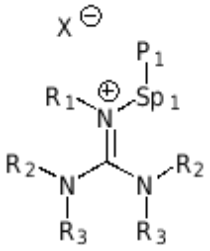
Claims

1. A guanidinium-based polymer or copolymer comprising more than one monomers containing at least one guanidinium group having a structure of:



wherein:

P_1 denotes a polymerizable group and is selected from the group consisting of styrene (or vinyl benzene), acrylate or methacrylate, vinyl ether, allyl ether, acrylamide or methacrylamide, ethylene oxide, propylene oxide, maleimides, siloxane, norbornene, a group containing C=C double bonds, and combinations thereof;

Sp_1 denotes a spacer group; preferably Sp_1 has a substituted or unsubstituted aliphatic moiety with a single bond at two terminal ends thereof;

R_1 is H, or a substituted or unsubstituted aliphatic moiety wherein CH_2 may be replaced by O, S or N in a way that no heteroatoms are connected to each other;

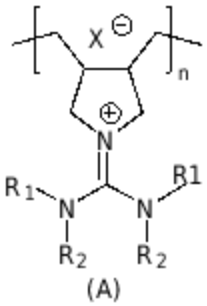
R_2 is H, or a substituted or unsubstituted aliphatic moiety; preferably R_2 is H, CH_3, or CH_2-CH_3;

R_3 is H, or a substituted or unsubstituted aliphatic moiety; wherein two R_3 groups can form a bridge between the nitrogen atoms building a five-, six- or seven-membered ring;

X^- denotes an anionic counterion and is selected from the group consisting of halide (F-, Cl-, Br-, or I-), BF_4-, PF_6-, carboxylate, malonate, citrate, carbonate, fumarate, $MeOSO_3$-, $MeSO_3$-, CF_3COO-, CF_3SO_3-, nitrate, and sulfate, wherein Me is methyl; and

the guanidinium-based polymer or copolymer is water soluble.

2. A guanidinium-based polymer or copolymer comprising more than one repeating unit having a structure (A):



(A)

wherein:

n denotes the number of the repeating units, and 1 <n< 4000, or 75<n< 1000;

R_1 is H, or a substituted or unsubstituted aliphatic moiety;

R_2 is H, or a substituted or unsubstituted aliphatic moiety; wherein two R_2 groups can form a bridge between the nitrogen atoms building a five-, six- or seven-membered ring;

X^- denotes an anionic counterion and is selected from the group consisting of halide (F-, Cl-, Br-, or I-), BF_4-, PF_6-, carboxylate, malonate, citrate, carbonate, fumarate, $MeOSO_3$-, $MeSO_3$-, CF_3COO-, CF_3SO_3-, nitrate, and sulfate, wherein Me is methyl;

and

the guanidinium-based polymer or copolymer is water soluble.

3. The guanidinium-based polymer or copolymer according to claim 1 or 2, wherein the guanidinium-based polymer or copolymer is selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide); poly(N-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride); and poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide); and 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.

4. A chemical mechanical planarization composition comprising the guanidinium-based polymer or copolymer according to any one of claims 1 to 3.

5. The chemical mechanical planarization composition of claim 4 further comprises at least one of:

an abrasive;
water;
an activator;
an oxidizing agent;
a corrosion inhibitor;
a dishing reducing agent;
a stabilizer; and
a pH adjusting agent.

6. The chemical mechanical planarization composition of claim 5, wherein the abrasive is selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, surface modified abrasive particles, and combinations thereof; and the abrasive ranges from 0.01 wt.% to 30 wt.%, or from 0.1 wt.% to 2 wt.%.

7. The chemical mechanical planarization composition according to claim 5 or 6, wherein the guanidinium-based polymer or copolymer is selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide); poly(N-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride); and poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide); and ranges from 0.00001 wt.% to 1.0 wt.%; or 0.0002 wt.% to 0.1 wt.%.

8. The chemical mechanical planarization composition according to any one of claims 5 to 7, 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, and 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, and 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, $KClO_4$, $KBrO_4$, and $KMnO_4$; 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.

9. The chemical mechanical planarization composition according to any one of claims 5 to 8, wherein the chemical mechanical planarization composition comprises silica particles or surface modified silica particles; the guanidinium-based polymer or copolymer selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide), poly(N-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride), poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide), and combinations thereof; iron (III) nitrate; malonic acid; hydrogen peroxide; and water; the pH of the composition is between 1 and 14 or 1 and 7.

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;
        the guanidinium-based polymer or copolymer according to any one of claims 1 to 3;
        water; and optionally at least one of
        an activator;
        an oxidizing agent;
        a corrosion inhibitor;
        a dishing reducing agent;
        a stabilizer; and
        a pH adjusting agent; and
    c) polishing the at least one surface containing tungsten with the chemical mechanical planarization composition.

11. The polishing method of claim 10, wherein the abrasive is 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; and the abrasive ranges from 0.01 wt.% to 30 wt.%, or from 0.1 wt.% to 2 wt.%; and the guanidinium-based polymer or copolymer is selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-*N*-(bis(dimethylamino)methylene-

N-methylpropan-1-aminium bromide); poly(*N*-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride); and poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide); and the guanidinium-based polymer or copolymer ranges from 0.00001 wt.% to 1.0 wt.%; or 0.0002 wt.% to 0.1 wt.%.

12. The polishing method according to claim 10 or 11, wherein the chemical mechanical planarization composition comprises silica particles or surface modified silica particles; the guanidinium-based polymer or copolymer selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide), poly(*N*-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride), poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide), and combinations thereof; iron (III) nitrate; malonic acid; hydrogen peroxide; 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;
        the guanidinium-based polymer or copolymer according to any one of claims 1 to 3;
        water; and optionally at least one of
        an activator;
        an oxidizing agent;
        a corrosion inhibitor;
        a dishing reducing agent;
        a stabilizer; and
        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.

14. The system of claim 13, wherein the chemical mechanical planarization composition has the 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; and ranging from 0.01 wt.% to 30 wt.%, or from 0.1 wt.% to 2 wt.%; and the guanidinium-based polymer or copolymer is selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-*N*-(bis(dimethylamino)methylene-*N*-methylpropan-1-aminium bromide); poly(*N*-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride); and poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide); and the guanidinium-based polymer or copolymer ranges from 0.00001 wt.% to 1.0 wt.%; or 0.0002 wt.% to 0.1 wt.%.

15. The system according to claim 13 or 14, wherein the chemical mechanical planarization composition comprises silica particles or surface modified silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; the guanidinium-based polymer or copolymer selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide), poly(*N*-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride), poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide), and combinations thereof; and water; the pH of the composition is between 1 and 7 or 1.5 and 4.

16. The guanidinium-based polymer or copolymer according to claim 2, wherein the guanidinium-based polymer or copolymer is selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide); poly(N-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride); and poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide); and 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.

17. A chemical mechanical planarization composition comprising the guanidinium-based polymer or copolymer according to claim 2.

18. The chemical mechanical planarization composition of claim 17, wherein the chemical mechanical planarization composition further comprises at least one of:

an abrasive ;
water;
an activator;
an oxidizing agent;
a corrosion inhibitor;
a dishing reducing agent;
a stabilizer; and
a pH adjusting agent;
and
the chemical mechanical planarization composition has a pH of 1 and 7 or 1.5 and 4.

19. The chemical mechanical planarization composition of claim 5, wherein the chemical mechanical planarization composition comprises silica particles or surface modified silica particles; the guanidinium-based polymer or copolymer selected from the group consisting of poly(vinylbenzyl-*N*-(bis(dimethylamino)methylene-*N*-methyl)methanaminium chloride), poly(3-acrylamido-N-(bis(dimethylamino)methylene-N-methylpropan-1-aminium bromide), poly(N-(1,3-dimethylimidazolidin-2-ylidene)-*N*-methyl-1-(4-vinylphenyl)methanaminium chloride), poly(1-(bis(dimethylamino)methylene)-3,4-ethylenepyrrolidin-1-ium bromide), and combinations thereof; and water; the pH of the composition is between 1 and 7 or 1.5 and 4.

20. The chemical mechanical planarization composition according to claim 9, wherein the pH of the composition is between 1.5 and 4.