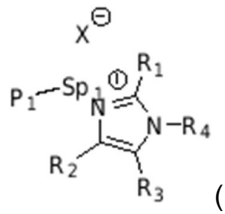
Claims

1. A polycationic polymer or copolymer formed by at least one first cationic monomer and at least one second cationic monomer;

wherein

the at least one first cationic monomer comprises a structure of (I):



(I);

wherein:

P_1 denotes a polymerizable group;

Sp_1 denotes a spacer group or a single bond;

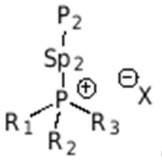
R_1, R_2, R_3 are each independently H; or substituted or unsubstituted aliphatic, aromatic, heteroaromatic or siloxane moieties wherein CH_2 not in the aromatic or heteroaromatic ring may be replaced by O, S or N in a way that no heteroatoms are connected to each other; and wherein hydrogen may be replaced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

R_4 is a substituted or unsubstituted linear, cyclic or branched aliphatic group;

X^- denotes an anionic counterion;

and

the at least one second cationic monomer comprises a structure of (II):



(II);

wherein:

P_2 denotes a polymerizable group;

Sp_2 denotes a spacer group or a single bond and can be selected from the group consisting of linear, branched and cyclic alkyl group; wherein CH2 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, hydrogen can be replaced by F, Cl or CN;

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

X^- denotes an anionic counterion.

2. The polycationic polymer or copolymer of claim 1, wherein at least one of the polymerizable groups P_1 and P_2 is selected from groups containing C=C double bonds.

3. The polycationic polymer or copolymer according to any one of claims 1 to 2, wherein the anionic counterions in (I) and (II) can be the same or different and each is selected from the group consisting of F-, Cl-, Br-, I-, BF_4-, PF_6-, carboxylate, malonate, citrate, carbonate, fumarate, $MeOSO_3$-, $MeSO_3$-, CF_3COO-, CF_3SO_3-, nitrate, and sulfate.

4. The polycationic polymer or copolymer according to any one of claims 1 to 3, wherein the at least one first cationic monomer comprises a cross linkable structure comprising R_5, wherein R_5 is selected from formula (a):

$$—Sp_3\text{-}P_3$$

(a)

wherein:

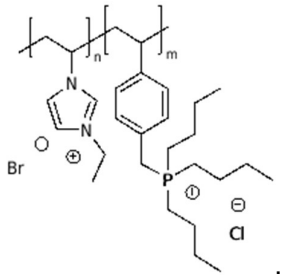
Sp_3 denotes at each occurrence a spacer group or a single bond and can be selected from the group consisting of linear, branched and cyclic alkyl group; wherein CH2 can be replaced by O, S or N in a way that no heteroatoms are connected to each other, hydrogen can be replaced by F, Cl or CN; and

P_3 is a polymerizable group which can be the same or different from P_1.

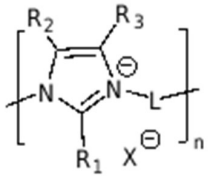
5. The polycationic polymer or copolymer according to any one of claims 1 to 4, wherein the polycationic polymer or copolymer is formed by a polymerization method selected from the group consisting of free radical polymerization, reversible addition-fragmentation chain-transfer polymerization (RAFT),

nitroxide-mediated polymerization (NMP), atomic transfer reaction polymerization (ATRP), ring opening polymerization (ROMP) and polycondensation reaction.

6. The polycationic polymer or copolymer according to any one of claims 1 to 5, wherein the polycationic polymer or copolymer is poly(vinyl-3-ethyl-1H-imidazol-3-ium-co-tributyl-(4-vinylbenzyl)-phosphonium) bromide chloride



7. A polycationic polymer or copolymer has at least one repeating unit of (A) and at least one repeating unit of (B):



(A)

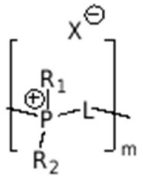
wherein:

L denotes at each occurrence a spacer group or a single bond;

R_1, R_2 and R_3 are each independently H or substituted or unsubstituted aliphatic, aromatic, heteroaromatic or siloxane moieties;

n is an integer from 1 to 500; and

X^- denotes an anionic counterion;



(B)

wherein

L denotes at each occurrence a spacer group or a single bond;

R_1, R_2 are each substituted or unsubstituted aliphatic, aromatic, heteroaromatic moieties;

m is an integer from 1 to 500; and

X^- denotes an anionic counterion.

8. The polycationic polymer or copolymer of claim 7, wherein the spacer group L is selected from substituted or unsubstituted, linear, cyclic or branched aliphatic groups; wherein CH_2 may be replaced by O, S or N in a way that no heteroatoms are connected to each other and wherein hydrogen may be replaced by F, Cl or CN.

9. The polycationic polymer or copolymer according to any one of claims 7 to 8, wherein the polycationic polymer or copolymer is formed by a polymerization method 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) and polycondensation reaction.

10. A chemical mechanical planarization composition comprising polycationic polymer or copolymer according to any one of claims 1-9.

11. A chemical mechanical planarization composition comprising :

0.01 wt.% to 30 wt.% or 0.01 wt.% to 10 wt.% of 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;

0.00001 wt.% to 5.0 wt.%, or 0.0005 wt.% to 1.0 wt.% of an activator;

0.01 wt.% to 30 wt.% , or 0.5 wt.% to 10 wt.% of an oxidizing agent;

0.00001 wt.% to 1.0 wt.%, or 0.00025 wt.% to 0.1 wt.% of an additive comprising the polycationic polymer or copolymer according to any one of claims 1 to 9;

water; and optionally at least one of

less than 1.0 wt.%, or less than 0.5 wt.% of a corrosion inhibitor;

0.001 wt.% to 2.0 wt. %, or 0.01 wt.% to 1.0 wt. % of a dishing reducing agent;
0.0001 to 5 wt.%, or 0.0005 to 1 wt.% of a stabilizer;
a pH adjusting agent; and
pH of the chemical mechanical planarization composition is between 1 and 14, or 1.5 and 4.

12. The chemical mechanical planarization composition of Claim 11, wherein 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;
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, and ammonium peroxymonosulfate; and non-peroxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof; 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 such as 1,3,5-Tris(2-hydroxyethyl), and combinations thereof;
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, such as polyethylene oxide (PEO); 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;

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 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.

13. The chemical mechanical planarization composition of Claim 11, wherein the chemical mechanical planarization composition comprises silica particles; poly(vinyl-3-ethyl-1H-imidazol-3-ium-co-tributyl-(4-vinylbenzyl)-phosphonium) bromide chloride, iron (III) nitrate, malonic acid, hydrogen peroxide, and water; the pH of the composition is between 1.5 and 4.

14. 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:

0.01 wt.% to 30 wt.% or 0.01 wt.% to 10 wt.% of 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;

0.00001 wt.% to 5.0 wt.%, or 0.0005 wt.% to 1.0 wt.% of an activator;

0.01 wt.% to 30 wt.%, or 0.5 wt.% to 10 wt.% of an oxidizing agent;

0.00001 wt.% to 1.0 wt.%, or 0.00025 wt.% to 0.1 wt.% of an additive comprising the polycationic polymer or copolymer according to any one of claims 1 to 9;

water; and optionally at least one of

less than 1.0 wt.%, or less than 0.5 wt.% of a corrosion inhibitor;
0.001 wt.% to 2.0 wt. %, or 0.01 wt.% to 1.0 wt. % of a dishing reducing agent;
0.0001 to 5 wt.%, or 0.0005 to 1 wt.% of a stabilizer;
a pH adjusting agent; and
pH of the chemical mechanical planarization composition is between 1 and 14, or 1.5 and 4;
and

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

15. The polishing method of Claim 14, wherein
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;
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, and ammonium peroxymonosulfate; and non-peroxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof;
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 such as 1,3,5-Tris(2-hydroxyethyl), and combinations thereof;
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, such as polyethylene oxide (PEO); 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;

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 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.

16. The polishing method of Claim 14, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; poly(vinyl-3-ethyl-1H-imidazol-3-ium-co-tributyl-(4-vinylbenzyl)-phosphonium) bromide chloride, and water; the pH of the composition is between 1.5 and 4.

17. The polishing method of Claim 14, wherein 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.

18. 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 polishing composition comprising:

0.01 wt.% to 30 wt.% or 0.01 wt.% to 10 wt.% of 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;

0.00001 wt.% to 5.0 wt.%, or 0.0005 wt.% to 1.0 wt.% of an activator;

0.01 wt.% to 30 wt.% , or 0.5 wt.% to 10 wt.% of an oxidizing agent;

0.00001 wt.% to 1.0 wt.%, or 0.00025 wt.% to 0.1 wt.% of an additive comprising the cationic polymer or copolymer according to any one of claims 1 to 9;

water; and optionally at least one of

less than 1.0 wt.%, or less than 0.5 wt.% of a corrosion inhibitor;

0.001 wt.% to 2.0 wt. %, or 0.01 wt.% to 1.0 wt. % of a dishing reducing agent;

0.0001 to 5 wt.%, or 0.0005 to 1 wt.% of a stabilizer;

a pH adjusting agent; and

pH of the chemical mechanical planarization composition is between 1 and 14, or 1.5 and 4; and

wherein the at least one surface containing tungsten is in contact with the polishing pad and the chemical mechanical planarization composition, thereby polishing the at least one surface containing tungsten with the chemical mechanical planarization composition.

19. The system of Claim 18, wherein

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;

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, and ammonium peroxymonosulfate; and non-peroxy compound selected from the group

consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof;
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 such as 1,3,5-Tris(2-hydroxyethyl), and combinations thereof;
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, such as polyethylene oxide (PEO); 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;
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 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.

20. The system of Claim 18, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; poly(vinyl-3-ethyl-1H-imidazol-3-ium-co-tributyl-(4-vinylbenzyl)-phosphonium) bromide chloride, and water; the pH of the composition is between 1.5 and 4.

21. A chemical mechanical planarization composition comprising polycationic polymer or copolymer according to Claim 7.