

CLAIMS

1. An etching solution suitable for the selective removal of polysilicon over p-doped silicon and/or polysilicon over silicon germanium alloy from a microelectronic device, comprising:
 - water;
 - at least one of NH_4OH or a quaternary ammonium hydroxide, and mixtures thereof;
 - at least one compound selected from benzoquinone or a derivative of benzoquinone; quinoline or a derivative of quinoline; an unsubstituted or substituted C_{6-20} aliphatic acid; a C_{4-12} alkylamine; and a polyalkylenimine; and mixtures thereof;
 - optionally at least one water-miscible organic solvent; and
 - optionally, at least one compound selected from an alkanolamine and a polyamine, and mixtures thereof.
2. The etching solution of claim 1 comprising:
 - from about 0.05 to about 15 wt % of said at least one of NH_4OH (neat) or a quaternary ammonium hydroxide (neat);
 - from about 0.01 to about 8 wt % of said at least one compound selected from a benzoquinone or a derivative of benzoquinone; quinoline or a derivative of quinoline; an unsubstituted or substituted C_{6-20} aliphatic acid; a C_{4-12} alkylamine and a polyalkylenimine, and mixtures thereof.
3. The etching solution of claim 1 or claim 2 wherein the etching solution comprises said at least one compound selected from benzoquinone or a derivative of benzoquinone.
4. The etching solution of any of the preceding claims wherein the etching solution comprises said at least one unsubstituted or substituted C_{6-20} aliphatic acid.
5. The etching solution of any of the preceding claims wherein the etching solution further comprises said at least one water-miscible organic solvent.

6. The etching solution of any of the preceding claims wherein the etching solution further comprises at least one polyamine.
7. The etching solution of any of the preceding claims wherein the etching solution further comprises at least one alkanolamine.
8. The etching solution of any of the preceding claims wherein the etching solution comprises said at least one compound selected from a quinoline or a derivative of quinoline.
9. The etching solution of any of the preceding claims wherein the etching solution comprises said at least one polyalkylenimine.
10. The etching solution of any of the preceding claims wherein the etching solution comprises said at least one C₄₋₁₂ alkylamine.
11. An etching solution suitable for the selective removal of polysilicon over p-doped silicon and/or polysilicon over silicon germanium alloy from a microelectronic device, comprising:
 - water;
 - at least one water-miscible organic solvent;
 - at least one of NH₄OH or a quaternary ammonium hydroxide;
 - at least one compound selected from the group consisting of an alkanolamine and a polyamine or mixtures thereof;
 - at least one benzoquinone or a derivative of benzoquinone;
 - optionally, at least one compound selected from the group consisting of a C₄₋₁₂ alkylamine, a polyalkylenimine, and an unsubstituted or substituted C₆₋₂₀ aliphatic acid;
 - optionally, at least one fluoride ion source;
 - optionally, a quinoline or derivatives of quinoline; and
 - optionally, a surfactant.

12. The etching solution of any of the preceding claims wherein the etching solution comprises from about 70 to about 99.9 wt% of said water.
13. The etching solution of any of claims 1-11 wherein the etching solution comprises from about 30 to about 70 wt% water.
14. The etching solution of any of the preceding claims wherein the water-miscible organic solvent is selected from the group consisting of sulfolane, DMSO, ethylene glycol, glycerol, dipropylene glycol monomethyl ether, and propylene glycol.
15. The etching solution of any of the preceding claims wherein the water-miscible organic solvent is dipropylene glycol monomethyl ether.
16. The etching solution of any of the preceding claims wherein the quaternary ammonium hydroxide compound is selected from tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, benzyltrimethyl ammonium hydroxide, ethyltrimethyl ammonium hydroxide (ETMAH), 2-hydroxyethyltrimethyl ammonium hydroxide, benzyltriethyl ammonium hydroxide, hexadecyltrimethyl ammonium hydroxide, and mixtures thereof.
17. The etching solution of any of the preceding claims wherein the alkanolamine compound is selected from N-methylethanolamine (NMEA), monoethanolamine (MEA), diethanolamine, triethanolamine, mono-isopropanolamine, triisopropanolamine, 2-(2-aminoethylamino)ethanol, 2-(2-aminoethoxy)ethanol (AEE), triethanolamine, N-ethyl ethanolamine, N,N-dimethylethanolamine, N,N-diethyl ethanolamine, N-methyl diethanolamine, N-ethyl diethanolamine, cyclohexylaminediethanol, diisopropanolamine, cyclohexylaminediethanol, and mixtures thereof.
18. The etching solution of any of the preceding claims wherein the polyalkylenimine is polyethylenimine.

19. The etching solution of any of the preceding claims wherein the substituted or unsubstituted C₆₋₂₀ aliphatic acid is selected from hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dedecanoic acid, 6-mercaptohexanoic acid, 7-mercaptoheptanoic acid, 8-mercaptooctanoic acid, 9-mercaptononanoic acid, 10-mercaptodecanoic acid, 11-mercaptoundecanoic acid, 12-mercaptododecanoic acid and 16-mercaptohexadecanoic acid.

20. The etching solution of any of the preceding claims wherein the unsubstituted or substituted C₆₋₂₀ aliphatic acid is a mercapto carboxylic acid.

21. The etching solution of any of the preceding claims wherein the benzoquinone or a derivative of benzoquinone is selected from 1,4-benzoquinone, o-benzoquinone, 2-methyl-1,4-benzoquinone, 2,5-dihydroxyl-p-benzoquinone, and 2-tert-butyl-1,4-benzoquinone, 2-phenyl-1,4-benzoquinone, 2-methoxy-1,4-benzoquinone; 2,6-dimethyl-1,4-benzoquinone; 2,3-dimethyl-1,4-benzoquinone; trimethyl-1,4-benzoquinone; 2,6-dimethoxy-1,4-benzoquinone; tetramethyl-1,4-benzoquinone; tetrafluoro-1,4-benzoquinone; 2,5-dichloro-1,4-benzoquinone; tetrachloro-1,4-benzoquinone; 2-chloro-1,4-benzoquinone; 1,4-naphthoquinone; 9,10-anthraquinone; 1,8-dichloro-9,10-anthraquinone; 2,3-dichloro-1,4-naphthoquinone; 3,5-di-tert-butyl-1,2-benzoquinone; 4-tert-butyl-1,2-benzoquinone; phenanthrenequinone; 1,2-naphthoquinone; 1,10-phenanthroline-5,6-dione; and tetrachloro-1,2-benzoquinone.

22. The etching solution of any of the preceding claims wherein the benzoquinone or a derivative of benzoquinone is present in the solution and is selected from p-benzoquinone, o-benzoquinone, 2-methyl-p-benzoquinone, 2,5-dihydroxyl-p-benzoquinone, and 2-t-butyl-p-benzoquinone.

23. The etching solution of any of the preceding claims wherein the polyamine is selected from pentamethyldiethylenetriamine (PMDETA), triethylenediamine (TEDA), triethylenetetramine (TETA), tetramethylethylenediamine (TMEDA), and diethylenetriamine (DETA).

24. The etching solution of any of the preceding claims wherein the quinoline or a derivative of quinoline is selected from quinoline, 8-hydroxy quinoline, 2-methyl-8-hydroxyquinoline and aminoquinoline.
25. The etching solution of any of the preceding claims wherein the C₄₋₁₂ alkylamine is selected from hexylamine, surfactant salts of hexylamine, octylamine, surfactant salts of octylamine, decylamine, surfactant salts of decylamine, and dodecylamine, and surfactant salts of dodecylamine.
26. The etching solution of claim 11 comprising
water;
methyl-p-benzoquinone;
propylene glycol;
diethylenetriamine; and
at least one quaternary ammonium hydroxide selected from the group consisting of ethyltrimethylammonium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, and benzyl trimethylammonium hydroxide.
27. The etching solution of claim 26 further comprising C₆₋₂₀ aliphatic acid.
28. A method for selectively enhancing the etch rate of polysilicon relative to p-doped silicon and/or polysilicon relative silicon germanium alloy in a composite semiconductor device comprising polysilicon and p-doped silicon and/or comprising polysilicon and germanium alloy, the method comprising the steps of:
contacting the composite semiconductor device comprising polysilicon and p-doped silicon and/or polysilicon and a silicon-germanium alloy with the aqueous composition of any of the preceding claims and
rinsing the composite semiconductor device after the polysilicon is at least partially removed.

29. The method of claim 28, wherein the selectivity of polysilicon relative to p-doped silicon is greater than 10.
30. The method of claim 29, wherein the selectivity of polysilicon relative to p-doped silicon is greater than 50.
31. The method of claim 29, wherein the selectivity of the etch for polysilicon relative to p-doped silicon is greater than 100.
32. The method of claim 28, wherein the selectivity of the etch for polysilicon over silicon-germanium alloy is greater than about 10.
33. The method of claim 28, wherein the selectivity of the etch for polysilicon over silicon-germanium alloy is greater than about 15.
34. The method of claim 28, wherein the selectivity of the etch for polysilicon over silicon-germanium alloy is greater than about 20.