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 titanium nitride and a second material; the composition comprising:

an amine salt buffer selected from the group consisting of ammonium chloride and ammonium bisulfate;

sodium persulfate;

hydrofluoric acid;

and

liquid carrier;
wherein

the composition comprises no hydrogen peroxide;

the composition has a pH < 4;

the second material is selected from the group consisting of Cu, W, aluminum nitride (AlNx with x=0.5 to 1), aluminum oxide(AlOx with x=1 to 1.5), low-k dielectric material, and combinations thereof; 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 amine salt buffer is present in the range of 0.5 to 10 wt%.

3. The composition of Claim 1, wherein the sodium persulfate is present in the range of 0.2 to 3 wt%.

4. The composition of Claim 1, wherein the liquid carrier is water; and the amount of hydrofluoric acid is < 4000ppm.

5. The composition of Claim 1, wherein the composition is a semi-aqueous composition having liquid carrier comprising water and dimethyl sulfone.

6. The composition of Claim 1 further comprising at least one selected from the group consisting of

a weakly coordinating anion is present in the 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($CF_3SO_3^-$), 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; and

a corrosion inhibitor in the range of < 2000 ppm selected from the group consisting of benzotriazole or substituated benzotriazole, polyethyleneimine, catechol, cysteine and cystine derivative, glycine, thiourea and thiobiuret, siloxane, aluminum chloride, aluminum fluoride, imidazole, triazole，boric acid，and combinations thereof.

7. The composition of Claim 1, wherein the pH of the composition is < 3; the composition offers a removal selectivity of TiN or TiNxOy vs. the second material > 5:1.

8. 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,

a composition for selectively removing the TiN or TiNxOy from the semiconductor device according to claim 1, 5, or 6.

9. The system of Claim 8, wherein the composition is a semi-aqueous composition having liquid carrier comprising water and dimethyl sulfone.

10. 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;

contacting the semiconductor device with a composition according to either claim 1, 5, or 6

wherein

the second material is selected from the group consisting of Cu, W, aluminum nitride (AlNx with x=0.5 to 1), aluminum oxide(AlOx with x=1 to 1.5), low-k dielectric material, and combinations thereof; and

TiN or TiNxOy is in direct contact with the composition; and removal selectivity of TiN or TiNxOy vs. the second material is > 1:1.

11. The process of Claim 10, wherein the liquid carrier in the composition is water; and the hydrofluoric acid is present in an amount < 4000ppm.

12. The process of Claim 10, wherein the composition is a semi-aqueous composition having liquid carrier comprising water and dimethyl sulfone.

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 titanium nitride and a second material; the composition comprising:

   an amine salt buffer;

   a non-ambient oxidizer; and

   liquid carrier;
   wherein

   the composition comprises no hydrogen peroxide;

   the composition has a pH < 4;

   the second material is selected from the group consisting of Cu, W, aluminum nitride (AlNx with x=0.5 to 1), aluminum oxide(AlOx with x=1 to 1.5), low-k dielectric material, and combinations thereof; 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 amine salt buffer is present in the range of 0.5 to10 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.

3. The composition of Claim 1, wherein the non-ambient oxidizer is present in the range of 0.2 to 3 wt % and is selected from the group consisting of salt of persulfate selected from the group consisting of sodium persulfate, ammonium persulfate, and

~~combinations thereof; salt of iodate, salt of periodate, Cl(I, III or V) compounds, Br(I,~~ III or V) compounds, and combinations thereof.

4. The composition of Claim 1, wherein the liquid carrier is water; and the composition further comprises < 4000ppm of an acidic fluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, fluorosilicic acid, fluoroboric acid, acid of hydrated fluoroaluminate, and combinations thereof.

5. The composition of Claim 4, wherein the amine salt buffer is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; the non-ambient oxidizer is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof; and the acidic fluoride is selected from the group consisting of ammonium bifluoride, hydrofluoric acid, and combinations thereof.

6. The composition of Claim 1, wherein the composition is a semi-aqueous composition having liquid carrier comprising water and at least one non-water liquid carrier selected from the group consisting of dimethyl sulfone, lactic acid, glycol, a polar aprotic solvent selected from the group consisting of sulfolanes, sulfoxides, nitriles, formamides and pyrrolidones, and combinations thereof; and the composition further comprises < 4000ppm of an acidic fluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, fluorosilicic acid, fluoroboric acid, acid of hydrated fluoroaluminate, and combinations thereof.

7. The composition of Claim 6, wherein the amine salt buffer is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; the non-ambient oxidizer is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof; and the acidic fluoride is selected from the group consisting of ammonium bifluoride, hydrofluoric acid, and combinations thereof.

8. The composition of Claim 1, wherein the composition is a semi-aqueous composition having liquid carrier consisting of water and a polar aprotic solvent selected from the

group consisting of sulfolane, sulfoxide, nitrile, formamide, pyrrolidone, and combinations thereof.

9. The composition of Claim 8, wherein the amine salt buffer is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; and the non-ambient oxidizer is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof.

10. The composition of Claim 1 further comprises at least one selected from the group consisting of

a weakly coordinating anion is present in the 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($CF_3SO_3^-$), 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; and

a corrosion inhibitor in the range of < 2000 ppm selected from the group consisting of benzotriazole or substituated benzotriazole, polyethyleneimine, catechol, cysteine and cystine derivative, glycine, thiourea and thiobiuret, siloxane, aluminum chloride, aluminum fluoride, imidazole, triazole，boric acid，and combinations thereof.

11. The composition of Claim 1, wherein the pH of the composition is < 3; the composition offers a removal selectivity of TiN or TiNxOy vs. the second material > 5:1.

12. 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,

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

0.5 to10 wt% of amine salt buffer 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 $N(R^1R^2R^3R^4)^+$; and 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;

0.2 to 3 wt % non-ambient oxidizer selected from the group consisting of salts of persulfates, salts of iodate, salts of periodate, Cl(I,III or V) compounds, Br(I, III or V) compounds, and combinations thereof; and

liquid carrier;

wherein

the composition comprises no hydrogen peroxide;

the composition has a pH < 4;

the second material is selected from the group consisting of Cu, W, aluminum nitride (AlNx with x=0.5 to 1), aluminum oxide(AlOx with x=1 to 1.5), low-k dielectric material, and combinations thereof; and

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

13. The system of Claim 12, wherein the liquid carrier in the composition is water; and the composition further comprises < 4000ppm of an acidic fluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, fluorosilicic acid, fluoroboric acid, acid of hydrated fluoroaluminate, and combinations thereof.

14. The system of Claim 13, wherein the amine salt buffer is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; the non-ambient oxidizer is selected from the group consisting of ammonium persulfate,

sodium persulfate, and combinations thereof; and the acidic fluoride is selected from the group consisting of ammonium bifluoride, hydrofluoric acid, and combinations thereof.

15. The system of Claim 12, wherein the composition is a semi-aqueous composition having liquid carrier comprising water and at least one non-water liquid carrier selected from the group consisting of dimethyl sulfone, lactic acid, glycol, a polar aprotic solvent selected from the group consisting of sulfolanes, sulfoxides, nitriles, formamides and pyrrolidones, and combinations thereof; and the composition further comprises < 4000ppm of an acidic fluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, fluorosilicic acid, fluoroboric acid, acid of hydrated fluoroaluminate, and combinations thereof.

16. The system of Claim 15, wherein the amine salt buffer in the composition is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; the non-ambient oxidizer in the composition is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof; and the acidic fluoride in the composition is selected from the group consisting of ammonium bifluoride, hydrofluoric acid, and combinations thereof.

17. The system of Claim 12, wherein the composition is a semi-aqueous composition having liquid carrier consisting of water and a polar aprotic solvent selected from the group consisting of sulfolane, sulfoxide, nitrile, formamide, pyrrolidone, and combinations thereof.

18. The system of Claim 17, wherein the amine salt buffer in the composition is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; and the non-ambient oxidizer in the composition is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof.

19. 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;

contacting the semiconductor device with a composition comprising:

0.5 to10 wt% of amine salt buffer 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 $N(R^1R^2R^3R^4)^+$; and 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;

0.2 to 3 wt % non-ambient oxidizer selected from the group consisting of salts of persulfates, salts of iodate, salts of periodate, Cl(I,III or V) compounds, Br(I, III or V) compounds, and combinations thereof; and

liquid carrier;

wherein

the composition comprises no hydrogen peroxide;

the composition has a pH < 4;

and

selectively removing TiN or TiNxOy ;

wherein

the second material is selected from the group consisting of Cu, W, aluminum nitride (AlNx with x=0.5 to 1), aluminum oxide(AlOx with x=1 to 1.5), low-k dielectric material, and combinations thereof; and

TiN or TiNxOy is in direct contact with the composition; and removal selectivity of TiN or TiNxOy vs. the second material is > 1:1.

20. The process of Claim 19, wherein the liquid carrier in the composition is water; and the composition further comprises < 4000ppm of an acidic fluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, fluorosilicic acid, fluoroboric acid, acid of hydrated fluoroaluminate, and combinations thereof.

21. The process of Claim 20, wherein the amine salt buffer is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; the non-ambient oxidizer is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof; and the acidic fluoride is selected from the group consisting of ammonium bifluoride, hydrofluoric acid, and combinations thereof.

22. The process of Claim 19, wherein the composition is a semi-aqueous composition having liquid carrier comprising water and at least one non-water liquid carrier selected from the group consisting of dimethyl sulfone, lactic acid, glycol, a polar aprotic solvent selected from the group consisting of sulfolanes, sulfoxides, nitriles, formamides and pyrrolidones, and combinations thereof; and the composition further comprises < 4000ppm of an acidic fluoride selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, aqueous hydrogen fluoride, fluorosilicic acid, fluoroboric acid, acid of hydrated fluoroaluminate, and combinations thereof.

23. The process of Claim 22, wherein the amine salt buffer in the composition is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; the non-ambient oxidizer in the composition is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof; and the acidic fluoride in the composition is selected from the group consisting of ammonium bifluoride, hydrofluoric acid, and combinations thereof.

24. The process of Claim 19, wherein the composition is a semi-aqueous composition having liquid carrier consisting of water and a polar aprotic solvent

~~selected from the group consisting of sulfolane, sulfoxide, nitrile, formamide,~~ pyrrolidone, and combinations thereof.

25. The process of Claim 24, wherein the amine salt buffer in the composition is selected from the group consisting of ammonium chloride, ammonium bisulfate and combinations thereof; and the non-ambient oxidizer in the composition is selected from the group consisting of ammonium persulfate, sodium persulfate, and combinations thereof.