

CLAIMS

1. An etching composition suitable for the selective removal of titanium nitride over molybdenum from a microelectronic device, comprising
 - (a) about 10 wt% to about 80 wt% water;
 - (b) about 0.5 wt% to about 15 wt% neat HNO₃;
 - (c) a base that is one or more of
 - (i) about 1 wt% to about 7 wt% of one or more alkanolamine; and
 - (ii) about 0.7 wt% to about 2 wt% f neat NH₄OH; and
 - (d) a halogen ion source that is one or more of
 - (i) about 1 wt% to about 30 wt% of one or more chloride ion source;and
 - (ii) about 0.02 wt% to about 0.15 wt% of one or more fluoride ion source.
2. The etching composition of claim 1, wherein the halogen ion source that is one or more of:
 - (i) about 3 wt% to about 30 wt% NH₄Cl;
 - (ii) about 1 wt% to about 25 wt% of neat HCl;
 - (iii) about 0.02 wt% to about 0.15 wt% of neat HF; and
 - (iv) about 0.02 wt% to about 0.15 wt% of neat NH₄F.
3. The etching composition of claim 1, wherein the base comprises about 1 wt% to about 7 wt% of alkanolamine.
4. The etching composition of claim 1, wherein the base comprises about 0.7 wt% to about 2 wt% of neat NH₄OH.
5. The etching composition of claim 1, wherein the halogen ion source comprises about 3 wt% to about 30 wt% NH₄Cl.
6. The etching composition of claim 1, wherein the halogen ion source comprises about 1 wt% to about 21 wt% of neat HCl.
7. The etching composition of claim 1, wherein the halogen ion source comprises about 0.02 wt% to about 0.15 wt% of neat HF.
8. The etching composition of claim 1, wherein the halogen ion source comprises about 0.02 wt% to about 0.15 wt% of neat NH₄F.
9. The etching composition of any of claims 1-8, wherein the base is one or more alkanolamine selected from the group of N-methylethanolamine (NMEA), monoethanolamine (MEA), diethanolamine, mono-, di- and triisopropanolamine, 2-(2-aminoethylamino)ethanol,

2-(2-aminoethoxy)ethanol, triethanolamine, N-ethyl ethanolamine, N,N-dimethylethanolamine, N,N-diethyl ethanolamine, N-methyl diethanolamine, N-ethyl diethanolamine, cyclohexylaminediethanol, and mixtures thereof.

10. The etching composition of any of claims 1-8, wherein the base is one or more alkanolamine selected from the group of triethanolamine (TEA), diethanolamine, N-methyl diethanolamine, diisopropanolamine, monoethanol amine, amino(ethoxy) ethanol (AEE), N-methyl ethanol amine, monoisopropanol amine, cyclohexylaminediethanol, and mixtures thereof.

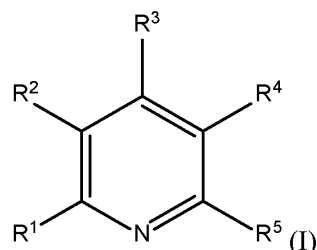
11. The etching composition of any of claims 1-8, wherein the base comprises amino(ethoxy) ethanol.

12. The etching composition of any of claims 1-8 further comprising about 70 wt % and about 80 wt % of neat acetic acid.

13. The etching composition of any of claims 1-8 further comprising at least one heteroaromatic compound.

14. The etching composition of any of claims 1-8 further comprising at least one heteroaromatic compound that is a six-membered heteroaromatic ring having one or more nitrogen atoms as one or more heteroatoms constituting the ring.

15. The etching composition of any of claims 1-8 further comprising at least one heteroaromatic compound that is a six-membered heteroaromatic ring having one or more nitrogen atoms as one or more heteroatoms constituting the ring comprises a pyridine compound represented by Formula (I):



wherein R^1 to R^5 each independently represent hydrogen, an amino group-containing substituent, or a hydrocarbon derivation group which is other than any amino group-containing substituent and has 1 to 10 carbon atoms, provided that at least one of R^1 to R^5 represents the amino group-containing substituent; and these substituents may be bonded to one another to form a cyclic structure.

16. The etching composition of any of claims 1-8 further comprising at least one heteroaromatic compound that is a six-membered heteroaromatic ring having one or more

nitrogen atoms as one or more heteroatoms constituting the ring selected from the group of 3-aminopyridine, 2-aminopyridine, 4-aminopyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-(aminomethyl)pyridine, 3-amino-4-methylpyridine, 5-amino-2-methylpyridine, 4-amino-3-methylpyridine, 3-amino-2-methylpyridine, 4-amino-2-methylpyridine, 3-amino-5-methylpyridine, 2-(methylamino)pyridine, 4-(methylamino)pyridine, 3-(aminomethyl)pyridine, 4-(aminomethyl)pyridine, 2,3-diaminopyridine, 3,4-diaminopyridine, 2,6-diaminopyridine, 2-amino-5-cyanopyridine, 2-amino-3-cyanopyridine, 2-aminopyridine-3-carboxyaldehyde, pyridine-2-carboxamide, 2-amino-4,6-dimethylpyridine, 4-(2-aminoethyl)pyridine, 3-(2-aminoethyl)pyridine, 2-(2-aminoethyl)pyridine, 4-dimethylaminopyridine, 2-dimethylaminopyridine, 2-(ethylamino)pyridine, 2-amino-3-(hydroxymethyl)pyridine, 4-acetamidopyridine, 2-acetamidopyridine, 3-acetamidopyridine, 4-(ethylaminomethyl)pyridine, 2-aminoquinoline, 3-aminoquinoline, 5-aminoquinoline, 6-aminoquinoline, 8-aminoquinoline, 4-dimethylamino-1-neopentylpyridinium chloride and mixtures thereof.

17. The etching composition of any of claims 1-8 further comprising at least one heteroaromatic compound that is a six-membered heteroaromatic ring having one or more nitrogen atoms as one or more heteroatoms constituting the ring selected from the group of 2-aminopyridine, 2,6-diaminopyridine, 2-(aminomethyl)pyridine, 2,6-(aminomethyl)pyridine, 2,6-(aminoethyl)pyridine, 2-amino-4-picoline, 2,6-diamino-4-picoline, 2-amino-3,5-lutidine, 2-aminoquinoline, 8-aminoquinoline, 2-aminoisoquinoline, acriflavine, 4-aminophenanthridine, 4,5-(aminomethyl)phenothiazine, 4,5-(aminomethyl)dibenzoxazine, 10-amino-7,8-benzoquinoline, bis(2-pyridylmethane)amine, tris(2-pyridyl)amine, bis(4-(2-pyridyl)-3-azabutane)amine, bis(N,N-(2-(2-pyridyl)ethane)aminomethane)amine, 4-(N,N-dialkylaminomethyl)morpholine and mixtures thereof.

18. The etching composition of any of claims 1-8 further comprising at least one heteroaromatic compound that is a six-membered heteroaromatic ring having one or more nitrogen atoms as one or more heteroatoms constituting the ring comprising 8-aminoquinoline.

19. The etching composition of any of claims 1-8 further comprising at least one water-miscible solvent selected from the group of diethylene glycol butyl ether, sulfolane, and propylene carbonate.

20. The etching composition of any of claims 1-8 further comprising diethylene glycol butyl ether.

21. The etching composition of any of claims 1-8 further comprising sulfolane.

22. The etching composition of any of claims 1-8 further comprising propylene carbonate.
23. The etching composition of any of claims 1-8 further comprising (i) 8-aminoquinoline and (ii) at least one water-miscible solvent selected from the group of diethylene glycol butyl ether, sulfolane and propylene carbonate.
24. The etching composition of any of claims 1-8, wherein the composition has a titanium nitride molybdenum metal etch selectivity ratio of from about 1:3 to about 15.1:1.
25. The etching composition of claim 1, wherein the composition comprises
- (a) about 60 wt% to about 70 wt% water;
 - (b) about 4.8 wt% of neat HNO₃;
 - (c) a base comprising about 1 wt % of amino(ethoxy) ethanol; and
 - (d) a halogen ion source comprising
 - (i) about 27 wt% NH₄Cl;
 - (ii) about 2.1 wt% neat of HCl; and
 - (iii) about 0.025 wt% of neat HF.
26. The etching composition of claim 1, wherein the composition comprises
- (a) about 60 wt% to about 71 wt% water;
 - (b) about 4.8 wt% of neat HNO₃;
 - (c) a base comprising about 1 wt % of amino(ethoxy) ethanol; and
 - (d) a halogen ion source comprising
 - (i) about 22.5 wt% NH₄Cl;
 - (ii) about 1.05 wt% of neat HCl; and
 - (iii) about 0.025 wt% of neat HF.
27. The etching composition of claim 1, wherein the composition comprises
- (a) about 60 wt% to about 72 wt% water;
 - (b) about 9.6 wt% of neat HNO₃;
 - (c) a base comprising about 2 wt % of amino(ethoxy) ethanol; and
 - (d) a halogen ion source comprising
 - (i) about 16.5 wt% NH₄Cl; and
 - (ii) about 0.02 wt% of neat HF.
28. The etching composition of claim 1, wherein the composition comprises
- (a) about 60 wt% to about 70 wt% water;
 - (b) about 9.6 wt% of neat HNO₃;
 - (c) a base comprising about 2 wt % of amino(ethoxy) ethanol; and

- (d) a halogen ion source comprising
 - (i) about 20 wt% NH_4Cl ; and
 - (ii) about 0.035 wt% of neat HF.
- 29. The etching composition of claim 1, wherein the composition comprises
 - (a) about 60 wt% to about 70 wt% water;
 - (b) about 9.6 wt% of neat HNO_3 ;
 - (c) a base comprising about 0.7 wt % of neat NH_4OH ; and
 - (d) a halogen ion source comprising
 - (i) about 20 wt% NH_4Cl ; and
 - (ii) about 0.035 wt% of neat HF.
- 30. The etching composition of claim 1, wherein the composition comprises
 - (a) about 70 wt% to about 80 wt% water;
 - (b) about 0.6 wt% of neat HNO_3 ;
 - (c) a base comprising about 1.45 wt % of neat NH_4OH ; and
 - (d) a halogen ion source comprising
 - (i) about 21 wt% neat HCl; and
 - (ii) about 0.12 wt% of neat NH_4F .
- 31. The etching composition of claim 1, wherein the composition comprises
 - (a) about 10 wt% to about 15 wt% water;
 - (b) about 4.8 wt% of neat HNO_3 ;
 - (c) a base comprising about 7 wt % of amino(ethoxy) ethanol;
 - (d) a halogen ion source comprising about 0.05 wt% of neat HF; and
 - (e) about 75 wt % of neat acetic acid.
- 32. The etching composition of claim 1, wherein the composition comprises
 - (a) about 10 wt% to about 15 wt% water;
 - (b) about 4.8 wt% of neat HNO_3 ;
 - (c) a base comprising about 6 wt % of amino(ethoxy) ethanol;
 - (d) a halogen ion source comprising about 0.05 wt% of neat HF; and
 - (e) about 76 wt % of neat acetic acid.
- 33. The etching composition of claim 1, wherein the composition comprises
 - (a) about 10 wt% to about 15 wt% water;
 - (b) about 4.8 wt% of neat HNO_3 ;
 - (c) a base comprising about 6 wt % of amino(ethoxy) ethanol;

- (d) a halogen ion source comprising about 0.04 wt% of neat HF; and
 - (e) about 78 wt % of neat acetic acid.
34. The etching composition of claim 1, wherein the composition comprises
- (a) about 10 wt% to about 15 wt% water;
 - (b) about 9 wt% of neat HNO₃;
 - (c) a base comprising about 2.03 wt % of neat NH₄OH;
 - (d) a halogen ion source comprising about 0.05 wt% of neat HF; and
 - (e) about 77 wt % of sulfolone.
35. An etching composition suitable for the selective removal of titanium nitride over molybdenum from a microelectronic device, comprising
- (a) about 88 wt% to about 96 wt% water;
 - (b) about 2 wt% to about 15 wt% of neat HNO₃;
 - (c) a halogen ion source comprising about 0.02 wt% to about 0.10 wt% of one or more fluoride ion source;
 - (d) about 70 wt% to about 95 wt% of one or more water-miscible solvents selected from diethyl glycol butyl ether, sulfolane and propylene carbonate.
36. The etching composition of claim 35, wherein the halogen ion source comprises about 0.02 wt% to about 0.10 wt% of neat HF.
37. The etching composition of claim 35, wherein the halogen ion source comprises about 0.05 of neat HF.
38. The etching composition of claim 35, wherein the one or more water-miscible solvents comprises about 70 wt% to about 80 wt% of diethyl glycol butyl ether.
39. The etching composition of claim 35, wherein the one or more water-miscible solvents comprises about 70 wt% to about 80 wt% of sulfolane.
40. The etching composition of claim 35, wherein the one or more water-miscible solvents comprises about 85 wt% to about 95 wt% of propylene carbonate.
41. The etching composition of claim 35, further comprising 8-aminoquinoline.
42. The etching composition of claim 35, further comprising triethanolamine.
43. The etching composition of claim 35, comprising
- (a) about 90 wt% to about 92 wt% water;
 - (b) about 12 wt% of neat HNO₃;
 - (c) a halogen ion source comprising about 0.05 wt% of HF;
 - (d) about 79 wt% of diethyl glycol butyl ether.

44. The etching composition of claim 35, comprising
- (a) about 88 wt% to about 90 wt% water;
 - (b) about 15 wt% of neat HNO₃;
 - (c) a halogen ion source comprising about 0.05 wt% of HF;
 - (d) about 74 wt% of diethyl glycol butyl ether; and
 - (e) about 0.05 wt% of 8-aminoquinoline.
45. An etching composition suitable for the selective removal of titanium nitride over molybdenum from a microelectronic device, comprising
- (a) about 4 wt% to about 5 wt% water;
 - (b) about 2.0 to about 3.0 wt% of neat HNO₃;
 - (c) a halogen ion source comprising about 0.10 wt% to about 0.12 wt% of HF;
 - (d) about 90 wt% to about 93 wt% of propylene carbonate; and
 - (e) about 0.4 wt% to about 0.6 wt% of triethanolamine.
46. The etching composition of claim 45, comprising
- (a) about 4 wt% to about 5 wt% water;
 - (b) about 2.4 of neat HNO₃;
 - (c) a halogen ion source comprising about 0.12 wt% of HF;
 - (d) about 92 wt% to about 93 wt% of propylene carbonate; and
 - (e) about 0.6 wt% of triethanolamine.
47. An etching composition suitable for the selective removal of titanium nitride over molybdenum from a microelectronic device, comprising
- (a) about 35 wt% to about 50 wt% water;
 - (b) about 6.0 to about 12.0 wt% of neat HNO₃;
 - (c) a base comprising about 15 wt% to about 45 wt% of NH₄H₂PO₄; and
 - (d) a halogen ion source comprising one or more of (i) about 1 wt% to about 7.5 wt% of neat HCl and (ii) about 2.5 wt% to about 5 wt% NH₄Cl.
48. The etching composition of claim 47, comprising
- (a) about 44 wt% to about 45 wt% water;
 - (b) about 12.0 wt% of neat HNO₃;
 - (c) a base comprising about 40 wt% of NH₄H₂PO₄; and
 - (d) a halogen ion source comprising about 3.0 wt% to about 3.5 wt% of neat HCl.
49. The etching composition of claim 47, comprising
- (a) about 46 wt% to about 48 wt% water;

- (b) about 6.0 wt% of neat HNO₃;
 - (c) a base comprising about 40 wt% of NH₄H₂PO₄; and
 - (d) a halogen ion source comprising about 6.5 wt% to about 7.5 wt% of neat HCl.
- 50.** The etching composition of claim 47, comprising
- (a) about 46 wt% to about 48 wt% water;
 - (b) about 9.0 wt% of neat HNO₃;
 - (c) a base comprising about 45 wt% of NH₄H₂PO₄; and
 - (d) a halogen ion source comprising (i) about 5 wt% to about 5.5 wt% of neat HCl and (ii) about 2.5 wt% to about 3.5 wt% NH₄Cl.
- 51.** An etching composition suitable for the selective removal of titanium nitride over molybdenum from a microelectronic device, comprising
- (a) about 35 wt% to about 80 wt% water;
 - (b) about 0.1 wt% to about 5 wt% neat HNO₃;
 - (c) a base that includes one or more of:
 - (i) about 1 wt% to about 7 wt% of one or more alkanolamine, and
 - (ii) about 0.7 wt% to about 2 wt% of neat NH₄OH; and
 - (d) a halogen ion source that includes one or more of:
 - (i) about 3 wt% to about 30 wt% NH₄Cl,
 - (ii) about 1 wt% to about 21 wt% of neat HCl,
 - (iii) about 0.02 wt% to about 0.15 wt% of neat HF, and
 - (iv) about 0.02 wt% to about 0.15 wt% of neat NH₄F.
- 52.** A method of selectively enhancing the etch rate of titanium nitride and molybdenum on a composite semiconductor device comprising titanium nitride and molybdenum, the method comprising the step of:
- (i) contacting the composite semiconductor device comprising titanium nitride and molybdenum with a composition of any of claims 1-51,
- wherein the titanium nitride is selectively etched over the molybdenum metal at a ratio of from about 1:3 to about 15.1:1 .