CLAIMS

What is claimed is:

1. A composition useful for removing residue from a semiconductor substrate, the composition comprising:
   a) from about ~~15%~~35% to about 50% by weight of water;
   b) from about 10% to about ~~65%~~30% by weight of a water-miscible organic solvent, wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof;
   c) from about ~~1%~~8% to about 50% by weight of ~~an amine compound selected from the group consisting of a at least one alkanolamine and aminopropylmorpholine~~an alkanolamine selected from the group consisting 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;
   d) from about ~~1%~~6% to about ~~25%~~10% by weight of an organic acid; and
   e) from about ~~0.01%~~1% to about 8% by weight of a fluoride ion source~~, wherein the water-miscible organic solvent is not an ether~~, wherein the composition is capable of providing a copper etch rate of 3 Å/min or less.

2. The composition of claim 1 further comprising from about 0.1% to about 15% by weight of a corrosion inhibitor selected from the group consisting of benzotriazole, amino-benzotriazole, L-ascorbic acid, gallic acid, vanillin, diethylhydroxylamine, and mixtures thereof.

~~3. The composition of claim 1 wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof.~~

43. The composition of claim ~~3~~1 wherein the water-miscible organic solvent is dimethylacetamide.

~~5~~4. The composition of claim ~~3~~1 wherein the water-miscible organic solvent is propylene glycol.

~~6~~5. The composition of claim ~~3~~1 wherein the water-miscible organic solvent is glycerol.

~~7~~6. The composition of claim 1 wherein the fluoride ion source is selected from the group consisting of ammonium fluoride and a quaternary ammonium compound.

~~8~~7. The composition of claim ~~7~~6 wherein the fluoride ion source is ammonium fluoride.

~~9~~8. The composition of claim ~~7~~6 wherein the fluoride ion source is a quaternary ammonium compound selected from the group consisting of tetramethylammonium fluoride and tetrabutylammonium fluoride.

~~10. The composition of claim 1 wherein the amine compound is an alkanolamine selected from the group consisting 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.~~

~~11~~9. The composition of claim ~~10~~ 1 wherein the alkanolamine is monoethanolamine.

~~12~~10. The composition of claim ~~10~~ 1 ~~wherein the amine compound is~~further comprising aminopropylmorpholine.

~~13~~11. The composition of claim ~~10~~ 1 wherein the alkanolamine ~~amine compound~~ is triethanolamine.

~~14~~12. The composition of claim ~~10~~ 1 wherein the alkanolamine ~~amine compound~~ is a mixture of triethanolamine and 2-(2-aminoethoxy)ethanol.

~~15. The composition of claim 1 wherein the composition comprises:~~

~~a) from about 35% to about 50% by weight of water;~~

~~b) from about 10% to about 30% by weight of the water-miscible organic solvent;~~
~~c) from about 8% to about 50% by weight of the amine compound selected from the group consisting of a at least one alkanolamine and aminopropylmorpholine;~~
~~d) from about 6% to about 10% by weight of the organic acid; and~~
~~e) from about 1% to about 8% by weight of the fluoride ion source.~~

~~16~~13. A method for removing residue from a semiconductor substrate, the method comprising the steps of:
contacting the semiconductor substrate with a cleaning composition of claim 1, wherein the semiconductor substrate comprises a porous dielectric material having a dielectric constant;
rinsing the cleaning composition from the semiconductor substrate; and
drying the semiconductor substrate,
wherein the dielectric constant of the porous dielectric material does not increase more than 0.50.

~~17~~14. The method of claim ~~16~~ 13 wherein the dielectric constant of the porous dielectric material does not increase more than 0.25.

~~18~~15. The method claim ~~16~~ 13 wherein the cleaning composition provides a copper etch rate of 42 Å/min or less.

~~19~~16. A replenishment composition to be added to a cleaning composition, said replenishment composition comprises a) from about 20% to about 84% by weight of water; b) from about 15% to about 40% by weight of a water-miscible organic solvent, ~~wherein the water-miscible solvent is not an ether~~wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof; c) from about 1% to about 5% by weight of ~~an amine compound selected from the group consisting of at least one alkanolamine and at least one aminopropylmorpholine~~an alkanolamine selected from the group consisting 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, wherein the composition is capable of providing a copper etch rate of 3 Å/min or less.

~~20~~17. The replenishment composition of claim ~~19~~16, further comprising from about 4% to about 35% by weight of diethyl hydroxylamine, and said water is from about 20 to about 80% of the replenishment composition.

~~21~~18. A method for removing unwanted residues from a semiconductor substrate comprising the steps of: contacting the semiconductor substrate with a cleaning composition comprising: a) from about 15% to about 50% by weight of water; b) from about 10% to about 65% by weight of a water-miscible organic solvent, ~~wherein the water-miscible solvent is not an ether~~wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof; c) from about 1% to about 20% by weight of ~~an amine compound selected from the group consisting of at least one alkanolamine and at least one aminopropylmorpholine~~an alkanolamine selected from the group consisting 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; d) from about 1% to about 25% by weight of at least one organic acid; and e) from about 0.01% to about 8% by weight of a fluoride ion source, wherein said contacting step results in a loss of a portion of said cleaning composition; and adding a replenishment composition to said cleaning composition; said replenishment composition comprising: a) from about 20% to about 84% by weight of water; b) from about 15% to about 40% by weight of a water-miscible organic solvent, ~~wherein the water-miscible solvent is not an ether~~wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof; c) from about 1% to about 5% by weight of ~~an amine compound selected from the group consisting of at least one alkanolamine and at least one aminopropylmorpholine~~an alkanolamine selected from the group consisting 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.

~~22~~19. The method of claim ~~21~~ 18 further comprising the steps of rinsing the cleaning composition from the semiconductor substrate; and drying the semiconductor substrate, wherein the semiconductor substrate comprises a porous dielectric material having a dielectric constant; and wherein after said contacting, rinsing and drying steps the dielectric constant of the porous dielectric material does not increase more than 0.50.

~~23~~20. The method of claim ~~22~~ 19 wherein the dielectric constant of the porous dielectric material does not increase more than 0.25.

2421. The method of claim 2118, wherein the cleaning composition used in the method may further comprise from about 1 to about 15% by weight of diethyl hydroxylamine, and the replenishment composition used in the method may further comprises from about 4% to about 35% of diethyl hydroxylamine, and said water is from about 20 to about 80% of the replenishment composition.

2522. A composition useful for removing residue from a semiconductor substrate, the composition consisting essentially of:

a) from about 15%35% to about 50% by weight of water;

b) from about 10% to about 65%30% by weight of a water-miscible organic solvent, ~~wherein the water-miscible solvent is not an ether~~wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof;

c) from about 1%8% to about 50% by weight of ~~an amine compound selected from the group consisting of at least one alkanolamine and at least one aminopropylmorpholine~~an alkanolamine selected from the group consisting 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;

d) from about 1%6% to about 25%10% by weight of an organic acid;

e) from about 0.01%1% to about 8% by weight of a fluoride ion source; and

f) optionally, from about 0.1% to about 15% by weight of a corrosion inhibitor selected from the group consisting of benzotriazole, amino-benzotriazole, L-ascorbic acid, gallic acid, vanillin, diethylhydroxylamine, and mixtures thereof,

wherein the composition is capable of providing a copper etch rate of 3 Å/min or less.

~~26. The composition of claim 25 wherein the water-miscible organic solvent is selected from the group consisting of propylene glycol, glycerol, dimethylacetamide, tetrahydrofuryl alcohol, ethylene glycol, hexylene glycol, and mixtures thereof.~~

2723. The composition of claim 26 22 wherein the water-miscible organic solvent is dimethylacetamide.

2824. The composition of claim 26 22 wherein the water-miscible organic solvent is propylene glycol.

2925. The composition of claim ~~26~~ 22 wherein the water-miscible organic solvent is glycerol.

3026. The composition of claim ~~25~~ 22 wherein the fluoride ion source is selected from the group consisting of ammonium fluoride and a quaternary ammonium compound.

3127. The composition of claim ~~30~~ 26 wherein the fluoride ion source is ammonium fluoride.

3228. The composition of claim ~~30~~ 26 wherein the fluoride ion source is a quaternary ammonium compound selected from the group consisting of tetramethylammonium fluoride and tetrabutylammonium fluoride.

~~33. The composition of claim 25 wherein the amine compound is an alkanolamine selected from the group consisting 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.~~

3429. The composition of claim ~~33~~ 22 wherein the alkanolamine is monoethanolamine.

~~35. The composition of claim 33 wherein the amine compound is aminopropylmorpholine.~~

3630. The composition of claim ~~33~~ 22 wherein the alkanolamine ~~amine compound~~ is triethanolamine.

3731. The composition of claim ~~33~~ 22 wherein the alkanolamine ~~amine compound~~ is a mixture of triethanolamine and 2-(2-aminoethoxy)ethanol.