A system of chemical mechanical polishing, comprising
    a semiconductor substrate having a surface containing copper or Through Vias (TSV) copper;
    providing a non-porous solid polishing pad;
    providing a chemical mechanical polishing (CMP) composition comprising:
        abrasives,
        micron-size polyurethane (PU) beads ranging from 2 to 100 μm or 20 to 70 μm;
        silicone-containing dispersing agent;
        at least one chelating agent;
        corrosion inhibitor;
        and optionally
        organic quaternary ammonium salt;
        a biocide;
        pH adjuster;
        an oxidizer added at the point of use;
        liquid carrier such as water; and
        the pH of the composition is from 3.0 to 12.0; or 5.5 to 8;

wherein the chelating agent is selected from the group consisting of amino acid, amino acid derivative, organic amine, and combinations thereof;

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

18. The system of claim 17, wherein the abrasives in the CMP composition are selected from the group consisting of colloidal silica; colloidal silica particles doped by other metal oxide within lattice of the colloidal silica; colloidal aluminum oxide selected from the group consisting of alpha-, beta-, and gamma-types of aluminum oxides; colloidal and photoactive titanium dioxide; cerium oxide, colloidal cerium oxide; zirconium oxide, nano-sized diamond particles; nano-sized silicon nitride particles; mono-modal, bi-modal, or multi-modal colloidal abrasive particles; organic polymer-based soft abrasives; surface-coated or modified abrasives; and mixtures thereof; and the abrasives range from .0025 wt.% to 25 wt.% or 0.0025 wt.% to 2.5 wt.%;
the micron-size polyurethane (PU) beads in the CMP composition range from 0.01 wt.% to 2.0 wt.% or 0.025 wt.% to 1.0 wt.%;
the silicone-containing dispersing agent in the CMP composition comprises a silicone polyether containing both a water-insoluble silicone backbone and water-soluble polyether pendant groups including repeating units of ethylene oxide (EO) and propylene oxide (PO) (EO-PO) functional groups; and the silicone-containing dispersing agent ranges from 0.01 wt.% to 2.0 wt.% or 0.001 wt.% to 2.0 wt.%; and the at least one chelating agent in the CMP composition 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, 2,2-dimethyl-1,3-propanediamine and 2,2-dimethyl-1,4-butanediamine, ethylenediamine, 1,3-diaminepropane, 1,4-diaminebutane, and combinations thereof; and the at least one chelating agent ranges from 0.1 wt.% to 18 wt.% or 0.5 wt.% to 15 wt.%.

19. The system of claim 17, wherein the corrosion inhibitor in the CMP composition is selected from the group consisting of 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; and the corrosion inhibitor ranges from 0.001 wt.% to 1.0 wt.% or 0.005 wt.% to 0.5 wt.%;

the biocide in the CMP composition 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 biocide ranges from 0.0001 wt.% to 0.05 wt.% or 0.0001 wt.% to 0.025 wt.%;

the oxidizing agent in the CMP composition 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 mixtures thereof; and the oxidizing agent ranges from 0.1 wt.% to 10 wt.% or 0.25 wt.% to 7 wt.%;

the organic quaternary ammonium salt in the CMP composition is selected from the group consisting of choline salt having different counter ions selected from the group consisting of choline bicarbonate, choline hydroxide, choline dihydrogen citrate salt, choline ethanolamine, choline bitartrate, and combinations thereof; and the organic quaternary ammonium salt ranges from 0.005 wt.% to 0.5 wt.% or 0.001 wt.% to 0.25 wt.%; and

the pH adjusting agent in the CMP composition is selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, other inorganic or organic acids, and other chemical reagents that are able to be used to adjust pH towards acidic direction; or is selected from the group consisting of sodium hydroxide, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic amines, and other chemical reagents that are able to be used to adjust pH towards alkaline direction.

20. The system of claim 17, wherein the CMP composition comprises at least one of chelating agent selected from the group consisting of glycine, glycine, D-alanine, L-alanine, DL-alanine, ethylenediamine, 1,3-diaminepropane, 1,4-diaminebutane, and combinations; the corrosion inhibitor is selected from the group consisting of 3-amino-1,2,4-triazole, 1,2,4-triazole, imidazole and imidazole derivatives, and combinations; choline bicarbonate or choline hydroxide; biocide; and colloidal silica

particles; silicone-containing dispersing agent, and 30 to 50 μm polyurethane (PU) beads.

21. The system of claim 17, wherein the CMP composition comprises glycine and alanine, 3-amino-1,2,4-triazole, ethylenediamine, choline bicarbonate, biocide, and colloidal silica particles, silicone-containing dispersing agent, and 30 μm to 50 μm polyurethane (PU) beads.