CLAIMS

1. An aqueous composition for selectively removing titanium nitride (TiN or TiNxOy, where x = 1 to 1.3 and y = 0 to 2) from a semiconductor device comprising Cu, W, low-k dielectric material and the titanium nitride,

comprising:

a weakly coordinating anion having negative charge highly dispersed throughout its structure selected from the group consisting of hexafluorosilicate and hexafluorotitanate or combinations thereof;

an amine salt buffer;

at least two non-oxidizing trace metal ions selected from the group consisting of Fe(II) ion, Cu(I) ion, Cu(II) ion, Ni(II) ion, and combinations thereof and

~~the remaining is solvent selected from the group consisting of water, glycol, propylene glycol, lactic acid, acetic acid, sulfolanes, dimethyl sulfoxide, alkyl sulfone, and combinations thereof;~~

wherein the aqueous composition (1) contains no non-ambient oxidizer; (2) is exposed to air, and (3) the aqueous composition has a pH less than 7.

2. The aqueous composition of Claim 1, wherein the weakly coordinating anion is in the range of 1.0-10.0 wt%~~; and is selected from the group consisting of p-toluenesulfonate ($C_7H_8SO_3^-$); sulfate (SO_4^{2-}); nitrate(NO_3^-); triflate($CF_3SO_3^-$); perfluorosulfonates ($R_fSO_3^-$), in R_f is a perfluoroalkylgroup from C_1 to C_4); perfluorosulfonimides; ($(R_f)_2NSO_2^-$), wherein R_f is a perfluoroalkylgroup from C_1 to C_4); hexafluorosilicate(SiF_6^{2-}); hexafluorotitanate (TiF_6^{2-}); tetrafluoroborate(BF_4^-); hexafluorophosphate (PF_6^-); hexafluoroantimonate (SbF_6^-) ; perfluoroalkylaluminates($(R_fO)_4Al^-$), wherein R_f is a perfluoroalkyl group; and combinations thereof~~.

3. The aqueous composition of Claim 1, wherein the amine salt buffer is in the range of 0.5 – 10.0 wt%; and is selected from the group consisting of ammonium chloride; ammonium bisulfate; ammonium phosphates; ammonium oxalate; ammonium perfluorosulfonates; ammonium tetrafluoroborate; ammonium hexafluorotitanate or ammonium hexafluorosilicate(which may be formed from ammonium hydroxide and hexafluorosilicic acid); and ammonium salts of organic acid selected from the group consisting of ammonium citrate; ammonium acetate; ammonium lactate; and combinations thereof;

wherein the ammonium has a form of $N(R^1R^2R^3R^4)^+$; and each of 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 aqueous composition of Claim 1, wherein each of the at least two non-oxidizing trace metal ions is in the range of <500 ppm; ~~and is independently selected from the group consisting of Fe(II) ion, Cu(I) ion, Cu(II) ion, Co(II) ion, Cr(II) ion, Mn(II) ion, Ni(II) ion, and combinations thereof.~~

5. The aqueous composition of Claim 1 further comprising a corrosion inhibitor in amount of < 2000 ppm; and is selected from the group consisting of benzotriazole and substituted benzotriazole; alkyl amine and alkyl amine including hexyl and octyl amine; polyethyleneimine and polyethyleneimine with carboxylic acids including citric and malonic acid; imidazole; cysteine and substituted cysteine; cystine and substituted cystine; triazole and substituted triazole; iminodiacetic acid; thiourea; benzimidazole; vanillin; catechols; and combinations thereof.

6. The aqueous composition of Claim 1 further comprising bifluoride in amount of < 4000 ppm.

7. The aqueous composition of Claim 1, wherein the pH is < 4.

8. A system for selectively removing titanium nitride (TiN or TiNxOy, where x = 1 to 1.3 and y = 0 to 2) from a microelectronic device, comprising:
the semiconductor device comprising Cu, W, low-k dielectric material and the titanium nitride;
an aqueous composition for selectively removing the titanium nitride from the semiconductor device comprising:
a weakly coordinating anion having negative charge highly dispersed throughout its structure selected from the group consisting of hexafluorosilicate and hexafluorotitanate or combinations thereof;
an amine salt buffer;
at least two non-oxidizing trace metal ions selected from the group consisting of Fe(II) ion, Cu(I) ion, Cu(II) ion, Ni(II) ion, and combinations thereof and
the remaining is solvent selected from the group consisting of water~~, glycol,~~ propylene glycol, lactic acid, acetic acid, sulfolanes, dimethyl sulfoxide, alkyl sulfone, and combinations thereof;
wherein the aqueous composition contains (1) contains no non-ambient oxidizer,(2) is exposed to air, and (3) the aqueous composition has a pH less than 7;

and

the titanium nitride is in direct contact with the aqueous composition but is not in direct in contact with W.

9. The system of Claim 8, wherein the weakly coordinating anion is in the range of 1.0-10.0 wt%; and is selected from the group consisting of p-toluenesulfonate ($C_7H_8SO_3^-$); sulfate (SO_4^{2-}); nitrate(NO_3^-); triflate($CF_3SO_3^-$); perfluorosulfonates ($R_fSO_3^-$), in R_f is a perfluoroalkylgroup from C_1 to C_4); perfluorosulfonimides; ($(R_f)_2NSO_2^-$), wherein R_f is a perfluoroalkylgroup from C_1 to C_4); hexafluorosilicate(SiF_6^{2-}); hexafluorotitanate (TiF_6^{2-}); tetrafluoroborate(BF_4^-); hexafluorophosphate (PF_6^-); hexafluoroantimonate (SbF_6^-) ; perfluoroalkylaluminates($(R_fO)_4Al^-$), wherein R_f is a perfluoroalkyl group; and combinations thereof.

10. The system of Claim 8, wherein the amine salt buffer is in the range of 0.5 – 10.0 wt%; and is selected from the group consisting of ammonium chloride; ammonium bisulfate; ammonium phosphates; ammonium oxalate; ammonium perfluorosulfonates; ammonium tetrafluoroborate; ammonium hexafluorotitanate or ammonium hexafluorosilicate(which may be formed from ammonium hydroxide and hexafluorosilicic acid); and ammonium salts of organic acid selected from the group consisting of ammonium citrate; ammonium acetate; ammonium lactate; and combinations thereof;
wherein the ammonium has a form of $N(R^1R^2R^3R^4)^+$; and each of 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.

11. The system of Claim 8, wherein each of the at least two non-oxidizing trace metal ions is in the range of <500 ppm; and is independently selected from the group consisting of Fe(II) ion, Cu(I) ion, Cu(II) ion, Co(II) ion, Cr(II) ion, Mn(II) ion, Ni(II) ion, and combinations thereof.

12. The system of Claim 8, wherein the aqueous composition further comprising a corrosion inhibitor in amount of < 2000 ppm; and is selected from the group consisting of benzotriazole and substituted benzotriazole; alkyl amine and alkyl amine including hexyl and octyl amine; polyethyleneimine and polyethyleneimine with carboxylic acids including citric and malonic acid; imidazole; cysteine and substituted

cysteine; cystine and substituted cystine; triazole and substituted triazole; iminodiacetic acid; thiourea; benzimidazole; vanillin; catechols; and combinations thereof.

13. The system of Claim 8, wherein the aqueous composition further comprising bifluoride in amount of < 4000ppm.

14. The system of Claim 8, wherein the aqueous composition has a pH < 4.

15. A process of selectively removing titanium nitride (TiN or TiNxOy (where x = 1 to 1.3 and y = 0 to 2) from a microelectronic device comprising Cu, W, low-k dielectric material and the titanium nitride, comprising:

contacting the semiconductor device with an aqueous composition comprising:

a weakly coordinating anion having negative charge highly dispersed throughout its structure selected from the group consisting of hexafluorosilicate and hexafluorotitanate or combinations thereof;

an amine salt buffer;

at least two non-oxidizing trace metal ions selected from the group consisting of Fe(II) ion, Cu(I) ion, Cu(II) ion, Ni(II) ion, and combinations thereof and

~~the remaining is solvent selected from the group consisting of water, glycol, propylene glycol, lactic acid, acetic acid, sulfolanes, dimethyl sulfoxide, alkyl sulfone, and combinations thereof~~;

wherein the aqueous composition contains (1) contains no non-ambient oxidizer,(2) is exposed to air, and (3) the aqueous composition has a pH less than 7;

and

removing the titanium nitride;

wherein the titanium nitride is in direct contact with the aqueous composition and is not in direct in contact with W.

16. The process of Claim 15, wherein the weakly coordinating anion is in the range of 1.0-10.0 wt%~~; and is selected from the group consisting of p-toluenesulfonate ($C_7H_8SO_3^-$); sulfate (SO_4^{2-}); nitrate(NO_3^-); triflate($CF_3SO_3^-$); perfluorosulfonates ($R_fSO_3^-$), in R_f is a perfluoroalkylgroup from C_1 to C_4); perfluorosulfonimides; ($(R_f)_2NSO_2^-$), wherein R_f is a perfluoroalkylgroup from C_1 to C_4); hexafluorosilicate(SiF_6^{2-}); hexafluorotitanate (TiF_6^{2-}); tetrafluoroborate(BF_4^-); hexafluorophosphate (PF_6^-); hexafluoroantimonate (SbF_6^-); perfluoroalkylaluminates($(R_fO)_4Al^-$), wherein R_f is a perfluoroalkyl group; and combinations thereof~~.

17. The process of Claim 15, wherein the amine salt buffer is in the range of 0.5 – 10.0 wt%; and is selected from the group consisting of ammonium chloride; ammonium bisulfate; ammonium phosphates; ammonium oxalate; ammonium perfluorosulfonates; ammonium tetrafluoroborate; ammonium hexafluorotitanate or ammonium hexafluorosilicate(which may be formed from ammonium hydroxide and hexafluorosilicic acid); and ammonium salts of organic acid selected from the group consisting of ammonium citrate; ammonium acetate; ammonium lactate; and combinations thereof;
wherein the ammonium has a form of $N(R^1R^2R^3R^4)^+$; and each of 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.

18. The process of Claim 15, wherein each of the at least two non-oxidizing trace metal ions is in the range of <500 ppm; ~~and is independently selected from the group consisting of Fe(II) ion, Cu(I) ion, Cu(II) ion, Co(II) ion, Cr(II) ion, Mn(II) ion, Ni(II) ion, and combinations thereof~~.

19. The process of Claim 15, wherein the aqueous composition further comprising a corrosion inhibitor in amount of < 2000 ppm; and is selected from the group consisting of benzotriazole and substituted benzotriazole; alkyl amine and alkyl amine including hexyl and octyl amine; polyethyleneimine and polyethyleneimine with carboxylic acids including citric and malonic acid; imidazole; cysteine and substituted cysteine; cystine and substituted cystine; triazole and substituted triazole; iminodiacetic acid; thiourea; benzimidazole; vanillin; catechols; and combinations thereof.

20. The process of Claim 15, wherein the aqueous composition further comprising bifluoride in amount of < 4000ppm.

21. The process of Claim 15, wherein the aqueous composition has a pH < 4.