CLAIMS

1. A composition for selectively removing titanium nitride (TiN or TiNxOy; where x = 0 to 1.3 and y = 0 to 2) from a semiconductor device comprising TiN or TiNxOy and a second material selected from the group consisting of Cu, W, low-k dielectric material, and combinations thereof, the composition comprising:

a weakly coordinating anion having negative charge highly dispersed throughout its structure selected from the group consisting of hexafluorosilicate (SiF_6^{2-}), hexafluorotitanate (TiF_6^{2-}), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), and combinations thereof;

an amine salt buffer;

a non-oxidizing trace metal ion selected from the group consisting of Fe(II) ion~~,~~ with Cu(I) ion, Fe (II) ion with Cu(II) ion, and combinations thereof;

a non-stoichiometric non-ambient trace oxidizer selected from the group consisting of Fe(III) compounds, Ce(IV), Vanadium (V), Mn (V, VI or VII) compounds, Cr (V or VI) compounds, Cl (I, III or V) compounds, Br (I or III) compounds, and combinations thereof; and

the remaining being solvent selected from the group consisting of water, sulfolane, dimethyl sulfide, lactic acid, glycol, and mixtures thereof;

wherein

the composition is hydrogen peroxide-free;

the composition is exposed to air;

the composition has a pH < 4; and

the composition offers a removal selectivity of TiN or TiNxOy vs. the second material > 1:1.

2. The composition of Claim 1, wherein the weakly coordinating anion is present in a range of 1 to 10 wt% ~~and is selected from the group consisting of: p-toluenesulfonate ($C_7H_8SO_3^-$), sulfate (SO_4^{2-}), nitrate(NO_3^-), triflate($CF_3SO_3^-$), fluorosulfate, perfluorosulfonates ($R_fSO_3^-$; where R_f is a perfluoroalkylgroup from C1 to C4), perfluorosulfonimides; ($(R_f)_2NSO_2^-$; where R_f is a perfluoroalkylgroup from C1 to C4), hexafluorosilicate(SiF_6^{2-}), hexafluorotitanate (TiF_6^{2-}), tetrafluoroborate(BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), perfluoroalkylaluminates($(R_fO)_4Al^-$, R_f is a perfluoroalkyl group), and combinations thereof~~.

3. The composition of Claim 1, wherein the amine salt buffer is present in a range of 0.5 to 10 wt% and is selected from the group consisting of:
ammonium chloride; ammonium bisulfate; ammonium phosphates; ammonium oxalate; ammonium perfluorosulfonates; ammonium tetrafluoroborate; ammonium hexafluorotitanate; ammonium hexafluorosilicate; ammonium salts of organic acid selected from ammonium citrate, ammonium acetate, ammonium lactate; and combinations thereof;
wherein the ammonium having a form of $N(R^1R^2R^3R^4)^+$;
wherein R^1, R^2, R^3, R^4 is independently selected from the group consisting of H, CH_3, C_2H_5, and C_3H_7.

4. The composition of Claim 1, wherein the non-oxidizing trace metal ion is present at <500 ppm~~, and is selected from the group consisting of: Fe(II) ion, Cu(I) ion, Cu(II) ion and combinations thereof~~.

5. The composition of Claim 1, wherein the non-stoichiometric non-ambient trace oxidizer is present in a range of 5-200 ppm~~, and is selected from the group consisting of Fe(III) compounds, Ce(IV), Vanadium (V), Mn(V,VI or VII) compounds, Cr(V or VI) compounds, Cl(I, III or V) compounds, Br(I or III) compounds, and combinations thereof~~.

6. The composition of Claim 1 further comprises < 4000ppm solvolyzing bifluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluorides aqueous hydrogen fluoride, and combinations thereof.

7. The composition of Claim 1 further comprises < 10000 ppm corrosion inhibitor selected from the group consisting of benzotriazole and substituated benzotriazole, polyethyleneimine, catechol, cysteine and cystine derivative, glycine, thiourea and thiobiuret, siloxane, aluminum chloride, aluminum fluoride, imidazole, triazole， boric acid, and combinations thereof.

8. The composition of Claim 1, wherein the removal selectivity of TiN or TiNxOy vs. the second material is > 10:1 .

9. The composition of Claim 1, wherein the weakly coordinating anion is hexafluorosilicate, the amine salt buffer is ammonium chloride; the non-oxidizing trace metal ion is $Cu(II)Cl_2$; the non-ambient trace oxidizer is non-stoichiometric $Fe(III)Cl_3$, and the removal selectivity of TiN or TiNxOy vs. the second material is > 10:1 .

10. The composition of Claim 9 further comprises ammonium bifluoride and polyethyleneimine.

11. A system for selectively removing titanium nitride (TiN or TiNxOy, where x = 0 to 1.3 and y = 0 to 2) from a surface of a microelectronic device, comprising:

the semiconductor device comprising TiN or TiNxOy and a second material selected from Cu, W, low-k dielectric material and combinations thereof,

a composition for selectively removing the TiN or TiNxOy from the semiconductor device comprising:

a weakly coordinating anion having negative charge highly dispersed throughout its structure selected from the group consisting of hexafluorosilicate (SiF_6^{2-}), hexafluorotitanate (TiF_6^{2-}), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), and combinations thereof;

an amine salt buffer;

a non-oxidizing trace metal ion selected from the group consisting of Fe(II) ion, with Cu(I) ion, Fe(II) ion with Cu(II) ion, and combination thereof;

a non-stoichiometric non-ambient trace oxidizer selected from the group consisting of Fe(III) compounds, Ce(IV), Vanadium (V), Mn (V, VI or VII) compounds, Cr (V or VI) compounds, Cl (I, III or V) compounds, Br (I or III) compounds, and combinations thereof; and

the remaining being solvent selected from the group consisting of water, sulfolane, dimethyl sulfide, lactic acid, glycol, and mixtures thereof;

wherein

the composition is hydrogen peroxide-free;

the composition is exposed to air;

the composition has a pH < 4; and

the composition offers a removal selectivity of TiN or TiNxOy vs. the second material > 1:1;

and

wherein TiN or TiNxOy is in direct contact with the composition and the TiN or TiNxOy is not in direct in contact with W if the second material is W.

12. The system of Claim 11, wherein the weakly coordinating anion is present in a range of 1 to 10 wt% ~~and is selected from the group consisting of: p-toluenesulfonate ($C_7H_8SO_3^-$), sulfate (SO_4^{2-}), nitrate(NO_3^-), triflate($CF_3SO_3^-$), fluorosulfate, perfluorosulfonates ($R_fSO_3^-$; where R_f is a perfluoroalkylgroup from C1 to C4), perfluorosulfonimides; ($(R_f)_2NSO_2^-$; where R_f is a perfluoroalkylgroup from C1 to C4), hexafluorosilicate(SiF_6^{2-}), hexafluorotitanate (TiF_6^{2-}), tetrafluoroborate(BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), perfluoroalkylaluminates($(R_fO)_4Al^-$, R_f is a perfluoroalkyl group), and combinations thereof~~.

13. The system of Claim 11, wherein the amine salt buffer is present in a range of 0.5 – 10 wt% and is selected from the group consisting of:

ammonium chloride; ammonium bisulfate; ammonium phosphates; ammonium oxalate; ammonium perfluorosulfonates; ammonium tetrafluoroborate; ammonium hexafluorotitanate; ammonium hexafluorosilicate; ammonium salts of organic acid selected from ammonium citrate, ammonium acetate, ammonium lactate; and combinations thereof;

wherein the ammonium having a form of $N(R^1R^2R^3R^4)^+$;

wherein R^1, R^2, R^3, R^4 is independently selected from the group consisting of H, CH_3, C_2H_5, and C_3H_7.

14. The system of Claim 11, wherein the non-oxidizing trace metal ion is in an amount of <500 ppm ~~and is selected from the group consisting of: Fe(II) ion, Cu(I) ion, Cu(II) ion and combinations thereof~~.

15. The system of Claim 11, wherein the non-stoichiometric non-ambient trace oxidizer is present in a range of 5-200 ppm ~~and is selected from the group consisting of Fe(III) compounds, Ce(IV), Vanadium (V), Mn(V,VI or VII) compounds, Cr(V or VI)~~

~~compounds, Cl(I, III or V) compounds, Br(I or III) compounds, and combinations thereof.~~

16. The system of Claim 11, wherein the composition further comprises < 4000ppm of solvolyzing bifluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, and combinations thereof.

17. The system of Claim 11, wherein the composition further comprises < 10000 ppm of a corrosion inhibitor selected from the group consisting of benzotriazole and substituated benzotriazole, polyethyleneimine, catechol, cysteine and cystine derivative, glycine, thiourea and thiobiuret, siloxane, aluminum chloride, aluminum fluoride, imidazole, triazole， boric acid， and combinations thereof.

18. The system of Claim 11, wherein the removal selectivity of TiN or TiNxOy vs. the second material is > 10:1.

19. The system of Claim 11, wherein the weakly coordinating anion is hexafluorosilicate, the amine salt buffer is ammonium chloride; the non-oxidizing trace metal ion is $Cu(II)Cl_2$; the non-ambient trace oxidizer is non-stoichiometric $Fe(III)Cl_3$, and the removal selectivity of TiN or TiNxOy vs. the second material is > 10:1 .

20. The system of Claim 19, wherein the composition further comprises ammonium bifluoride, and polyethyleneimine.

21. A process of selectively removing titanium nitride (TiN or TiNxOy, where x = 0 to 1.3 and y = 0 to 2) comprising:

providing a semiconductor device comprising TiN or TiNxOy and a second material selected from Cu, W, low-k dielectric material;

contacting the semiconductor device with a composition comprising:

a weakly coordinating anion having negative charge highly dispersed throughout its structure selected from the group consisting of hexafluorosilicate (SiF_6^{2-}), hexafluorotitanate (TiF_6^{2-}), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), and combinations thereof;

an amine salt buffer;

a non-oxidizing trace metal ion selected from the group consisting of Fe(II) ion~~,~~ with Cu(I) ion, Fe(II) ion with Cu(II) ion, and combination thereof;

a non-stoichiometric non-ambient trace oxidizer selected from the group consisting of Fe(III) compounds, Ce(IV), Vanadium (V), Mn (V, VI or VII) compounds, Cr (V or VI) compounds, Cl (I, III or V) compounds, Br (I or III) compounds, and combinations thereof; and

the remaining being solvent selected from the group consisting of water, sulfolane, dimethyl sulfide, lactic acid, glycol, and mixtures thereof;

wherein

the composition is hydrogen peroxide-free;

the composition is exposed to air; and

the composition has a pH < 4;

and

selectively removing TiN or TiNxOy ;

wherein TiN or TiNxOy is in direct contact with the composition and the TiN or TiNxOy is not in direct in contact with W if the second material is W; and removal selectivity of TiN or TiNxOy vs. the second material is > 1:1.

22. The process of Claim 21, wherein the weakly coordinating anion is present in a range of 1 to 10 wt% ~~and is selected from the group consisting of: p-toluenesulfonate ($C_7H_8SO_3^-$), sulfate (SO_4^{2-}), nitrate(NO_3^-), triflate($CF_3SO_3^-$), fluorosulfate, perfluorosulfonates ($R_fSO_3^-$; where R_f is a perfluoroalkylgroup from C1 to C4), perfluorosulfonimides; ($(R_f)_2NSO_2^-$; where R_f is a perfluoroalkylgroup from C1 to C4), hexafluorosilicate(SiF_6^{2-}), hexafluorotitanate (TiF_6^{2-}), tetrafluoroborate(BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), perfluoroalkylaluminates($(R_fO)_4Al^-$, R_f is a perfluoroalkyl group), and combinations thereof~~.

23. The process of Claim 21, wherein the amine salt buffer is present in a range of 0.5 – 10 wt% and is selected from the group consisting of: ammonium chloride; ammonium bisulfate; ammonium phosphates; ammonium oxalate; ammonium perfluorosulfonates; ammonium tetrafluoroborate; ammonium hexafluorotitanate; ammonium hexafluorosilicate; ammonium salts of organic acid selected from

ammonium citrate, ammonium acetate, ammonium lactate; and combinations thereof;

wherein the ammonium having a form of $N(R^1R^2R^3R^4)^+$;

wherein R^1, R^2, R^3, R^4 is independently selected from the group consisting of H, CH_3, C_2H_5, and C_3H_7.

24. The process of Claim 21, wherein the non-oxidizing trace metal ion is <500 ppm ~~and is selected from the group consisting of: Fe(II) ion, Cu(I) ion, Cu(II) ion and combinations thereof~~.

25. The process of Claim 21, wherein the non-stoichiometric non-ambient trace oxidizer is present in a range of 5-200 ppm ~~and is selected from the group consisting of Fe(III) compounds, Ce(IV), Vanadium(V), Mn(V,VI or VII) compounds, Cr(V or VI) compounds, Cl(I, III or V) compounds, Br(I or III) compounds, and combinations thereof~~.

26. The process of Claim 21, wherein the composition further comprises < 4000ppm of solvolyzing bifluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluorides, aqueous hydrogen fluoride, and combinations.

27. The process of Claim 21, wherein the composition further comprises < 10000 ppm corrosion inhibitor selected from the group consisting of benzotriazole and substituated benzotriazole, polyethyleneimine, catechol, cysteine and cystine derivative, glycine, thiourea and thiobiuret, siloxane, aluminum chloride, aluminum fluoride, imidazole, triazole， boric acid, and combinations thereof.

28. The process of Claim 21, wherein the removal selectivity of TiN or TiNxOy vs. the second material is > 10:1.

29. The process of Claim 21, wherein the weakly coordinating anion is hexafluorosilicate, the amine salt buffer is ammonium chloride; the non-oxidizing trace metal ion is $Cu(II)Cl_2$; the non-ambient trace oxidizer is non-stoichiometric $Fe(III)Cl_3$, and the removal selectivity of TiN or TiNxOy vs. the second material is > 10:1 .

30. The process of Claim 29, wherein the composition further comprises ammonium bifluoride, and polyethyleneimine.