CLAIMS

1. An etching solution suitable for the selective removal of TiSiN over hafnium oxide from a microelectronic device, which comprises:

water;

about 3.8 wt.% to about 5.6 wt.% of a mixture of ~~at least one~~ alkaline ammonium compounds comprising ~~selected from the group consisting of~~ ammonium hydroxide~~, a quaternary ammonium hydroxide,~~ and about 0.4 wt.% to about 1.2 wt.% of neat ammonium fluoride~~, and a quaternary ammonium fluoride~~;

about 2.0 wt.% to about 8.0 wt.% of neat hydrogen peroxide~~at least one peroxide compound~~;

about 10 wt.% to about 15 wt.% of a water-miscible organic solvent selected from the group consisting of sulfolane, dimethylsulfoxide (DMSO), and propylene glycol;

about 0.4 wt.% to about 0.8 wt.% of pentamethyldiethylenetriamine (PMDETA)~~at least one nitrogen-containing compound selected from the group consisting of a C_{4-12} alkylamine, a polyalkylenimine, and a polyamine~~; and

optionally at least one chelating agent,

wherein "about" corresponds to ±5% of the stated value.

~~2. The etching solution of claim 1 wherein the quaternary ammonium hydroxide compound is selected from the group consisting of tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrabutylammonium hydroxide (TBAH), tetrapropylammonium hydroxide, trimethylethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide, (2-hydroxyethyl)triethylammonium hydroxide, (2-hydroxyethyl)tripropylammonium hydroxide, (1-hydroxypropyl)trimethylammonium hydroxide, ethyltrimethylammonium hydroxide, diethyldimethylammonium hydroxide, choline hydroxide, benzyltrimethylammonium hydroxide, and mixtures thereof.~~

~~3~~2. The etching solution of claim 1 wherein the mixture of ~~at least one~~ alkaline ammonium compounds comprises about 4.1 wt.% of neat ~~includes~~ ammonium hydroxide~~ and ammonium fluoride~~.

43. The etching solution of claim 1 ~~claim 3~~ wherein the water-miscible organic solvent comprises about 10 wt.% ~~is selected from the group consisting~~ of sulfolane, dimethylsulfoxide (DMSO)~~, and~~ or propylene glycol~~; and the at least one peroxide compound is hydrogen peroxide~~.

~~5. The etching solution of claim 4 wherein the at least one nitrogen containing compound is selected from pentamethyldiethylenetriamine (PMDETA), triethylenediamine (TEDA), triethylenetetramine (TETA), tetramethylethylenediamine (TMEDA), and diethylenetriamine (DETA).~~

~~6. The etching solution of claim 4 wherein the at least one nitrogen containing compound is octylamine.~~

~~7. The etching solution of claim 4 wherein the at least one nitrogen containing compound is the polyalkylenimine.~~

~~8. The etching solution of claim 7 wherein the polyalkylenimine is polyethylenimine.~~

~~9. The etching solution of claim 4 wherein the at least one nitrogen containing compound is pentamethyldiethylenetriamine (PMDETA).~~

~~10~~4. The etching solution of any of the preceding claims comprising at least one chelating agent selected from ethylenediaminetetraacetic acid (EDTA), butylenediaminetetraacetic acid, (1,2-cyclohexylenediamine)tetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DETPA), ethylenediaminetetrapropionic acid, (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), N, N,N', N'-ethylenediaminetetra(methylenephosphonic) acid (EDTMP), triethylenetetraminehexaacetic acid (TTHA), 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DHPTA), methyliminodiacetic acid, propylenediaminetetraacetic acid, nitrotriacetic acid (NTA), citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, oxalic acid, phthalic acid, maleic acid, mandelic acid, malonic acid, lactic acid, salicylic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, and cysteine.

~~11~~5. The etching solution of claim ~~10~~4, wherein said at least one chelating agent is ethylenediaminetetraacetic acid (EDTA).

~~12~~6. The etching solution of any of the preceding claims further comprising a surfactant.

~~13~~7. A method for selectively enhancing the etch rate of TiSiN relative to hafnium oxide in a composite semiconductor device comprising TiSiN and hafnium oxide, the method comprising the steps of:

contacting the composite semiconductor device comprising TiSiN and hafnium oxide with an etching solution ~~as set forth in any one of claims 1 to 12~~comprising:

water;

at least one alkaline ammonium compound selected from the group consisting of ammonium hydroxide, a quaternary ammonium hydroxide, ammonium fluoride, and a quaternary ammonium fluoride;

at least one peroxide compound;

a water-miscible organic solvent;

at least one nitrogen containing compound selected from the group consisting of a C_{4-12} alkylamine, a polyalkylenimine, and a polyamine; and

optionally at least one chelating agent

; and

rinsing the composite semiconductor device after the TiSiN is at least partially removed, wherein the selectivity of the etch for TiSiN over hafnium oxide is greater than 30.

~~14~~8. The method of claim ~~13~~ 7 further comprising the step of drying the semiconductor device.

~~15~~9. The method of claims ~~13~~ 7 or ~~14~~ 8 wherein the selectivity of the etch for TiSiN over hafnium oxide is greater than 500.

~~16~~10. The method of claims ~~13~~ 7 or ~~14~~ 8 wherein the selectivity of the etch for TiSiN over hafnium oxide is greater than 1,000.

~~17~~11. The method of any of claims ~~13~~ 7 to ~~16~~ 10 wherein the contacting step is performed at a temperature of about 60°C or greater.

~~18~~12. An etching solution suitable for the selective removal of TiSiN over hafnium oxide from a microelectronic device, comprising:

from about 3.7 wt.% to about 4.5 wt.% neat of at least one alkaline ammonium compound selected from the group consisting of ammonium hydroxide, a quaternary ammonium hydroxide, ammonium fluoride, and a quaternary ammonium fluoride;

from about 3.9 wt.% to about 4.5 wt.% neat of at least one peroxide compound;

from about 10 wt.% to about 15 wt.% of a water-miscible organic solvent;

from about 0.4 wt.% to about 1 wt.% of at least one nitrogen containing compound selected from the group consisting of a C_{4-12} alkylamine, a polyalkylenimine, and a polyamine; and

water;

wherein "about" corresponds to ±5% of the stated value.

~~19~~13. The etching solution of claim ~~18~~ 12 further comprising at least one chelating agent.

~~20~~14. The etching solution of claims ~~18~~ 12 or ~~19~~13, wherein

the at least one alkaline ammonium compound is ammonium hydroxide;

the at least one peroxide compound is hydrogen peroxide;

the water-miscible organic solvent is selected from the group consisting of sulfolane, propylene glycol, and dimethylsulfoxide (DMSO); and

the at least one nitrogen containing compound is selected from the group consisting of octylamine, pentamethyldiethylenetriamine (PMDETA), and polyethylenimine.

~~21~~15. An etching solution suitable for the selective removal of TiSiN over hafnium oxide from a microelectronic device, which comprises:

about 4.2 wt.% of ammonium hydroxide (neat);

about 4.3 wt.% of hydrogen peroxide (neat);

from about 0.4 wt.% to about 1.2 wt.% of ammonium fluoride (neat);

about 10 wt.% of a water-miscible organic solvent;

from about 0.30 wt.% to about 1 wt.% of at least one nitrogen containing compound selected from the group consisting of a C_{4-12} alkylamine, a polyalkylenimine, and a polyamine;

from about 0.30 wt.% to about 1 wt.% at least one chelating agent; and

water;

wherein "about" corresponds to ±5% of the stated value.

~~22~~16. The etching solution of claim ~~21~~15, wherein

the water-miscible organic solvent is selected from the group consisting of sulfolane, propylene glycol, and dimethylsulfoxide (DMSO);

the at least one nitrogen containing compound is selected from the group consisting of octylamine, pentamethyldiethylenetriamine (PMDETA), and polyethylenimine and

the composition comprises at least one chelating agent selected from ethylenediaminetetraacetic acid (EDTA), butylenediaminetetraacetic acid, (1,2-cyclohexylenediamine)tetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DETPA), ethylenediaminetetrapropionic acid, (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), N, N,N', N'-ethylenediaminetetra(methylenephosphonic) acid (EDTMP), triethylenetetraminehexaacetic acid (TTHA), 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DHPTA), methyliminodiacetic acid, propylenediaminetetraacetic acid, nitrotriacetic acid (NTA), citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, oxalic acid, phthalic acid, maleic acid, mandelic acid, malonic acid, lactic acid, salicylic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, and cysteine.

17. The etching solution of claim 15, wherein the etching solution comprises about 0.4 wt. % of neat ammonium fluoride.

18. The etching solution of claim 15, wherein the etching solution comprises about 0.8 wt.% of neat ammonium fluoride.

19. The etching solution of claim 15, wherein the etching solution comprises about 1.2 wt.% of neat ammonium fluoride.

20. The etching solution of claim 15, wherein the at least one nitrogen containing compound comprises pentamethyldiethylenetriamine (PMDETA).

21. The etching solution of claim 15, wherein the water-miscible organic solvent comprises sulfolane.

22. The etching solution of claim 15, wherein the at least one chelating agent comprises ethylenediaminetetraacetic acid (EDTA).

23. The etching solution of claim 15, wherein the etching solution comprises:

about 4.2 wt.% of ammonium hydroxide (neat);

about 4.3 wt.% of hydrogen peroxide (neat);

from about 0.4 wt.% to about 1.2 wt.% of ammonium fluoride (neat);

about 10 wt.% of sulfolane;

from about 0.70 wt.% of pentamethyldiethylenetriamine (PMDETA);

from about 0.60 wt.% ethylenediaminetetraacetic acid (EDTA); and

the balance water.