CLAIMS

1. A post Chemical Mechanical Planarization(CMP) cleaning composition comprising:

at least one organic acid or its salts;

at least two surfactants;

wherein at least one of the at least two surfactants is a first type surfactant having at least two sulfonic acid groups; and at least one of the at least two surfactants is a second type surfactant which is not the first type surfactant;

and

water;

optionally

fluoride compound;

water soluble polymer or copolymer;

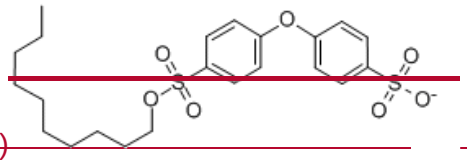
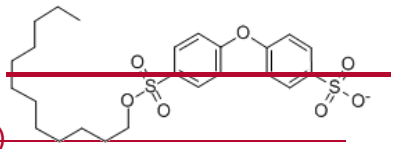
corrosion inhibitor;

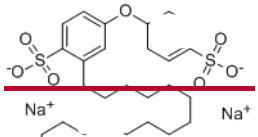
biological preservative; and

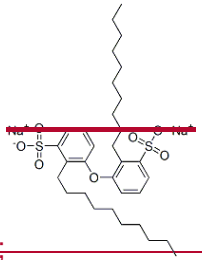
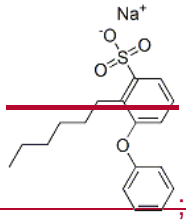
pH adjusting agent.

2. The post CMP cleaning composition of Claim 1, wherein the first type surfactant is a diphenyl disulfonic acid surfactant having diphenyl disulfonic acid or its salts.

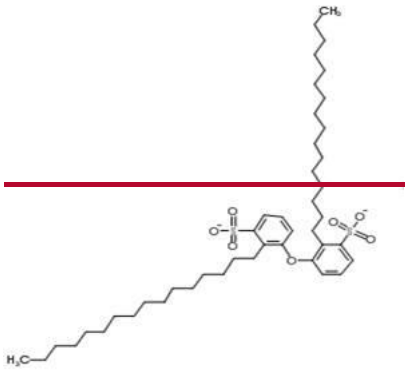
3. The post CMP cleaning composition of Claim 1, wherein the first type surfactant has a structure selected from the group consisting of

(a)  ; (b) 



(c) ; (d);  ;(e) 

;and (f)



4. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant increases zeta potential magnitude on surface containing dielectric material.

5. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant reduces contact angle on cleaning surfaces.

6. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant has a surface tension of < 50 dynes/cm at concentration of 0.01 wt.% in water, preferably <45 dynes/cm at concentration of 0.01 wt.% in water, or more preferably <40 dynes/cm at concentration of 0.01 wt.% in water.

7. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, non-ionic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant increases zeta potential magnitude on surface containing dielectric material.

8. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, non-ionic surfactant,

ampholytic surfactant, and combinations thereof; and the second type surfactant reduces contact angle on cleaning surfaces.

9. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, non-ionic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant has a surface tension of < 50 dynes/cm at concentration of 0.01 wt.% in water, or preferably <45 dynes/cm at concentration of 0.01 wt.% in water.

10. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, ampholytic surfactant showing anionic characteristics in the composition, and combinations thereof; and the second type surfactant increases zeta potential magnitude on surface containing dielectric material.

11. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, ampholytic surfactant showing anionic characteristics in the composition, and combinations thereof; and the second type surfactant reduces contact angle on cleaning surfaces.

12. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, ampholytic surfactant showing anionic characteristics in the composition, and combinations thereof; and the second type surfactant has a surface tension of < 50 dynes/cm at concentration of 0.01 wt.% in water, or preferably <45 dynes/cm at concentration of 0.01 wt.% in water .

13. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of non-ionic surfactants comprising ethylene oxide group or propylene oxide group or both groups.

14. The post CMP cleaning composition of Claim 1, wherein the at least one organic acid is selected from the group consisting of monocarboxylic acid, dicarboxylic acid, polyacrboxylic acid, hydroxycarboxylic acid, and combinations thereof.

15. The post CMP cleaning composition of Claim 1, wherein the at least one organic acid is selected from the group consisting of oxalic acid, citric acid, maleic acid, malic acid, malonic acid, gluconic acid, glutaric acid, ascorbic acid, formic acid, acetic acid, ethylene diamine tetraacetic acid, diethylene triamine pentaacetic acid, glycine, α-alanine, cystine, and combinations thereof.

16. The post CMP cleaning composition of Claim 1, wherein the at least one organic acid is selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof.

17. The post CMP cleaning composition of Claim 1, wherein the fluoride compound is selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium bifluoride, quaternary ammonium fluorides, and combinations thereof.

18. The post CMP cleaning composition of Claim 1, wherein the fluoride compound is ammonium fluoride.

19. The post CMP cleaning composition of Claim 1, wherein the water soluble polymer comprises a group selected from the group consisting of sulfonic acid group, acrylic acid group, and combinations thereof; and the water soluble copolymer comprises monomers having a group selected from the group consisting of sulfonic acid group, acrylic acid group, and combinations thereof.

20. The post CMP cleaning composition of Claim 1, wherein the water soluble polymer or copolymer is selected from the group consisting of acrylic acid-acrylamido propane sulfonic acid copolymer, poly(acrylic acid), poly(meth-acrylic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid, carboxymethyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose, poly-(1-vinylpyrroliddone-co-2-dimethylaminoethyl methacrylate), poly(sodium 4-styrenesulfonate), poly(ethylene oxide), poly(4-sytrenesulfonic acid), polyacrylamide, poly(acrylamide/acrylic acid) copolymer, and combinations thereof; wherein molecular weight of the water soluble polymer or copolymer ranges from 100 to 10,000,000, preferably .

21. The post CMP cleaning composition of Claim 1, wherein the corrosion inhibitor is selected from the group consisting of oligomer or polymer comprising of ethyleneimine,

propyleneimine, polyethyleneimine(PEI), and combinations thereof; wherein molecular weight of the oligomer or polymer ranges from between 500 to 1000000, preferably between 500 and 15000.

22. The post CMP cleaning composition of Claim 1, wherein the biological preservative is selected from the group consisting of tetramethylammonium chloride; tetraethylammonium chloride; tetrapropylammonium chloride; alkylbenzyldimethylammonium chloride; alkylbenzyldimethylammonium hydroxide; sodium chlorite; sodium hypochlorite; isothiazolinone compound selected from the group consisting of methylisothiazolinone, methylchloroisothiazolinone, benzisothiazolinone and combinations thereof; and combinations thereof.

23. The post CMP cleaning composition of Claim 1, wherein the pH adjusting agent is selected from the group consisting of inorganic acid nitric acid selected from the group consisting of sulfonic acid, or phosphoric acid; inorganic base selected from the group consisting of ammonia hydroxide, potassium hydroxide or sodium hydroxide; and organic base selected from the group consisting of quaternary ammonium hydroxide, and amine compound.

24. The post CMP cleaning composition of Claim 1, wherein the composition has a pH of between 1 to 7, preferably 2 to 6, or more preferably 3 to 6.

25. The post CMP cleaning composition of Claim 1, wherein the composition is diluted with water 2 to 500 times at point of use.

26. The post CMP cleaning composition of Claim 1, wherein the composition has turbidity less than 5 NTU, preferably 2.5NTU, more preferably 2NTU, or most preferably 1 NTU.

27. The post CMP cleaning composition of Claim 1, wherein the composition comprises at least one organic acid selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof; the first type surfactant comprising two or more sulfonic acid groups is a diphenyl disulfonic acid or its salt; the second type surfactant comprising a secondary alkane sulfonic acid with C_{12}-C_{17} hydrophobic chain.

28. The post CMP cleaning composition of Claim 1, wherein the composition comprises at least one organic acid selected from the group consisting of oxalic acid, citric acid,

malonic acid, and combinations thereof; the first type surfactant comprising two or more sulfonic acid groups is a diphenyl disulfonic acid or its salt; the second type surfactant comprising a secondary alkane sulfonic acid with C_{12}-C_{17} hydrophobic chain; and the fluoride compound selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium bifluoride, quaternary ammonium fluorides, and combinations thereof.

29. The post CMP cleaning composition of Claim 1, wherein the composition comprises at least one organic acid selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof; the first type surfactant comprising two or more sulfonic acid groups is a diphenyl disulfonic acid or its salt; the second type surfactant comprising a secondary alkane sulfonic acid with C_{12}-C_{17} hydrophobic chain; the fluoride compound selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium bifluoride, quaternary ammonium fluorides, and combinations thereof; and the water soluble polymer comprising acrylic acid group or the water soluble copolymer comprising monomers having acrylic acid group.

30. A method of post Chemical Mechanical Planarization (CMP) cleaning semiconductor wafer comprising at least one surface selected from the group consisting of metallic film, dielectric film, and combinations thereof, comprising

providing the semiconductor wafer;

providing the post Chemical Mechanical Planarization (CMP) cleaning composition of any one of claims 1 to 29; and

cleaning the semiconductor wafer using the post CMP cleaning composition;

wherein the metallic film is selected from the group consisting of tungsten, copper, cobalt, ruthenium, aluminum, and combinations thereof.

31. The method of post Chemical Mechanical Planarization (CMP) cleaning of claim 30; where the method removes metallic residues selected from the group consisting of Fe, W, Ti, TiN and combinations thereof from the at least one surface.

32. A system for post Chemical Mechanical Planarization (CMP) cleaning semiconductor wafer comprising at least one surface selected from the group consisting of metallic film, dielectric film, and combinations thereof, comprising

the semiconductor wafer; and

the post Chemical Mechanical Planarization (CMP) cleaning composition of any one of claims 1 to 29; and

wherein the at least one surface is in touch with the post CMP cleaning composition and the metallic film is selected from the group consisting of tungsten, copper, cobalt, ruthenium, aluminum, and combinations thereof.

CLAIMS

1. A post Chemical Mechanical Planarization(CMP) cleaning composition comprising:

at least one organic acid or its salts;

at least two surfactants;

wherein at least one of the at least two surfactants is a first type surfactant having at least two sulfonic acid groups; and at least one of the at least two surfactants is a second type surfactant which is not the first type surfactant and is selected from the group consisting of non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant increases zeta potential magnitude on surface containing dielectric material, reduces contact angle on cleaning surfaces, and has a surface tension of < 50 dynes/cm at concentration of 0.01 wt.% in water;

and

water;

optionally at least one selected from the group consisting of

fluoride compound;

water soluble polymer or copolymer;

corrosion inhibitor;

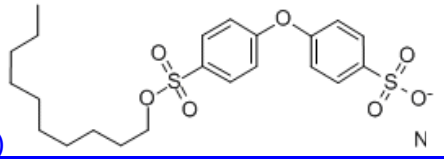
biological preservative; and

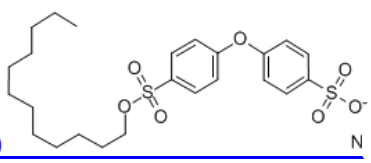
pH adjusting agent;

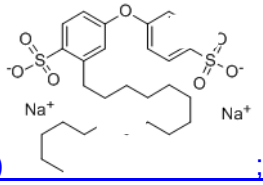
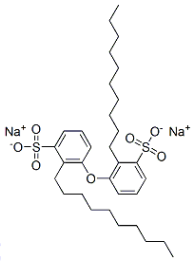
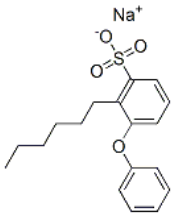
wherein the composition has a pH of between 1 to 7.

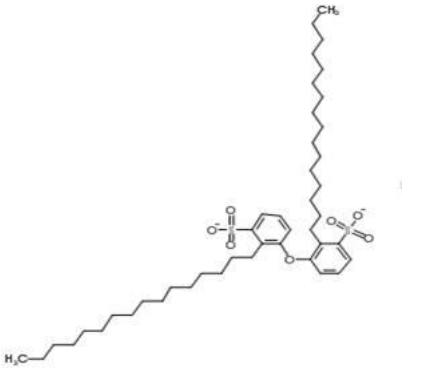
2. The post CMP cleaning composition of Claim 1, wherein the first type surfactant is a diphenyl disulfonic acid surfactant having diphenyl disulfonic acid or its salts.

3. The post CMP cleaning composition of Claim 1, wherein the first type surfactant has a structure selected from the group consisting of

(a) 

(b) 

(c)  ; (d);  ;(e)  ;and (f)



.

4. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of anionic surfactant, non-ionic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant has a surface tension of <45 dynes/cm at concentration of 0.01 wt.% in water.

5. The post CMP cleaning composition of Claim 1, wherein the second type surfactant is selected from the group consisting of non-ionic surfactants comprising ethylene oxide group or propylene oxide group or both groups.

6. The post CMP cleaning composition of Claim 1, wherein the at least one organic acid is selected from the group consisting of monocarboxylic acid, dicarboxylic acid, polyacrboxylic acid, hydroxycarboxylic acid, and combinations thereof.

7. The post CMP cleaning composition of Claim 1, wherein the at least one organic acid is selected from the group consisting of oxalic acid, citric acid, maleic acid, malic acid, malonic acid, gluconic acid, glutaric acid, ascorbic acid, formic acid, acetic acid, ethylene diamine tetraacetic acid, diethylene triamine pentaacetic acid, glycine, α-alanine, cystine, and combinations thereof.

8. The post CMP cleaning composition of Claim 1, wherein the at least one organic acid is selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof.

9. The post CMP cleaning composition of Claim 1, wherein

the fluoride compound is selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium bifluoride, quaternary ammonium fluorides, and combinations thereof;

the water soluble polymer comprises a group selected from the group consisting of sulfonic acid group, acrylic acid group, and combinations thereof; and the water soluble copolymer comprises monomers having a group selected from the group consisting of sulfonic acid group, acrylic acid group, and combinations thereof;

the corrosion inhibitor is selected from the group consisting of oligomer or polymer comprising of ethyleneimine, propyleneimine, polyethyleneimine(PEI), and combinations thereof; wherein molecular weight of the oligomer or polymer ranges from between 500 and 15000;

the biological preservative is selected from the group consisting of tetramethylammonium chloride; tetraethylammonium chloride; tetrapropylammonium chloride; alkylbenzyldimethylammonium chloride; alkylbenzyldimethylammonium hydroxide; sodium chlorite; sodium hypochlorite; isothiazolinone compound selected from the group consisting of methylisothiazolinone, methylchloroisothiazolinone, benzisothiazolinone and combinations thereof; and combinations thereof; and

the pH adjusting agent is selected from the group consisting of inorganic acid nitric acid selected from the group consisting of sulfonic acid, or phosphoric acid; inorganic base selected from the group consisting of ammonia hydroxide, potassium hydroxide or sodium hydroxide; and organic base selected from the group consisting of quaternary ammonium hydroxide, and amine compound.

10. The post CMP cleaning composition of Claim 1, wherein the fluoride compound is ammonium fluoride.

11. The post CMP cleaning composition of Claim 1, wherein the water soluble polymer or copolymer is selected from the group consisting of acrylic acid-acrylamido propane sulfonic acid copolymer, poly(acrylic acid), poly(meth-acrylic acid), poly(2-acrylamido-2-methyl-1-propanesulfonic acid, carboxymethyl cellulose, methyl cellulose, hydroxypropyl methyl cellulose, poly-(1-vinylpyrroliddone-co-2-dimethylaminoethyl methacrylate), poly(sodium 4-styrenesulfonate), poly(ethylene oxide), poly(4-sytrenesulfonic acid), polyacrylamide, poly(acrylamide/acrylic acid) copolymer, and combinations thereof; wherein molecular weight of the water soluble polymer or copolymer ranges from 100 to 10,000,000.

12. The post CMP cleaning composition of Claim 1, wherein the composition has a pH of 2 to 6.

13. The post CMP cleaning composition of Claim 1, wherein the composition is diluted with water 2 to 500 times at point of use.

14. The post CMP cleaning composition of Claim 1, wherein the composition has turbidity less than 2.5NTU.

15. The post CMP cleaning composition of Claim 1, wherein the composition comprises at least one organic acid selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof; the first type surfactant comprising two or more sulfonic acid groups is a diphenyl disulfonic acid or its salt; the second type surfactant comprising a secondary alkane sulfonic acid with C_{12}-C_{17} hydrophobic chain.

16. The post CMP cleaning composition of Claim 1, wherein the composition comprises at least one organic acid selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof; the first type surfactant comprising two or more sulfonic acid groups is a diphenyl disulfonic acid or its salt; the second type surfactant comprising a secondary alkane sulfonic acid with C_{12}-C_{17} hydrophobic chain; and the fluoride compound selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium bifluoride, quaternary ammonium fluorides, and combinations thereof.

17. The post CMP cleaning composition of Claim 1, wherein the composition comprises at least one organic acid selected from the group consisting of oxalic acid, citric acid, malonic acid, and combinations thereof; the first type surfactant comprising two or more sulfonic acid groups is a diphenyl disulfonic acid or its salt; the second type surfactant comprising a secondary alkane sulfonic acid with C_{12}-C_{17} hydrophobic chain; the fluoride compound selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium bifluoride, quaternary ammonium fluorides, and combinations thereof; and the water soluble polymer comprising acrylic acid group or the water soluble copolymer comprising monomers having acrylic acid group.

18. A method of post Chemical Mechanical Planarization (CMP) cleaning semiconductor wafer comprising at least one surface selected from the group consisting of metallic film, dielectric film, and combinations thereof, comprising

providing the semiconductor wafer;

providing a post Chemical Mechanical Planarization (CMP) cleaning composition comprising of:

at least one organic acid or its salts;
at least two surfactants; wherein at least one of the at least two surfactants is a first type surfactant having at least two sulfonic acid groups; and at least one of the at least two surfactants is a second type surfactant which is not the first type surfactant and is selected from the group consisting of non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and combinations thereof; and the second type surfactant increases zeta potential magnitude on surface containing dielectric material,
reduces contact angle on cleaning surfaces, and has a surface tension of < 50 dynes/cm at concentration of 0.01 wt.% in water;
and
water;
optionally at least one selected from the group consisting of
fluoride compound;
water soluble polymer or copolymer;

corrosion inhibitor;

biological preservative; and

pH adjusting agent;

wherein the composition has a pH of between 1 to 7;

and

cleaning the semiconductor wafer using the post CMP cleaning composition;

wherein the metallic film is selected from the group consisting of tungsten, copper, cobalt, ruthenium, aluminum, and combinations thereof.

19. The method of post Chemical Mechanical Planarization (CMP) cleaning of claim 18; where the method removes metallic residues selected from the group consisting of Fe, W, Ti, TiN and combinations thereof from the at least one surface.

20. A system for post Chemical Mechanical Planarization (CMP) cleaning semiconductor wafer comprising at least one surface selected from the group consisting of metallic film, dielectric film, and combinations thereof, comprising

the semiconductor wafer; and

the post Chemical Mechanical Planarization (CMP) cleaning composition of claim 1; and

wherein the at least one surface is in touch with the post CMP cleaning composition and the metallic film is selected from the group consisting of tungsten, copper, cobalt, ruthenium, aluminum, and combinations thereof.