THE CLAIMS

What is claimed is:

1. A semi-aqueous composition comprising:

at least one oxidizing agent, wherein the oxidizing agent is present in amount ranging from 0.001 wt% to 0.2 wt% and comprises a species selected from the group consisting of periodic acid, iodic acid, vanadium (V) oxide, vanadium (IV,V) oxide, ammonium vanadate 1,4-benzoquinone, dimethyl-1,4-benzoquinone, and combinations thereof,

from 0.1 wt% to 2.5 wt% of at least one etchant,

from 0.001 wt% to about 2 wt% of at least one corrosion inhibitor selected from the group consisting of myristyltrimethylammonium bromide, benzalkonium chloride, hexadecyltrimethylammonium p-toluenesulfonate, hexadecyltrimethylammonium hydroxide, 5-benzyl-lH-tetrazole, and combinations thereof,

from 0.01 wt% to 2 wt% of at least one source of silica selected from the group consisting of methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, tetraethoxysilane (TEOS), N-propyltrimethoxysilane, N-propyltriethoxysilane, hexyltrimethoxysilane, hexyltriethoxysilane, ammonium hexafluororosilicate, sodium silicate, tetramethyl ammonium silicate (TMAS), and combinations thereof,

from 85 wt% to 99 wt% water, and

from 1 wt% to 15 wt% of at least one organic solvent;

said composition substantially devoid of amines, chemical mechanical polishing abrasive materials, and hydrogen peroxide, the composition characterized by a TiN to tungsten selectivity of greater than 40: 1 and a tungsten removal rate less than about 1 Å min^{-1} when tungsten and TiN coupons are immersed in said composition at 50˚C.

2. The composition of claim 1, wherein the etchant comprises a species selected from the group consisting of H_2ZrF_6, H_2TiF_6, HPF_6, HF, ammonium fluoride, ammonium bifluoride, tetrafluoroboric acid, hexafluorosilicic acid, tetrabutylammonium tetrafluoroborate (TBA-BF_4), ammonium hexafluorosilicate, ammonium hexafluorotitanate, tetraalkylammonium fluoride ($NR_1R_2R_3R_4F$), tetraalkylammonium hydroxide ($NR_1R_2R_3R_4OH$), where R_1, R_2, R_3, R_4 may be the same as or different from one another and is selected from the group consisting of straight-chained or branched C_1-C_6 alkyl groups, weak bases, and combinations thereof.

3. The composition of claim 1, wherein the etchant comprises tetrafluoroboric acid, hexafluorosilicic acid, HF, or combinations thereof.

4. The composition of claim 1, further comprising a source of silica, wherein the source of silica comprises at least one species selected from the group consisting of methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, tetraethoxysilane (TEOS), N-propyltrimethoxysilane, N-propyltriethoxysilane, hexyltrimethoxysilane, hexyltriethoxysilane, ammonium hexafluororosilicate, tetramethyl ammonium silicate (TMAS), and combinations thereof.

5. The composition of claim 1, wherein the at least one organic solvent comprises a species selected from the group consisting of methanol, ethanol, isopropanol, butanol, pentanol, hexanol, 2-ethyl-1-hexanol, heptanol, octanol, ethylene glycol, 1,2- and 1,3-propylene glycol, 1,2-, 1,3-, and 1,4-butanediol, tetrahydrofurfuryl alcohol (THFA), butylene carbonate, ethylene carbonate, propylene carbonate, dipropylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, ethylene glycol phenyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether (DPGME), tripropylene glycol methyl ether (TPGME), dipropylene glycol dimethyl ether, dipropylene glycol ethyl ether, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether (DPGPE), tripropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, 2,3-dihydrodecafluoropentane, ethyl perfluorobutylether, methyl perfluorobutylether, alkyl carbonates, alkylene carbonates, 4-methyl-2-pentanol, tetramethylene glycol dimethyl ether, dimethyl sulfoxide, and combinations thereof.

6. The composition of claim 1, wherein the composition further comprises at least one low-k passivating agent selected from the group consisting of boric acid, ammonium pentaborate, sodium tetraborate, 3-hydroxy-2-napthoic acid, malonic acid, and iminodiacetic acid.

7. The composition of claim 1, wherein the composition is further substantially devoid of metal halides, and combinations thereof.

8. The composition of claim 1, wherein the composition has a TiN to tungsten selectivity of greater than 50:1 and a tungsten removal rate less than about 1 Å min^{-1} and a TiN to copper selectivity of greater than 20:1 and a copper removal rate less than about 2 Å min^{-1} at temperatures in a range from about 45ºC to about 60°C.

9. The composition of claim 1, wherein the pH of the composition is in a range from about 0 to about 4.

10. A semi-aqueous composition for selectively removing titanium nitride and/or photoresist etch residue material from the surface of a microelectronic device having same thereon, said composition comprising:

at least one oxidizing agent present in amount ranging from 0.001 wt% to 0.2 wt% and selected from the group consisting of periodic acid, iodic acid, vanadium (V) oxide, vanadium (IV,V) oxide, ammonium vanadate, 1,4-benzoquinone, dimethyl-1 ,4-benzoquinone, and combinations thereof,

from 0.1 wt% to 2.5 wt% of at least one etchant,

from 0.001 wt% to 2 wt% of at least one corrosion inhibitor selected from the group consisting of myristyltrimethylammonium bromide, benzalkonium chloride, hexadecyltrimethylammonium p-toluenesulfonate, hexadecyltrimethylammonium hydroxide, 5-benzyl-lH-tetrazole, and combinations thereof,

from 0.01 wt% to 2 wt% of at least one source of silica selected from the group consisting of methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, tetraethoxysilane (TEOS), N-propyltrimethoxysilane, N-propyltriethoxysilane, hexyltrimethoxysilane, hexyltriethoxysilane, ammonium hexafluororosilicate, sodium silicate, tetramethyl ammonium silicate (TMAS), and combinations thereof,

from 85 wt% to 95 wt% water, and

from 1 wt% to 15 wt% of at least one organic solvent;

wherein the composition is substantially devoid of hydrogen peroxide.

11. A method comprising contacting a surface of a microelectronic device comprising titanium nitride material, copper, tungsten, and low-k dielectric materials with a semi-aqueous composition, comprising:

at least one oxidizing agent present in amount ranging from 0.001 wt% to 0.2 wt% and selected from the group consisting of periodic acid, iodic acid, vanadium (V) oxide, vanadium (IV,V) oxide, ammonium vanadate, 1,4-benzoquinone, dimethyl-1 ,4-benzoquinone, and combinations thereof;

from 0.1 wt% to 2.5 wt% of at least one etchant;

from 0.001 wt% to 2 wt% of at least one corrosion inhibitor selected from the group consisting of myristyltrimethylammonium bromide, benzalkonium chloride, hexadecyltrimethylammonium p-toluenesulfonate, hexadecyltrimethylammonium hydroxide, 5-benzyl-lH-tetrazole, and combinations thereof,

from 0.01 wt% to 2 wt% of at least one source of silica selected from the group consisting of methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, tetraethoxysilane (TEOS), N-propyltrimethoxysilane, N-propyltriethoxysilane, hexyltrimethoxysilane, hexyltriethoxysilane, ammonium hexafluororosilicate, sodium silicate, tetramethyl ammonium silicate (TMAS), and combinations thereof,

from 85 wt% to 95 wt% water, and

from 1 wt% to 15 wt% of at least one organic solvent;

said composition substantially devoid of amines, chemical mechanical polishing abrasive materials, and hydrogen peroxide, the composition characterized by a TiN to tungsten selectivity of greater than 40: 1 and a tungsten removal rate less than about 1 Å min^{-1} when tungsten and TiN coupons are immersed in said composition at 50˚C.

12. The method of claim 11, wherein the contacting comprises time in a range from about 0.3 minute to about 30 minutes at temperature in a range of from about 20ºC to about 100ºC.

13. The method of claim 11, wherein the composition is rinsed from the surface following the desired etching action.

14. The method of claim 11, wherein the composition has a TiN to tungsten selectivity of greater than 40:1 and a tungsten removal rate less than about 1 Å min^{-1} and a TiN to copper selectivity of greater than 20:1 and a copper removal rate less than about 2 Å min^{-1} at temperatures in a range from about 45ºC to about 60°C.