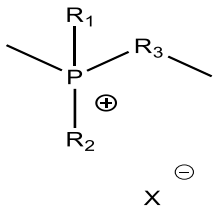
Claims

1. A cationic polymer or copolymer formed by at least one cationic monomer containing at least one phosphonium group, wherein the cationic monomer comprises a structure selected from the group consisting of:

(1)



wherein:

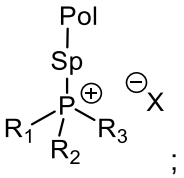
the at least one phosphonium group is in backbone of the cationic polymer or copolymer;

R_1 and R_2 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other;

R_3 is a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic, heteroaromatic, or siloxane moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F^-, Cl^-, Br^-, and I^-; BF_4^-; PF_6^-; carboxylate $RCOO^-$ with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate RSO_3^- with R = H, alkyl or aryl; CF_3COO^-; $CF_3SO_3^-$; nitrate; sulfate; carbonate; and hydrogen carbonate;

(2)



;

wherein:

the at least one phosphonium group is in a side chain or side chains of the cationic polymer or copolymer;

Sp denotes at each occurrence a spacer or a single bond which chemically links the at least one phosphonium group to backbone of the cationic polymer or copolymer; wherein the spacer is a substituted or unsubstituted alkyl chain having 1 to 20, preferably 1 to 10 carbon atoms and is optionally mono- or polysubstituted by F, Cl, Br, I or CN; wherein one or more non-adjacent CH_2 groups each can be independently replaced by -O-, -S-, -NH-, -NR- in a way that no heteroatoms are connected to each other;

Pol denotes backbone of the cationic polymer or copolymer and the backbone type is selected from the group consisting of vinyl, styrene, acrylic or methacrylic, acrylamide, methacrylamide, ethylene glycol, vinyl ether, siloxane, phenol, norbornene type backbone, and combinations thereof;

R_1, R_2, R_3 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

and

anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F-, Cl-, Br-, and I-; BF_4-; PF_6-; carboxylate RCOO- with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate RSO_3^- with R = H, alkyl or aryl; CF_3COO-; CF_3SO_3-; nitrate; sulfate; carbonate; and hydrogen carbonate;

and

(3) combinations of (1) and (2).

2. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is formed with at least one non-ionic monomer in addition to the at least one cationic monomer, and the at least one non-ionic monomer is selected from the group consisting of acrylate or methacrylate type monomer, acrylamide or methacrylamide type monomer, maleimide type monomer, vinyl benzene type monomer, vinyl-type monomer, ethylene glycol type monomer, siloxane type monomer, norbornene type monomer, and combinations thereof.

3. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is a cationic copolymer or a block-copolymer.

4. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer has functional anions selected from bromide, chloride, nitrate, sulfate, phosphate as counter ions.

5. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, and poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide.

6. The cationic polymer or copolymer of Claim 1, wherein polymerization of the cationic polymer or copolymer is selected from the group consisting of free radical polymerization, reversible addition-fragmentation chain-transfer polymerization (RAFT), nitroxide-mediated polymerization (NMP), atomic transfer reaction polymerization (ATRP), ring opening polymerization (ROMP), polycondensation reaction, and combinations thereof.

7. A chemical mechanical planarization composition comprising:
an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;
an activator;
an oxidizing agent;
an additive comprising the cationic polymer or copolymer of any one of claims 1 to 6;
water; and optionally
a corrosion inhibitor;
a dishing reducing agent;
a stabilizer;
a pH adjusting agent.

8. The chemical mechanical planarization composition of Claim 7, wherein the abrasive ranges from 0.05 wt.% to 20 wt.% or 0.01 wt.% to 10 wt.%; the additive comprising the cationic polymer or copolymer ranges from 0.0001 wt.% to 0.025 wt.% or 0.0002wt.% to 0.02 wt.%; the oxidizing agent is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof and the oxidizing agent ranges from 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%; the activator is selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof and the activator ranges from 0.0001 wt.% to 2.0 wt.% or 0.0005 wt.% to 1.0 wt.%: the corrosion inhibitor is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate, and combinations thereof and the corrosion inhibitor ranges from less than 1.0 wt.% or less than 0.25 wt.%; the pH adjusting agent is selected from the group consisting of (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH; the dishing reducing agent is selected from the group consisting of sarcosinate and

related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units; ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds; sulfide; oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; and sulfonic acid polymer; and combinations thereof; and the dishing reducing agent ranges from 0.001 wt.% to 2.0 wt. % or 0.01 wt.% to 1.0 wt. %; and

the stabilizer is selected from the group consisting of adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; phosphoric acid; substituted or unsubstituted phosphonic acids; nitriles; and combinations thereof and the stabilizer ranges from 0.0001 to 5 wt.% or 0.0005 to 1 wt.%.

9. The chemical mechanical planarization composition of Claim 7, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate, malonic acid, hydrogen peroxide, a cationic polymer or copolymer selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide, and combinations thereof; and water; the pH of the composition is between 1 and 7 or 1.5 and 4.

10. A polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing tungsten, comprising the steps of:

a) providing a polishing pad;

b) providing a chemical mechanical planarization composition comprising:

an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;

an activator;

an oxidizing agent;

an additive comprising the cationic polymer or copolymer of any one of claims 1 to 6;

water; and optionally

a corrosion inhibitor;

a dishing reducing agent;

a stabilizer;

a pH adjusting agent; and

c) polishing the at least one surface containing tungsten with the chemical mechanical planarization composition;

wherein the at least one surface containing tungsten comprises a dishing topography of less than 2000 or less than 1000 Angstroms and an erosion topography of less than 2000 or less than 1000 Angstroms.

11. The polishing method of Claim 10, wherein

the abrasive ranges from 0.05 wt.% to 20 wt.% or 0.01 wt.% to 10 wt.%;

the additive comprising the cationic polymer or copolymer ranges from 0.0001 wt.% to 0.025 wt.% or 0.0002wt.% to 0.02 wt.%;

the oxidizing agent is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof and the oxidizing agent ranges from 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%;

the activator is selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and

ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof and the activator ranges from 0.0001 wt.% to 2.0 wt.% or 0.0005 wt.% to 1.0 wt.%:

the corrosion inhibitor is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate~~,~~ and combinations thereof and the corrosion inhibitor ranges from less than 1.0 wt.% or less than 0.25 wt.%;

the pH adjusting agent is selected from the group consisting of (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH;

the dishing reducing agent is selected from the group consisting of sarcosinate and related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units; ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds; sulfide; oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; and sulfonic acid polymer; and combinations thereof; and the dishing reducing agent ranges from 0.001 wt.% to 2.0 wt. % or 0.01 wt.% to 1.0 wt. %; and

the stabilizer is selected from the group consisting of adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; phosphoric acid; substituted or unsubstituted phosphonic acids; nitriles; and combinations thereof and the stabilizer ranges from 0.0001 to 5 wt.% or 0.0005 to 1 wt.%.

12. The polishing method of Claim 10, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; a cationic polymer or copolymer selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide, and combinations thereof; and water; the pH of the composition is between 1 and 7 or 1.5 and 4.

13. A system for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing tungsten, comprising:

a) a polishing pad; and

b) a chemical mechanical planarization composition comprising:

an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;

an activator;

an oxidizing agent;

an additive comprising the cationic polymer or copolymer of any one of claims 1 to 6;

water; and optionally

a corrosion inhibitor;

a dishing reducing agent;

a stabilizer;

a pH adjusting agent; and

wherein the at least one surface containing tungsten is in contact with the polishing pad and the chemical mechanical planarization composition polishing the at least one surface containing tungsten with the chemical mechanical planarization composition and the at least one surface containing tungsten comprises a dishing topography of less than 2000 or less than 1000 Angstroms and an erosion topography of less than 2000 or less than 1000 Angstroms.

14. The system of claim 13, wherein

the abrasive ranges from 0.05 wt.% to 20 wt.% or 0.01 wt.% to 10 wt.%;

the additive comprising the cationic polymer or copolymer ranges from 0.0001 wt.% to 0.025 wt.% or 0.0002wt.% to 0.02 wt.%;

the oxidizing agent is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof and the oxidizing agent ranges from 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%;

the activator is selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof and the activator ranges from 0.0001 wt.% to 2.0 wt.% or 0.0005 wt.% to 1.0 wt.%:

the corrosion inhibitor is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate~~,~~ and combinations thereof and the corrosion inhibitor ranges from less than 1.0 wt.% or less than 0.25 wt.%;

the pH adjusting agent is selected from the group consisting of (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH;

the dishing reducing agent is selected from the group consisting of sarcosinate and

related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units; ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds; sulfide; oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; and sulfonic acid polymer; and combinations thereof; and the dishing reducing agent ranges from 0.001 wt.% to 2.0 wt. % or 0.01 wt.% to 1.0 wt. %; and
the stabilizer is selected from the group consisting of adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; phosphoric acid; substituted or unsubstituted phosphonic acids; nitriles; and combinations thereof and the stabilizer ranges from 0.0001 to 5 wt.% or 0.0005 to 1 wt.%.

15. The system of claim 13, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; a cationic polymer or copolymer selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide, and combinations thereof; and water; the pH of the composition is between 1 and 7 or 1.5 and 4.

16. The chemical mechanical planarization composition of Claim 7, wherein the additive comprising cationic polymer or copolymer is formed with at least one non-ionic monomer in addition to the at least one cationic monomer, and the at least one non-ionic monomer is selected from the group consisting of acrylate or methacrylate type monomer, acrylamide or methacrylamide type monomer, maleimide type monomer, vinyl benzene type monomer, vinyl-type monomer, ethylene glycol type monomer, siloxane type monomer, norbornene type monomer, and combinations thereof.

17. The chemical mechanical planarization composition of Claim 7, wherein the additive comprising cationic polymer or copolymer has functional anions selected from bromide, chloride, nitrate, sulfate, phosphate as counter ions.

18. The polishing method of Claim 10, wherein the additive comprising cationic polymer or copolymer is formed with at least one non-ionic monomer in addition to the at least one cationic monomer, and the at least one non-ionic monomer is selected from the group consisting of acrylate or methacrylate type monomer, acrylamide or methacrylamide type monomer, maleimide type monomer, vinyl benzene type monomer, vinyl-type monomer, ethylene glycol type monomer, siloxane type monomer, norbornene type monomer, and combinations thereof.

19. The polishing method of Claim 10, wherein the additive comprising cationic polymer or copolymer has functional anions selected from bromide, chloride, nitrate, sulfate, phosphate as counter ions.

20. The system of claim 13, wherein the additive comprising cationic polymer or copolymer is formed with at least one non-ionic monomer in addition to the at least one cationic monomer, and the at least one non-ionic monomer is selected from the group consisting of acrylate or methacrylate type monomer, acrylamide or methacrylamide type monomer, maleimide type monomer, vinyl benzene type monomer, vinyl-type monomer, ethylene glycol type monomer, siloxane type monomer, norbornene type monomer, and combinations thereof.

21. The system of claim 13, wherein the additive comprising cationic polymer or copolymer has functional anions selected from bromide, chloride, nitrate, sulfate, phosphate as counter ions.