CLAIMS

1. An etching composition suitable for the selective removal of tantalum nitride over titanium nitride from a microelectronic device, which comprises:

from ~~about~~ 40% to ~~about~~ 80% by weight water;

from ~~about~~ 10% to ~~about~~ 50% by weight phosphorous-containing inorganic acid or salt thereof ~~(neat)~~;

from ~~about~~ 0.1% to ~~about~~ 6% by weight fluoride ion source ~~(neat)~~; and

from ~~about~~ 12% to ~~about~~ 35% by weight water-miscible organic solvent,

wherein the fluoride ion source is selected from the group consisting of hydrofluoric acid, ammonium fluoride, quaternary ammonium fluorides, fluoroborates, fluoroboric acid, tetrabutylammonium tetrafluoroborate, aluminum hexafluoride, and a fluoride salt of an aliphatic primary, secondary or tertiary amine having the formula:

$R^1NR^2R^3R^4F$,

wherein R^1, R^2, R^3 and R^4 individually represent H or a C_1-C_4 alkyl group,

wherein the water-miscible solvent is selected from the group consisting of ethylene glycol, propylene glycol, butyl diglycol, 1,4-butanediol, tripropylene glycol methyl ether, propylene glycol propyl ether, diethylene glycol n-butyl ether, hexyloxypropylamine, poly(oxyethylene)diamine, dimethylsulfoxide, tetrahydrofurfuryl alcohol, glycerol, alcohols, sulfoxides, or mixtures thereof, and

wherein said etching solution is substantially free of oxidizing agents.

~~2. The etching composition of claim 1 wherein the water-miscible solvent is selected from the group consisting of ethylene glycol, propylene glycol, butyl diglycol, 1,4-butanediol, tripropylene glycol methyl ether, propylene glycol propyl ether, diethylene glycol n-butyl ether, hexyloxypropylamine, poly(oxyethylene)diamine, dimethylsulfoxide, tetrahydrofurfuryl alcohol, glycerol, alcohols, sulfoxides, or mixtures thereof.~~

~~3~~2. The etching composition of claim 1 wherein the water-miscible solvent is selected from the group consisting of butyl diglycol, glycerol or propylene glycol or mixtures thereof.

~~4. The etching composition of claim 1 wherein the fluoride ion source is selected from the~~

~~group consisting of hydrofluoric acid, ammonium fluoride, quaternary ammonium fluorides such as, for example, fluoroborates, fluoroboric acid, tetrabutylammonium tetrafluoroborate, aluminum hexafluoride, and a fluoride salt of an aliphatic primary, secondary or tertiary amine having the formula:~~

~~$R^1NR^2R^3R^4F$,~~

~~wherein R^1, R^2, R^3 and R^4 individually represent H or a (C_1-C_4) alkyl group.~~

~~5~~3. The etching composition of claim ~~4~~1 wherein the fluoride ion source is selected from the group consisting of ammonium fluoride, ammonium bifluoride, tetramethylammonium fluoride, tetraethylammonium fluoride, methyltriethylammonium fluoride, and tetrabutylammonium fluoride and mixtures thereof.

~~6~~4. The etching composition of claim ~~5~~3 wherein said fluoride ion source comprises ammonium fluoride.

~~7~~5. The etching composition of claim 1 wherein the phosphorous-containing inorganic acid is selected from the group consisting of phosphoric acid (H_3PO_4), hypophosphorus acid (H_3PO_2), phosphorus acid (H_3PO_3), hypophosphoric acid ($H_4P_2O_6$), metaphosphoric acid (HPO_3), peroxophosphoric acid (H_3PO_5), pyrophosphoric acid ($H_4P_2O_7$), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$), trimetaphosphoric acid ($H_3P_3O_9$), and phosphoric anhydride (P_4O_{10}), and salts thereof and mixtures thereof.

~~8~~6. The etching composition of claim 1 wherein the phosphorous-containing inorganic acid comprises phosphoric acid (H_3PO_4).

~~9~~7. The etching composition of claim 1 wherein the composition comprises

from ~~about~~ 50% to ~~about~~ 80% by weight water;

from ~~about~~ 10% to ~~about~~ 30% by weight of said phosphorous-containing inorganic acid or salt thereof ~~(neat)~~; and

from ~~about~~ 0.6% to ~~about~~ 5% by weight fluoride ion source ~~(neat)~~.

~~10~~8. The etching composition of claim 1 wherein the composition comprises

from ~~about~~ 50% to ~~about~~ 70% by weight water;

from ~~about~~ 10% to ~~about~~ 25% by weight of said phosphorous-containing inorganic acid or salt thereof ~~(neat)~~;

from ~~about~~ 1% to ~~about~~ 5% by weight fluoride ion source ~~(neat)~~; and

from ~~about~~ 20% to ~~about~~ 30% by weight water-miscible organic solvent.

~~11~~9. The etching composition of claim 1 wherein the composition comprises

from ~~about~~ 55% to ~~about~~ 65% by weight water;

from ~~about~~ 10% to ~~about~~ 20% by weight of said phosphorous-containing inorganic acid or salt thereof ~~(neat)~~;

from ~~about~~ 1% to ~~about~~ 5% by weight fluoride ion source ~~(neat)~~; and

from ~~about~~ 20% to ~~about~~ 30% by weight water-miscible organic solvent.

~~12~~10. The etching composition of claim 1 wherein the composition provides a tantalum nitride over titanium nitride etch selectivity of at least 5.

~~13~~11. A method of selectively enhancing the etch rate of tantalum nitride relative to titanium nitride on a microelectronic device comprising tantalum nitride and titanium nitride, the method comprising the steps of:

contacting the microelectronic device comprising tantalum nitride and titanium nitride with an etching composition comprising from ~~about~~ 40% to ~~about~~ 80% by weight water; from ~~about~~ 10% to ~~about~~ 50% by weight phosphorous-containing inorganic acid or salt thereof ~~(neat)~~; from ~~about~~ 0.1% to ~~about~~ 6% by weight fluoride ion source ~~(neat)~~; and from ~~about~~ 12% to ~~about~~ 35% by weight water-miscible organic solvent;

wherein the fluoride ion source is selected from the group consisting of hydrofluoric acid, ammonium fluoride, quaternary ammonium fluorides, fluoroborates, fluoroboric acid, tetrabutylammonium tetrafluoroborate, aluminum hexafluoride, and a fluoride salt of an aliphatic primary, secondary or tertiary amine having the formula:

$R^1NR^2R^3R^4F$,

wherein R^1, R^2, R^3 and R^4 individually represent H or a C_1-C_4 alkyl group;

wherein the water-miscible solvent is selected from the group consisting of ethylene glycol, propylene glycol, butyl diglycol, 1,4-butanediol, tripropylene glycol methyl ether, propylene glycol propyl ether, diethylene glycol n-butyl ether, hexyloxypropylamine,

poly(oxyethylene)diamine, dimethylsulfoxide, tetrahydrofurfuryl alcohol, glycerol, alcohols, sulfoxides, or mixtures thereof; and

wherein said etching solution is substantially free of oxidizing agents;

and

rinsing the microelectronic device after the tantalum nitride is at least partially removed, wherein the selectivity of the etch for tantalum nitride over titanium nitride is greater than 3.

~~14~~12. The method of claim ~~13~~11 further comprising the step of drying the microelectronic device.

~~15~~13. The method of claim ~~13~~11 wherein the selectivity of the etch for tantalum nitride over titanium nitride is between ~~about~~ 9 and ~~about~~ 125.

~~16~~14. The method of claim ~~13~~11 wherein the contacting step is performed at a temperature of from ~~about~~ 25 °C. to ~~about~~ 150 °C.

~~17. The method of claim 13 wherein the water-miscible solvent is selected from the group consisting of ethylene glycol, propylene glycol, butyl diglycol, 1,4-butanediol, tripropylene glycol methyl ether, propylene glycol propyl ether, diethylene glycol n-butyl ether, hexyloxypropylamine, poly(oxyethylene)diamine, dimethylsulfoxide, tetrahydrofurfuryl alcohol, glycerol, alcohols, sulfoxides, or mixtures thereof.~~

~~18. The method of claim 13 wherein the fluoride ion source is selected from the group consisting of hydrofluoric acid, ammonium fluoride, quaternary ammonium fluorides such as, for example, fluoroborates, fluoroboric acid, tetrabutylammonium tetrafluoroborate, aluminum hexafluoride, and a fluoride salt of an aliphatic primary, secondary or tertiary amine having the formula:~~

~~$R^1NR^2R^3R^4F$,~~

~~wherein R^1, R^2, R^3 and R^4 individually represent H or a (C_1-C_4) alkyl group.~~

~~19~~15. The method of claim ~~13~~11 wherein the fluoride ion source is selected from the group consisting of ammonium fluoride, ammonium bifluoride, tetramethylammonium fluoride, tetraethylammonium fluoride, methyltriethylammonium fluoride, and tetrabutylammonium fluoride.

~~20~~16. The method of claim ~~13~~11 wherein the phosphorous-containing inorganic acid is selected from the group consisting of hypophosphorus acid (H_3PO_2), phosphorus acid (H_3PO_3), hypophosphoric acid ($H_4P_2O_6$), metaphosphoric acid (HPO_3), peroxophosphoric acid (H_3PO_5), pyrophosphoric acid ($H_4P_2O_7$), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$), trimetaphosphoric acid ($H_3P_3O_9$), and phosphoric anhydride (P_4O_{10}), and salts thereof and mixtures thereof.

~~21~~17. The etching composition of claim 1 wherein the composition is substantially free of hydrogen fluoride.

~~22~~18. The etching composition of claim ~~3~~2 wherein the phosphorous-containing inorganic acid comprises phosphoric acid (H_3PO_4) and wherein said fluoride ion source comprises ammonium fluoride.

~~23~~19. The etching composition of claim 1, wherein the water-miscible solvent is selected from the group consisting of propylene glycol, butyl diglycol, 1,4-butanediol, tripropylene glycol methyl ether, propylene glycol propyl ether, diethylene glycol n-butyl ether, glycerol, or mixtures thereof.

~~24~~20. The etching composition of claim 1, wherein the composition provides a tantalum nitride over titanium nitride etch selectivity of greater than 3.