

NANOELECTRONIC AND MICROELECTRONIC

CLEANING COMPOSITIONS

FIELD OF THE INVENTION

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[0001] This invention relates to methods and cleaning compositions for cleaning nanoelectronic and microelectronic substrates with supercritical fluid compositions, and particularly to such cleaning compositions useful with and having improved compatibility with nanoelectronic and microelectronic substrates characterized by silicon dioxide, sensitive low- κ or high- κ dielectrics and copper, tungsten, tantalum, nickel, gold, cobalt, palladium, platinum, chromium, ruthenium, rhodium, iridium, hafnium, titanium, molybdenum, tin and other metallization, as well as substrates of Al or Al(Cu) metallizations and advanced interconnect technologies, and particularly such substrates having high aspect ratio openings, including difficult submicron crevices, grooves, trenches and vias. The invention also relates to the use of such cleaning compositions for stripping photoresists, and cleaning residues from plasma process generated organic, organometallic and inorganic compounds, and cleaning residues from planarization processes such as chemical mechanical polishing (CMP) and as additives in planarization slurry/liquids.

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BACKGROUND TO THE INVENTION

[0002] Many photoresist strippers and residue removers have been proposed for use in the microelectronics field as downstream or back end of the manufacturing line cleaners. In the manufacturing process a thin film of photoresist is deposited on a wafer substrate, and then circuit design is imaged on the thin film. Following baking, the exposed portion of the positive resist or the unexposed portion of the negative resist is removed with a photoresist developer. The resulting image is then transferred to the underlying material, which is generally a dielectric or metal, by way of reactive plasma etch gases or chemical

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etchant solutions. The etchant gases or chemical etchant solutions selectively attack the photoresist-unprotected area of the substrate. As a result of the plasma etching process, photoresist, etching gas and etched material by-products are deposited as residues around or on the sidewall of the etched openings on the substrate.

[0003] Additionally, following termination of the etching step, the resist mask must be removed from the protected area of the wafer so that the final finishing operation can take place. This can be accomplished in a plasma ashing step by the use of suitable plasma ashing gases or wet chemical strippers. Finding a suitable cleaning composition for removal of this resist mask material without adversely affecting, e.g., corroding, dissolving or dulling, the metal circuitry has also proven problematic.

[0004] As microelectronic fabrication integration levels have increased and patterned nanoelectronic and microelectronic device dimensions have decreased for the production of current and future generation nanoelectronic and microelectronic semiconductor devices and other items such as flat panel displays, it has become increasingly common in the art to employ copper metallizations, low- κ (both porous and non-porous) and high- κ dielectrics. These materials have presented additional challenges to find acceptable cleaner compositions. Many process technology compositions that have been previously developed for "traditional" or "conventional" semiconductor devices containing Al/SiO₂, Al(Cu)/SiO₂, or Al/Mo/SiO₂ structures cannot be employed with copper, tungsten, tantalum, nickel, gold, cobalt, palladium, platinum, chromium, ruthenium, rhodium, iridium, hafnium, titanium, molybdenum, tin and other metallized, and low- κ or high- κ dielectric structures. For example, hydroxylamine based stripper or residue remover compositions are successfully used for cleaning devices with Al metallizations, but are practically unsuitable for those with copper and other

metallizations. Similarly, many copper metallized/ low- κ strippers are not suitable for Al metallized devices unless significant adjustments in the compositions are made.

5 **[0005]** Removal of these etch and/or ash residues following the plasma etch and/or ashing process has proved problematic. Failure to completely remove or neutralize these residues can result in the absorption of moisture and the formation of undesirable materials that can cause corrosion to the metal structures or electrical defects to the integrated circuitry. The circuitry materials are corroded by
10 the undesirable materials and produce discontinuances in the circuitry wiring and undesirable increases in electrical resistance. This problem is also especially evident in removing sidewall deposited photoresist or residues and surface-hardened photoresist hardened due to UV radiation, reactive ion etching or ion implantation processes. There is also a problem of removing photoresist and
15 other residues when they are present in structures having high aspect ratio openings, including difficult submicron grooves and narrow crevices.

[0006] The current back end cleaners show a wide range of compatibility with certain, sensitive dielectrics and metallizations, ranging from totally unacceptable to
20 marginally satisfactory. Many of the current strippers or residue cleaners are not acceptable for advanced interconnect materials such as porous and low- κ dielectrics and copper metallizations. Additionally, the typical alkaline cleaning solutions employed are overly aggressive towards porous and low- κ and high- κ dielectrics and/or copper metallizations. Moreover, many of these alkaline cleaning
25 compositions contain organic solvents that show poor product stability, especially at higher pH ranges and at higher process temperatures.

[0007] In an attempt to at least partially address these problems, it has been proposed to employ supercritical fluids to remove such organic and inorganic

residues from such substrates. Examples of such proposals are found in the disclosure in U.S. Patent Nos. 6,242,165B1, 6,306,564B1, 6,500,605B1 and 6,653,236B2. In these patents it is proposed to clean substrates with supercritical fluids such as carbon dioxide, ammonia, nitrous oxide, carbon monoxide, and inert gases such as nitrogen, helium, neon, argon, krypton and xenon, and particularly carbon dioxide. It is proposed to employ supercritical fluids alone or with various simple modifiers, such as oxidizers (U.S. 6,242,265B1), carbon dioxide with chemical solvents (U.S. 6,306,564B1), and carbon dioxide, an amine and a solvent (U.S. 6,500,605B1). However, the cleaning efficiencies and capabilities of the supercritical fluids alone or with the simple modifiers have been limited in removing bulk photoresist and difficult-to-remove plasma generated residues.

BRIEF SUMMARY OF THE INVENTION

[0008] There is, therefore, a need for reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions that are suitable for semiconductor and flat panel display cleaning operations with supercritical fluids, which compositions are effective cleaners and are applicable for stripping photoresists and cleaning residues from plasma process generated organic, organometallic and inorganic compounds, cleaning residues from planarization processes, such as CMP, and which can be used for advanced interconnect materials employing copper and other metallizations, including but not limited to tungsten, tantalum, nickel, gold, cobalt, palladium, platinum, chromium, ruthenium, rhodium, iridium, hafnium, titanium, molybdenum, and tin metallization, and porous or non-porous low- κ (i.e., a κ value of 3 or less) or high- κ (i.e., a κ value of 20 or greater) dielectrics as well as useful for cleaning conventional devices, such as those with aluminum or aluminum(copper) metallizations containing silicon dioxide, low- κ or high- κ dielectrics.

[0009] It has been discovered that effective nanoelectronic and microelectronic

supercritical fluid cleaning compositions for cleaning microelectronic substrates under supercritical fluid conditions, and particularly cleaning compositions useful with and having improved compatibility with microelectronic substrates characterized by silicon dioxide, sensitive low- κ or high- κ dielectrics and copper, tungsten, tantalum, nickel, gold, cobalt, palladium, platinum, chromium, ruthenium, rhodium, iridium, hafnium, titanium, molybdenum, tin and other metallization, as well as substrates of Al or Al(Cu) metallizations and advanced interconnect technologies, are provided by such reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions that are generally effective cleaners for cleaning such devices. Such reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention are provided by compositions comprising: (1) a supercritical main fluid reaching a supercritical fluid state at a temperature of 250°C or less and a pressure of 600 bars or less (592.2 atm, 8702.3 psi), and (2) as a secondary fluid, a modifier formulation selected from the following formulations:

- a) a formulation comprising: an oxidizing agent; a polar organic solvent selected from the group consisting of amides, sulfones, sulfolenes, selenones and saturated alcohols; and optionally other components;
- b) a silicate free formulation comprising: a polar organic solvent selected from the group consisting of amides, sulfones, selenones and saturated alcohols; a strong alkaline base; and optionally other components;
- c) a formulation comprising: from about 0.05% to 30% by weight of one or more non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions; from about 0.5 to about 99.95% by weight of one or more corrosion inhibiting solvent compounds, said corrosion inhibiting solvent compound having at least two sites capable of complexing with metals; and optionally other components;
- d) a formulation comprising: from about 0.05 to 20% by weight of one or more non-ammonium producing, non-HF producing fluoride salt; from about 5 to about 99.95% by weight of water, organic solvent or both water and organic solvent;

and optionally other components; and

e) a formulation comprising: from about 0.05% to 30% by weight of one or more non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions; from about 5 to about 99.95% by weight of one or more steric hindered amide solvents; and optionally other components. More preferably such reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention for use under supercritical fluid conditions are provided by compositions comprising: (1) a supercritical main fluid reaching a supercritical fluid state at a temperature of 250°C or less, preferably at a temperature of 150°C or less, and a pressure of 600 bars (592.2 atm, 8702.3 psi), preferably a pressure of 400 bars (394.8 atm, 5801.5 psi) or less, more preferably a pressure of 300 bars (296.1 atm, 4351.1 psi) or less, and (2) as a secondary fluid, a modifier formulation selected from the following formulations:

a) a formulation comprising:

an oxidizing agent;

polar organic solvent selected from the group consisting of amides, sulfones, sulfolenes, selenones and saturated alcohols;

and optionally one or more of the following components:

an acid;

an alkaline base;

a corrosion-inhibiting co-solvent;

a chelating or metal complexing agent;

an oxidizer stabilizing agent;

a corrosion-inhibiting agent;

a metal corrosion inhibitor;

a fluoride compound;

a surfactant; and

water;

b) a silicate free formulation comprising:

polar organic solvent selected from the group consisting of amides, sulfones, selenones and saturated alcohols; and

a strong alkaline base;

and optionally one or more of the following components:

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an acid;

a corrosion-inhibiting co-solvent;

a chelating or metal complexing agent;

an oxidizer stabilizing agent;

a corrosion-inhibiting agent;

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a metal corrosion inhibitor;

a fluoride compound;

a surfactant; and

water;

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c) a formulation comprising:

from about 0.05% to 30% by weight of one or more non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions;

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from about 0.5 to about 99.95% by weight of one or more corrosion inhibiting solvent compounds, said corrosion inhibiting solvent compound having at least two sites capable of complexing with metals;

from about 0 to about 99.45% by weight water or other organic co-solvent;

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from about 0 to 40% by weight a steric hindered amine or alkanolamine;

from about 0 to 40% by weight an organic or inorganic acid;

from about 0 to 40% by weight of an other metal corrosion inhibitor compounds;

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from about 0 to 5% by weight a surfactant;

from about 0 to 10% by weight of a metal ion free silicate compound;

from about 0 to 5% by weight of a metal chelating agent; and
from about 0 to 10% by weight of a fluoride compound;

d) a formulation comprising:

- 5 from about 0.05 to 20% by weight of one or more non-ammonium
producing, non-HF producing fluoride salt;
from about 5 to about 99.95% by weight of water, organic solvent or
both water and organic solvent;
from about 0 to about 80% by weight of a metal corrosion inhibiting
10 solvent;
from about 0 to 40% by weight a steric hindered amine or
alkanolamine;
from about 0 to 40% by weight of an organic or inorganic acid;
from about 0 to 40% by weight of an other metal corrosion inhibitor
15 compound;
from about 0 to 5% by weight of a surfactant;
from about 0 to 10% by weight of a metal ion free silicate compound;
and
from about 0 to 5% by weight of a metal chelating agent; and

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e) a formulation comprising:

- from about 0.05% to 30% by weight of one or more non-ammonium
producing strong base containing non-nucleophilic, positively charged counter
ions;
25 from about 5 to about 99.95% by weight of one or more steric hindered
amide solvents;
from about 0 to about 95% by weight water or other organic co-solvent;
from about 0 to 40% by weight a steric hindered amine or
alkanolamine;
30 from about 0 to 40% by weight an organic or inorganic acid;

from about 0 to 40% by weight of an other metal corrosion inhibitor compounds;

from about 0 to 5 % by weight a surfactant.;

from about 0 to 10 % by weight of a metal ion free silicate compound;

5 from about 0 to 5 % by weight of a metal chelating agent; and

from about 0 to 10 % by weight of a fluoride compound.

The invention also comprises the use of such nanoelectronic and microelectronic cleaning compositions to clean nanoelectronic and microelectronic substrates.

10 **[0010]** These reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention provide improved and superior cleaning and stripping photoresist and provide for organic and inorganic residue removal with surprisingly good compatibilities with many sensitive substrates, under elevated temperatures and pressures that are required
15 for many common supercritical fluid operations. Such reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention provide particular advantageous capabilities for nanoelectronic and microelectronic cleaning applications, residue removal, cleaning residues from planarization processes, such as chemical mechanical
20 polishing, and for use as additives in planarization slurry/liquids.

[0011] The nanoelectronic and microelectronic cleaning compositions of this invention are suitable for stripping photoresists and cleaning residues from plasma process generated organic, organometallic and inorganic compounds, and have
25 improved compatibility with microelectronic substrates characterized by silicon dioxide, sensitive low- κ or high- κ dielectrics and copper, tungsten, tantalum, nickel, gold, cobalt, palladium, platinum, chromium, ruthenium, rhodium, iridium, hafnium, titanium, molybdenum, tin and other metallization, as well as substrates of Al or Al(Cu) metallizations, and advanced interconnect technologies. Additionally, the
30 cleaning compositions of this invention are particularly suitable for cleaning difficult

5 samples containing very stubborn plasma etch and ash residues and also hardened (e.g., polymerized) photoresists that are generated in the manufacturing process for producing Cu/low- κ and high- κ dielectrics structures. The cleaning compositions of this invention may be used alone or coupled with other cleaning solutions.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

- 10 **[0012]** The reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention are provided by compositions comprising: (1) a supercritical main fluid reaching a supercritical fluid state at a temperature of 250°C or less and a pressure of 600 bars or less (592.2 atm, 8702.3 psi), and (2) as a secondary fluid, a modifier formulation selected from
- 15 the following formulations:
- a) a formulation comprising: an oxidizing agent; a polar organic solvent selected from the group consisting of amides, sulfones, sulfolenes, selenones and saturated alcohols; and optionally other components;
 - b) a silicate free formulation comprising: a polar organic solvent selected from
 - 20 the group consisting of amides, sulfones, selenones and saturated alcohols; a strong alkaline base; and optionally other components;
 - c) a formulation comprising: from about 0.05% to 30% by weight of one or more non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions; from about 0.5 to about 99.95% by weight of one or more
 - 25 corrosion inhibiting solvent compounds, said corrosion inhibiting solvent compound having at least two sites capable of complexing with metals; and optionally other components;
 - d) a formulation comprising: from about 0.05 to 20% by weight of one or more non-ammonium producing, non-HF producing fluoride salt; from about 5 to about
 - 30 99.95% by weight of water, organic solvent or both water and organic solvent;

and optionally other components; and

e) a formulation comprising: from about 0.05% to 30% by weight of one or more non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions; from about 5 to about 99.95% by weight of one or more steric hindered amide solvents; and optionally other components. More preferably such reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention are provided by compositions comprising: (1) a supercritical main fluid reaching a supercritical fluid state at a temperature of 250°C or less, preferably at a temperature of 150°C or less, and a pressure of 600 bars (592.2 atm, 8702.3 psi), preferably a pressure of 400 bars (394.8 atm, 5801.5 psi) or less, more preferably a pressure of 300 bars (296.1 atm, 4351.1 psi) or less, and (2) as a secondary fluid a modifier formulation selected from the following formulations:

a) a formulation comprising:

an oxidizing agent;
polar organic solvent selected from the group consisting of amides, sulfones, sulfolenes, selenones and saturated alcohols;
and optionally one or more of the following components:
an acid;
an alkaline base;
a corrosion-inhibiting co-solvent;
a chelating or metal complexing agent;
an oxidizer stabilizing agent;
a corrosion-inhibiting agent;
a metal corrosion inhibitor;
a fluoride compound;
a surfactant; and
water;

b) a silicate free formulation comprising:

polar organic solvent selected from the group consisting of amides, sulfones, selenones and saturated alcohols; and

a strong alkaline base;

and optionally one or more of the following components:

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an acid;

a corrosion-inhibiting co-solvent;

a chelating or metal complexing agent;

an oxidizer stabilizing agent;

a corrosion-inhibiting agent;

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a metal corrosion inhibitor;

a fluoride compound;

a surfactant; and

water;

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c) a formulation comprising:

from about 0.05% to 30% by weight of one or more non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions;

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from about 0.5 to about 99.95% by weight of one or more corrosion inhibiting solvent compounds, said corrosion inhibiting solvent compound having at least two sites capable of complexing with metals;

from about 0 to about 99.45% by weight water or other organic co-solvent;

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from about 0 to 40% by weight a steric hindered amine or alkanolamine;

from about 0 to 40% by weight an organic or inorganic acid;

from about 0 to 40% by weight of an other metal corrosion inhibitor compounds;

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from about 0 to 5% by weight a surfactant;

from about 0 to 10% by weight of a metal ion free silicate compound;

from about 0 to 5% by weight of a metal chelating agent; and
from about 0 to 10% by weight of a fluoride compound;

d) a formulation comprising:

- 5 from about 0.05 to 20% by weight of one or more non-ammonium
producing, non-HF producing fluoride salt;
 from about 5 to about 99.95% by weight of water, organic solvent or
both water and organic solvent;
 from about 0 to about 80% by weight of a metal corrosion inhibiting
10 solvent;
 from about 0 to 40% by weight a steric hindered amine or
alkanolamine;
 from about 0 to 40% by weight of an organic or inorganic acid;
 from about 0 to 40% by weight of an other metal corrosion inhibitor
15 compound;
 from about 0 to 5% by weight of a surfactant;
 from about 0 to 10% by weight of a metal ion free silicate compound;
 and
 from about 0 to 5% by weight of a metal chelating agent; and

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e) a formulation comprising:

- from about 0.05% to 30% by weight of one or more non-ammonium
producing strong base containing non-nucleophilic, positively charged counter
ions;
25 from about 5 to about 99.95% by weight of one or more steric hindered
amide solvents;
 from about 0 to about 95% by weight water or other organic co-solvent;
 from about 0 to 40% by weight a steric hindered amine or
alkanolamine;
30 from about 0 to 40% by weight an organic or inorganic acid;

from about 0 to 40% by weight of an other metal corrosion inhibitor compounds;

from about 0 to 5 % by weight a surfactant.;

from about 0 to 10 % by weight of a metal ion free silicate compound;

5 from about 0 to 5 % by weight of a metal chelating agent; and

from about 0 to 10 % by weight of a fluoride compound.

10 [0013] The reasonably stable, homogeneous supercritical state nanoelectronic and microelectronic cleaning compositions of this invention will generally comprise from about 0.1% to about 50%, preferably from about 3%, to about 25%, and more preferably from about 5% to about 20%, by weight of the secondary fluid modifier formulation component (2) based on the weight of the supercritical main fluid component (1).

15 [0014] The supercritical main fluid component (1) is one reaching a supercritical fluid state at a temperature of 250°C or less, preferably at a temperature of 150°C or less, and a pressure of 600 bars (592.2 atm, 8702.3 psi), preferably a pressure of 400 bars (394.8 atm, 5801.5 psi) or less, more preferably a pressure of 300 bars (296.1 atm, 4351.1 psi) or less. Any suitable
20 material meeting this supercritical-fluid-criteria may be employed in the nanoelectronic and microelectronic cleaning compositions of this invention. Such materials include, but are not limited to, carbon dioxide, ammonia, argon, butane, carbon disulfide, chlorotrifluoromethane, 2, 2'-dimethylpropane, ethane, fluoromethane, hexane, hydrogen sulfide, methanol, nitrogen, nitrogen oxide,
25 pentane, propane, sulfur dioxide, trifluoromethane, 2-propanol, dichloromethane, sulfur hexafluoride, nitrous oxide, carbon monoxide, and inert gases such as nitrogen, helium, neon, argon, krypton and xenon. Carbon dioxide is generally preferred since it forms supercritical fluid readily with critical temperature of 31 °C and critical pressure of 73.77 bar (72.8 atm, 1,070 psi).

[0015] In formulation a) of component (2) of the cleaning compositions of this invention, the oxidizing agent of formulation a) may be any oxidizing agent suitable for use in nanoelectronic and microelectronic cleaning compositions. As
5 examples of such oxidizing agents there may be mentioned, for example, peroxides, particularly hydrogen peroxide, molecular adducts of peroxyhydrates from hydrogen peroxides and oxyacids, zirconyl acetate and azo compounds, e.g., sodium percarbonate, sodium perborates, as well as periodates (IO_4^-), perborates, permanganates (MnO_4^-), hydrogen persulfates, persulfates and alkyloxyhalides, for
10 example t-BuOCl. Other peroxy compounds from substitution reactions of H_2O_2 and organic molecules may be employed but are less preferred. Examples include alkylperoxides, peroxyacids, diacyl peroxides and ketone peroxides. Similar substitution products of H_2O_2 with inorganic molecules, such as peroxysulfuric acid, may also be employed. The oxidizing agent is employed in the formulation a) in an
15 amount of from about 0.1 to about 30 wt%, preferably from about 0.1 to about 5 wt%, and most preferably in an amount of from about 1 to about 5 wt% of formulation a). The preferred oxidizing agent is hydrogen peroxide (H_2O_2), preferably employed as a 3 to 30% aqueous solution.

[0016] In formulation a) of component (2), the organic solvent is a polar organic solvent with hydrogen bonding capability and which is minimally or non-reactive with the oxidizing agent. Such organic solvents include amides, sulfones, sulfolenes, selenones, and saturated alcohols. Among the preferred solvents there may be mentioned sulfolane (tetrahydrothiophene-1,1-dioxide), 3-methylsulfolane,
20 n-propyl sulfone, n-butyl sulfone, sulfolene (2,5-dihydrothiophene-1,1-dioxide), 3-methylsulfolene, amides such as 1-(2-hydroxyethyl) -2-pyrrolidinone (HEP), dimethylpiperidone (DMPD), N-methyl pyrrolidinone (NMP), and dimethylacetamide (DMAc), dimethylformamide (DMF), and saturated alcohols
25 such as ethanol, propanol, butanol, hexanol, ethylene glycol, propylene glycol,

glycerol, and hexafluoroisopropanol. The organic solvent component can include one or more of the solvents and is generally present in the formulation a) in an amount of from about 1 to about 99.9 wt%, preferably in an amount of from about 10 to about 90 wt%, and most preferably in an amount of from about 30 to 80 wt% of formulation a). These solvents are resistant to acidic and alkaline conditions and will not bind the oxidizing agent too tightly. Additionally, they are capable of stabilizing the oxidizing agent, such as hydrogen peroxide, by forming stable complexes through interaction such as hydrogen bonding.

[0017] Water can be present in the formulation a) of component (2) of the cleaning compositions of this invention and when present can be present in an amount of from about 0.1 to about 98 wt%, preferably in an amount of from about 10 to about 60 wt%, most preferably in an amount of from about 15 to about 50 wt% of the formulation a). The water can be present as part of the aqueous portion of the other components and/or as additional added water.

[0018] The alkaline base is present as an optional, but generally preferred component of the formulation a) of component (2) of the cleaning compositions of this invention. The alkaline base can be present in the formulation in an amount of from 0 to about 30 wt%, preferably in an amount of from about 0.1 to about 10 wt%, most preferably in an amount of from about 0.1 to about 5 wt% of formulation a). Any suitable alkaline base may be employed in formulation a) of the cleaning compositions. The base is preferably ammonia hydroxide or an ammonia or non-ammonia derived base. When the cleaning composition of this invention is intended to be used to clean copper metallized structures the base is preferably a non-ammonia derived base and when the cleaning composition of this invention is intended to be used to clean aluminum containing structures the alkaline base is preferably ammonium hydroxide, a ammonia derived base, or a non-ammonia derived base in combination with a corrosion-inhibiting co-solvent and/or corrosion-

inhibiting agent, as disclosed hereinafter. As examples of suitable non-ammonia derived bases there may be mentioned tetraalkylammonium hydroxides such as those of the formula $R_4N^+OH^-$ where each R is independently a substituted or unsubstituted alkyl groups, preferably of 1 to 22 carbon atoms and more preferably 1 to 4 carbon atoms. Among the non-ammonia derived alkaline bases useful in the formulation a) component there may be mentioned, for example, tetramethylammonium hydroxide, tetrabutylammonium hydroxide, choline hydroxide, and the like. Inorganic bases such as for example potassium hydroxide, sodium hydroxide and the like may also be used as the alkaline base.

[0019] As indicated before, the formulation a) of component (2) of the cleaning composition of this invention can also be employed under acid pH conditions and any suitable acid component can be employed in the necessary amount sufficient to provide the acidic pH to the composition, such as for example HCl or HF.

[0020] The formulation a) of component (2) of the cleaning composition may also optionally include one or more corrosion-inhibiting co-solvents. Preferred corrosion-inhibiting co-solvents useful in the formulation a) of this invention are those of the general formula



where R_1 and R_2 are each independently selected from H, alkyl, preferably alkyl of from 1 to 6 carbon atoms, aryl, preferably aryl of from 3 to 14 carbon atoms, OR_3 and SO_2R_4 ; n is a numeral of from 2 to 6, preferably 2 or 3; W and Y are each independently selected from OR_3 , and SO_2R_4 ; and R_3 and R_4 are each independently selected from H, alkyl, preferably alkyl of from 1 to 6 carbon atoms, and aryl, preferably aryl of from 3 to 14 carbon atoms. As examples of

such corrosion-inhibiting co-solvents there may be mentioned, for example, ethylene glycol, propylene glycol and glycerol and the like. If the required polar organic solvent component of the formulation a) is not a saturated alcohol within the above-mentioned formula, such a saturated alcohol may be present as a co-solvent. The co-solvents may be present in the formulation a) in an amount of from 0 to about 80 wt%, preferably from about 1 to about 50 wt%, most preferably from about 1 to 30 wt% of formulation a).

[0021] Formulation a) of component (2) of the cleaning compositions of this invention may also contain other corrosion-inhibiting agents, preferably aryl compounds containing two or more OH, OR₆, and/or SO₂R₆R₇ groups bonded directly to the aromatic ring, where R₆, R₇ and R₈ are each independently alkyl, preferably alkyl of from 1 to 6 carbon atoms, or aryl, preferably aryl of from 6 to 14 carbon atoms. As examples of such preferred corrosion-inhibiting agents there may be mentioned catechol, pyrogallol, gallic acid, resorcinol and the like. Such other corrosion-inhibiting agents may be present in formulation a) in an amount of from 0 to about 15 wt%, preferably from about 0.1 to about 10 wt%, most preferably from about 0.5 to about 5 wt% of formulation a).

[0022] Organic or inorganic chelating or metal complexing agents are not required in formulation a) of component (2), but offer substantial benefits, such as for example, improved product stability. Examples of suitable chelating or complexing agents include but are not limited to trans-1,2-cyclohexanediamine tetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, alkylidene-diphosphonic acid derivatives (e.g. ethane-1-hydroxy-1,1-diphosphonate), phosphonates containing ethylenediamine, diethylenetriamine or triethylenetetramine functional moieties [e.g. ethylenediamine tetra(methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), triethylenetetramine hexa(methylene phosphonic acid)]. The chelating agent will be

present in the composition in an amount of from 0 to about 5 wt%, preferably from about 0.1 to about 2 wt% of formulation a). Metal chelating or complexing agents of various phosphonates, such as ethylenediamine tetra(methylene phosphonic acid) (EDTMP) offer much improved stabilization of the cleaning compositions of the cleaning compositions of this invention containing oxidizing agents at acidic and alkaline conditions and thus are generally preferred.

[0023] Other stabilizers for oxidizing agents can also be employed in formulation a) of component (2) of the cleaning compositions of this invention if desired. These stabilizers may be employed in an amount ranging from 0 to about 10 wt%, preferably from about 0.1 to 5 wt% of formulation a). Examples of such stabilizer include but are not limited to acetanilide and silicates, preferably metal ion-free silicates such as tetraalkylammonium silicates (including hydroxy- and alkoxy alkyl groups) where the alkyl group, preferably contains from 1 to 4 carbon atoms. Among such silicates are tetraethylorthosilicate, tetramethylammonium silicate, tetrakis(2-hydroxyethyl) orthosilicate and the like.

[0024] Other metal corrosion inhibitors, such as benzotriazole, may be employed in formulation a) of component (2) in an amount of from 0 to about 5 wt%, preferably from about 0.1 to 2 wt% of formulation a).

[0025] Formulation a) of component (2) of the cleaning compositions of this invention optionally may also contain surfactants, such as for example dimethyl hexynol (Surfynol-61), ethoxylated tetramethyl decynediol (Surfynol-465), polytetrafluoroethylene cetoxypopylbetaine (Zonyl FSK), Zonyl FSH and the like. The surfactant will generally be present in formulation a) in an amount of from 0 to about 5 wt%, preferably 0.1 to about 3 wt% of formulation a).

[0026] Formulation a) of component (2) of the cleaning compositions of this invention may also optionally contain fluoride compounds in cleaning composition, such as for example, tetramethylammonium fluoride, tetrabutylammonium fluoride, and ammonium fluoride. Other suitable fluorides include, for example fluoroborates, tetrabutylammonium fluoroborates, aluminum hexafluorides, antimony fluoride and the like. The fluoride components will be present in formulation a) in an amount of from 0 to 10 wt%, preferably from about 0.1 to 5 wt% of formulation a).

[0027] Examples of formulation a) of component (2) of the cleaning compositions of this invention are set forth in the following formulations in Tables 1 to 9, in which the amount of the components are indicated in parts by weight of the formulation.

In the following Tables the abbreviations employed are as follows.

HEP= 1-(2-hydroxyethyl)-2-pyrrolidinone

TMAH= tetramethylammonium hydroxide

TMAF= tetramethylammonium fluoride

ACA= acetanilide

CyDTA= trans-1,2-cyclohexanediamine tetraacetic acid

TEOS= tetraethylorthosilicate

DMPD= dimethylpiperidone

SFL= sulfolane

TMAS= tetramethylammonium silicate

EG= ethylene glycol

CAT=catechol

EHDP= ethane-1-hydroxy-1,1-diphosphonate

EDTMP= ethylenediamine tetra(methylene phosphonic acid)

1N HCl= 1 normal hydrochloric acid

NH₄OH=ammonium hydroxide

CH=choline hydroxide

Water= additional water over water from aqueous solution of components.

5 Also in the following Tables the formulations XM-188, XM-188A and XM-191 refer to the following compositions in which the listed components are present in the parts by weight indicated in the parenthesis.

XM-188= SFL (300), Water (75), 25% TMAH (25), CyDTA (2.3)

XM-188A= SFL (150), Water (60), 25% TMAH (17.5), EDTMP (1.8)

XM-191= SFL (150), Water (60), 25% TMAH (17.5), EDTMP (1.8), EG (30)

TABLE 1
Formulations

Component	A	B	C	D	E	F	G
HEP	30	30	30	30		60	
25% TMAH	2	2.6	2	2	2	5	5
ACA	0.2	0.2					
CyDTA		0.2				0.4	0.4
TEOS			1				
DMPD					30		60
SFL							
EG							
CAT							
60% EHDP							
EDTMP							
TMAF							
10% TMAH							
29% NH ₄ OH							
30% H ₂ O ₂	2.5	2.5	2.5	2.5	2.5	5	5
Water	15	15	15	15	15	30	30
XM-188							
XM-188A							
XM-191							
1N HCl							
20% CH							

TABLE 2
Formulations

Component	H	I	J	K	L	M	N
HEP	30						
25% TMAH	1	10	8.8		4	3	4.9
ACA							
CyDTA		0.92			0.35		0.24
TEOS							
DMPD							
SFL		120			50	30	37
EG					10		
CAT							
60% EHDP						0.24	0.29
EDTMP							
TMAF							
10% TMAH	1						
29%NH ₄ OH							
30% H ₂ O ₂	2	10	8.8	2.5	4.2	2.5	4
Water	15	60					9
XM-188			40	40			
XM-188A							
XM-191							
1N HCl							
20% CH							

TABLE 3
Formulations

Component	O	P	Q	R	S	T	U
HEP							
25% TMAH	5	20	4.4		7.8		
ACA							
CyDTA							
TEOS							
DMPD							
SFL		200	37.5		42.5		
EG						10.3	15
CAT							
60% EHDP	1.5	2.6					
EDTMP			0.68				
TMAF							2
10% TMAH							
29% NH ₄ OH							
30% H ₂ O ₂	19.2	18.7	4.8	5	4.3		5
Water	20	70	22.5		10.6	3.5	
XM-188	200					40	
XM-188A				57.4			40
XM-191							
1N HCl							
20% CH							

TABLE 4
Formulations

Component	V	W	X	Y	Z	AA	BB
HEP							
25% TMAH							
ACA							
CyDTA	0.39				0.39		
TEOS							
DMPD							
SFL	50			50	50	50	40
EG		15	15				
CAT		3			3.5	3.5	1.5
60% EHDP							
EDTMP				0.6		0.6	0.6
TMAF							
10% TMAH							
29% NH ₄ OH	1.4			1.9	1.4	1.9	2
30% H ₂ O ₂	6.4	5.8	5.5	7.2	6.7	6.7	7.6
Water	12.5			20	12.5	20	30
XM-188		40	40				
XM-188A							
XM-191							
1N HCl							
20% CH							

TABLE 5
Formulations

Component	CC	DD	EE	FF	GG	HH	II
HEP							
25% TMAH			2				
ACA							
CyDTA	0.39						
TEOS							
DMPD							
SFL	50	50		60		60	
EG					50		
CAT							
60% EHDP							
EDTMP		0.6					
TMAF							
10% TMAH							
29%NH ₄ OH	1.7	2.2					
30% H ₂ O ₂	7	7.3	5	5	5	6.2	2.5
Water	12.5	20					
XM-188							40
XM-188A			57				
XM-191							
1N HCl						1	
20% CH							

TABLE 6
Formulations

Component	JJ	KK	LL	MM	NN	OO
HEP						
25% TMAH	5	5	6		5	6
ACA						
CyDTA						
TEOS						
DMPD						
SFL						
EG						
CAT						
60% EHDP						
EDTMP						
TMAF						
10% TMAH						
29%NH ₄ OH						
30% H ₂ O ₂	7	7.5	6	2.5	7	6
Water		5				
XM-188			80	40		80
XM-188A						
XM-191	62.5	64.5			62.5	
1N HCl						1
20% CH						

TABLE 7
Formulations

Component	PP	QQ	RR	SS	TT	UU	VV
HEP							
25% TMAH	25	25	20	25	17.5	17.5	2.5
ACA							
CyDTA	3	3	2.5	1.5			0.23
TEOS							
DMPD							
SFL	300	300	300	300	150	150	30
EG	5				40	20	15
CAT							3
60% EHDP							
EDTMP					1.8	1.8	
TMAF							
10% TMAS							
29% NH ₄ OH							
30% H ₂ O ₂	36.8	37.3	36.7	37.2	26	24	5.8
Water	35	45	45	45	50	50	7.5
XM-188							
XM-188A							
XM-191							
1N HCl							
20% CH							

TABLE 8
Formulations

Component	WW	XX	YY	ZZ	AAA	BBB	CCC
HEP							
25% TMAH					3.1	7.5	
ACA							
CyDTA	0.39		0.39		0.28	1.2	0.8
TEOS							
DMPD						7.5	
SFL	50	50	50	50	74		75
EG							
CAT	3.5	3.5					
60% EHDP							
EDTMP		0.6		0.6			
TMAF							
10% TMAH							
29% NH ₄ OH	1.4	1.9	1.4	1.9			
30% H ₂ O ₂	6.8	7.6	6.4	7.25	14.7	13.6	14
Water	12.5	20	12.5	20	40	25	25
XM-188							
XM-188A							
XM-191							
1N HCl							
20% CH							12

TABLE 9
Formulations

Component	DDD	EEE
HEP		75
25% TMAH	6.25	7.5
ACA		
CyDTA	0.6	1.2
TEOS		
DMPD		
SFL		
EG	75	
CAT		
60% EHDP		
EDTMP		
TMAF		
10% TMAH		
29% NH ₄ OH		
30% H ₂ O ₂	13.4	13.6
Water	25	25
XM-188		
XM-188A		
XM-191		
1N HCl		

[0028] In formulation b) of component (2) of the cleaning compositions of this invention, the polar organic solvent is a solvent with hydrogen bonding capability and which is minimally or non-reactive with the oxidizing agent. Such organic solvents include amides, sulfones, sulfolenes, selenones, and saturated alcohols. Among the preferred solvents there may be mentioned sulfolane (tetrahydrothiophene-1,1-dioxide), 3-methylsulfolane, n-propyl sulfone, n-butyl sulfone, sulfolene (2,5-dihydrothiophene-1,1-dioxide), 3-methylsulfolene, amides such as 1-(2-hydroxyethyl)-2-pyrrolidinone (HEP), dimethylpiperidone (DMPD), N-methyl pyrrolidinone (NMP), and dimethylacetamide (DMAc), dimethylformamide (DMF), and saturated alcohols such as ethanol, propanol, butanol, hexanol, ethylene glycol, propylene glycol, glycerol, and hexafluoroisopropanol. The organic solvent component of formulation b) can include one or more of the solvents and is generally present in the formulation b) in an amount of from about 1 to about 99.9 wt%, preferably in an amount of from about 10 to about 90 wt%, and most preferably in an amount of from about 30 to 80 wt% of formulation b). These solvents are resistant to acidic and alkaline conditions and will not bind with oxidizing agents too tightly. Additionally, when the formulation of this invention are combined with a oxidizing agent they are capable of stabilizing the oxidizing agent, such as hydrogen peroxide, by forming stable complexes through interaction such as hydrogen bonding.

[0029] The alkaline base in formulation b) of component (2) of the cleaning compositions of this invention can be present in an amount of from 0.1 to about 30 wt%, preferably in an amount of from about 0.1 to about 10 wt%, most preferably in an amount of from about 0.1 to about 5 wt% of formulation b). Any suitable alkaline base may be employed in formulation b) of component (2) of the cleaning compositions of this invention. The base is preferably ammonia hydroxide or an ammonia or non-ammonia derived base. When the cleaning composition of this invention is intended to be used to clean copper metallized structures the base is preferably a non-ammonia derived base and when the cleaning composition of this

invention is intended to be used to clean aluminum containing structures the alkaline base is preferably ammonium hydroxide, a ammonia derived base, or a non-ammonia derived base in combination with a corrosion-inhibiting co-solvent and/or corrosion-inhibiting agent, as disclosed hereinafter. As examples of suitable non-ammonia derived bases there may be mentioned tetraalkylammonium hydroxides such as those of the formula $R_4N^+OH^-$ where each R is independently a substituted or unsubstituted alkyl groups, preferably of 1 to 22 carbon atoms and more preferably 1 to 4 carbon atoms. Among the non-ammonia derived alkaline bases useful in the compositions there may be mentioned, for example, tetramethylammonium hydroxide, tetrabutylammonium hydroxide, choline hydroxide, and the like. Inorganic bases such as for example potassium hydroxide, sodium hydroxide and the like may also be used as the alkaline base.

[0030] Water can be present in formulation b) of component (2) of the cleaning compositions of this invention and when present can be present in an amount of from about 0.1 to about 98 wt%, preferably in an amount of from about 10 to about 60 wt%, most preferably in an amount of from about 15 to about 50 wt% of formulation b). The water can be present as part of the aqueous portion of the other components and/or as additional added water.

[0031] The cleaning composition of this invention can also be employed under acid pH conditions and any suitable acid component can be employed in formulation b) of component (2) of the cleaning compositions of this invention in the necessary amount sufficient to provide the acidic pH to the composition, such as for example HCl or HF.

[0032] Formulation b) of component (2) of the cleaning compositions of this invention may also optionally include one or more corrosion-inhibiting co-solvents. Preferred corrosion-inhibiting co-solvents useful in the compositions of this

invention are those of the general formula



5 where R_1 and R_2 are each independently selected from H, alkyl, preferably alkyl of from 1 to 6 carbon atoms, aryl, preferably aryl of from 3 to 14 carbon atoms, OR_3 and SO_2R_4 ; n is a numeral of from 2 to 6, preferably 2 or 3; W and Y are each independently selected from OR_3 , and SO_2R_4 ; and R_3 and R_4 , are each
10 independently selected from H, alkyl, preferably alkyl of from 1 to 6 carbon atoms, and aryl, preferably aryl of from 3 to 14 carbon atoms. As examples of such corrosion-inhibiting co-solvents there may be mentioned, for example, ethylene glycol, propylene glycol and glycerol and the like. If the required polar organic solvent component of the formulation b) is not a saturated alcohol within the above-mentioned formula, such a saturated alcohol may be present as a co-
15 solvent. The co-solvents may be present in the composition in an amount of from 0 to about 80 wt%, preferably from about 1 to about 50 wt%, most preferably from about 1 to 30 wt% of formulation b).

[0032] Formulation b) of component (2) of the cleaning compositions of this
20 invention may also contain other corrosion-inhibiting agents, preferably aryl compounds containing two or more OH, OR_5 and/or SO_2R_6 groups bonded directly to the aromatic ring, where R_5 , and R_6 are each independently alkyl, preferably alkyl of from 1 to 6 carbon atoms, or aryl, preferably aryl of from 6 to 14 carbon atoms. As examples of such preferred corrosion-inhibiting agents
25 there may be mentioned catechol, pyrogallol, gallic acid, resorcinol and the like. Such other corrosion-inhibiting agents may be present in formulation b) in an amount of from 0 to about 15 wt%, preferably from about 0.1 to about 10 wt%, most preferably from about 0.5 to about 5 wt% of formulation b)

5 **[0033]** Organic or inorganic chelating or metal complexing agents are not required, but offer substantial benefits, such as for example, improved product stability if present in formulation b) of component (2) of the cleaning compositions of this invention. Examples of suitable chelating or complexing agents include but are not limited to trans-1,2-cyclohexanediamine tetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, alkylidene-diphosphonic acid derivatives (e.g. ethane-1-hydroxy-1,1-diphosphonate), phosphonates containing ethylenediamine, diethylenetriamine or triethylenetetramine functional moieties [e.g. ethylenediamine tetra(methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), triethylenetetramine hexa(methylene phosphonic acid). The chelating agent will be present in formulation b) in an amount of from 0 to about 5 wt%, preferably from about 0.1 to about 2 wt% of formulation b). Metal chelating or complexing agents of various phosphonates, such as ethylenediamine tetra(methylene phosphonic acid) (EDTMP) offer much improved stabilization of the formulation b) when they are combined with oxidizing agents at acidic and alkaline conditions and thus are generally preferred.

20 **[0034]** Optionally other metal corrosion inhibitors, such as benzotriazole, may be employed in formulation b) of component (2) of the cleaning compositions of this invention an amount of from 0 to about 5 wt%, preferably from about 0.1 to 2 wt% of formulation b).

25 **[0035]** Formulation b) of component (2) of the cleaning compositions of this invention optionally may also contain surfactants, such as for example dimethyl hexynol (Surfynol-61), ethoxylated tetramethyl decynediol (Surfynol-465), polytetrafluoroethylene cetoxypropylbetaine (Zonyl FSK), Zonyl FSH and the like. The surfactant will generally be present in formulation b) in an amount of from 0 to

about 5 wt%, preferably 0.1 to about 3 wt% of formulation b).

[0036] Formulation b) of component (2) of the cleaning compositions of this invention may also optionally contain fluoride compounds in the formulation, such as for example, tetramethylammonium fluoride, tetrabutylammonium fluoride, and ammonium fluoride. Other suitable fluorides include, for example fluoroborates, tetrabutylammonium fluoroborates, aluminum hexafluorides, antimony fluoride and the like. The fluoride components will be present in formulation b) in an amount of from 0 to 10 wt%, preferably from about 0.1 to 5 wt% of formulation b).

[0037] Formulation b) of component (2) of the cleaning compositions of this invention can be employed in combination with oxidizing agents. Such formulations can contain any oxidizing agent suitable for use in nanoelectronic and microelectronic cleaning compositions. As examples of such oxidizing agents there may be mentioned, for example, peroxides, particularly hydrogen peroxide, molecular adducts of peroxyhydrates from hydrogen peroxides and oxyacids, zirconyl acetate and azo compounds, e.g., sodium percarbonate, sodium perborates, as well as periodates (IO_4^-), perborates, permanganates (MnO_4^-), hydrogen persulfates, persulfates and alkyloxyhalides, for example t-BuOCl. Other peroxy compounds from substitution reactions of H_2O_2 and organic molecules may be employed but are less preferred. Examples include alkylperoxides, peroxyacids, diacyl peroxides and ketone peroxides. Similar substitution products of H_2O_2 with inorganic molecules, such as peroxysulfuric acid, may also be employed. When the formulations b) of this invention are combined with an oxidizing agent the oxidizing agent is employed in the resulting cleaning compositions in an amount of from about 0.1 to about 30 wt%, preferably from about 0.1 to about 5 wt%, and most preferably in an amount of from about 0.5 to about 5 wt% of formulation b). The preferred oxidizing agent is hydrogen peroxide (H_2O_2), preferably employed as a 3 to 30% aqueous solution.

[0038] Examples of formulations b) of component (2) of the cleaning composition of this invention are set forth in the following Tables 10 to 13, in which the amount of the components are indicated in parts by weight of the formulation.

In the following Tables the abbreviations employed are as follows.

TMAH= 25% Tetramethylammonium hydroxide

HEP=1-(2hydroxyethyl)-2-pyrrolidinone.

CyDTA= trans-1,2-cyclohexanediamine tetraacetic acid

DMPD= dimethylpiperidone

SFL= sulfolane

EG= ethylene glycol

CAT=catechol

EDTMP= ethylenediamine tetra(methylene phosphonic acid)

NH₄OH= ammonium hydroxide

CH=choline hydroxide

Water= additional water over water from aqueous solution of
components.

TABLE 10
Formulations

Component	A	B	C	D	E	F
25% TMAH	25	17.5	10	2.5	2	9
HEP						
SFL	300	150		30	50	
CyDTA	2.3		0.9	0.23	0.19	1.15
EDTMP		1.8				
DMPD			120			
EG		30		15		200
CAT				3		
29% NH ₄ OH						
20% CH						
H ₂ O	75	60	60	7.5	12.5	

TABLE 11
Formulations

Component	G	H	I	J	K	L
25% TMAH	25	25	20	25	17.5	17.5
HEP						
SFL	300	300	300	300	150	150
CyDTA	3	3	2.5	1.5		
EDTMP					1.8	1.8
DMPD						
EG	5	30			40	20
CAT						
29% NH ₄ OH						
20% CH						
H ₂ O	35	45	45	45	50	50

TABLE 12
Formulations

Component	M	N	O	P	Q	R
25% TMAH	2.5					3.1
HEP						
SFL	30	50	50	50	50	74
CyDTA	0.23	0.39		0.39		0.28
EDTMP			0.6		0.6	
DMPD						
EG	15					
CAT	3	3.5	3.5			
29% NH ₄ OH		1.4	1.9	1.4	1.9	
20% CH						
H ₂ O	7.5	12.5	20	12.5	20	40

5

TABLE 13
Formulations

Component	S	T	U	V
25% TMAH	7.5	17.5	6.25	7.5
HEP				75
SFL		75		
CyDTA	1.2	0.8	0.6	1.2
EDTMP				
DMPD	75			
EG				
CAT				
29% NH ₄ OH				
20% CH		12		
H ₂ O	25	25	25	25

[0039] Formulation c) of component (2) of the cleaning compositions of this invention will comprise one or more of any suitable non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions and one or more of any suitable solvent stable under strong alkaline conditions and having a metal-corrosion inhibiting arm in the solvent compound. Among the suitable non-ammonia producing strong bases containing non-nucleophilic, positively charged counter ions suitable for use in the cleaning compositions of this invention there may be mentioned tetraalkylammonium hydroxides or salts of the formula $[(R)_4N^+]_p [X^{-q}]$, where each R is independently a substituted or unsubstituted alkyl, preferably alkyl of from 1 to 22, and more preferably 1 to 6, carbon atoms ($R \neq H$); and $X=OH$ or a suitable salt anion, such as carbonate and the like; p and q are equal and are integer of from 1 to 3. Suitable strong bases also include KOH and NaOH. Cleaning compositions of this invention containing a formulation c) as component (2) and containing the non-ammonium producing strong bases containing non-nucleophilic, positively charged counter ions show much improved compatibility with porous and low- κ dielectrics and copper metallization. Ammonia-free tetraalkylammonium hydroxides (TAAH) are very strong bases, yet they have been discovered to provide surprisingly improved compatibility with porous and low- κ dielectrics compared to cleaning compositions with ammonium hydroxide. Especially preferred are tetramethylammonium hydroxide, tetrabutylammonium hydroxide and choline hydroxide.

[0040] Formulation c) of component (2) of the cleaning compositions of this invention contain one or more "corrosion inhibiting solvent", i.e., a solvent compound that has at least two sites capable of complexing with metal is employed. Preferred as such corrosion inhibiting solvents are compounds having two or more sites capable of complexing with a metal and having one of the two following general formulae:



or



5 where W and Y are each independently selected from =O, -OR, -O-C(O)-R, -C(O)-, -C(O)-R, -S, -S(O)-R, -SR, -S-C(O)-R, -S(O)₂-R, -S(O)₂, -N, -NH-R, -NR₁R₂, -N-C(O)-R, -NR₁-C(O)-R₂, -P(O), -P(O)-OR and -P(O)-(OR)₂; X is
10 alkylene, cycloalkylene or cycloalkylene containing one or more hetero atoms selected from O, S, N and P atoms, and arylene or arylene containing one or more hetero atoms selected from O, S, N and P atoms; each R, R₁ and R₂ are each independently selected from hydrogen, alkyl, cycloalkyl or cycloalkyl containing one or more hetero atoms selected from O, S, N and P atoms, and aryl or aryl containing one or more hetero atoms selected from O, S, N and P
15 atoms; each of n₁ and n₂ is independently an integer of from 0 to 6; and z is an integer of from 1 to 6 when X is alkylene, cycloalkylene or arylene; and z is an integer of from 0 to 5 when X is cycloalkylene containing one or more hetero atoms selected from O, S, N and P atoms or arylene containing one or more hetero atoms selected from O, S, N and P atoms; T is selected from -O, -S, -N and -P; Z is selected from hydrogen, -OR₅, -N(R₅)₂, and -SR₅; each of R₃, R₄ and R₅ are each independently selected from hydrogen, alkyl, cycloalkyl or cycloalkyl containing one or more hetero atoms selected from O, S, N and P atoms, and aryl or aryl containing one or more hetero atoms selected from O, S, N and P
20 atoms; m is an integer of from 0 to 6 and y is an integer of from 1 to 6. In the above definitions alkyl and alkylene are preferably of from 1 to 6 carbon atoms, more preferably of from 1 to 3 carbon atoms, cycloalkyl and cycloalkylene preferably contain from 3 to 6 carbon atoms, and aryl and arylene preferably contain from about 3 to 14 carbon atoms, more preferably from about 3 to 10 carbon atoms. Alkyl is preferably methyl, ethyl or propyl; alkylene is preferably
25 methylene, ethylene or propylene; aryl is preferably phenyl; arylene is preferably phenylene; hetero-substituted cycloalkyl is preferably dioxyl, morpholinyl and pyrrolidinyl; and hetero-substituted aryl is preferably pyridinyl.
30

[0041] Some suitable examples are of such corrosion inhibiting solvents employed in formulation c) of component (2) of the cleaning compositions of this invention include, for example, but are not limited to ethylene glycol, diethylene glycol, glycerol, diethylene glycol dimethyl ether, monoethanolamine, diethanolamine, triethanolamine, N,N-dimethylethanolamine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 4-(2-hydroxyethyl)morpholine, 2-(methylamino)ethanol, 2-amino-2-methyl-1-propanol, 1-amino-2-propanol, 2-(2-aminoethoxy)-ethanol, N-(2-hydroxyethyl) acetamide, N-(2-hydroxyethyl) succinimide and 3-(diethylamino)-1,2-propanediol.

[0042] Formulation c) of component (2) of the cleaning compositions of this invention containing the non-ammonium producing strong bases can be formulated into aqueous, semi-aqueous or organic solvent-based compositions. The non-ammonium producing, strong bases containing non-nucleophilic, positively charged counter ions can be used with corrosion inhibiting solvents alone or in combination with other stable solvents, preferably one or more polar organic solvents resistant to strong bases and that do not contain unhindered nucleophiles, such as dimethyl sulfoxide (DMSO), sulfolane (SFL), and dimethyl piperidone. The formulation c) of component (2) of the cleaning compositions of this invention may also optionally contain organic or inorganic acids, preferably weak organic or inorganic acids, hindered amines, hindered alkanolamines, and hindered hydroxylamines. Formulation c) of component (2) of the cleaning compositions of this invention can also contain other metal corrosion inhibitors, such as benzotriazole, and aryl compounds containing 2 or more OH or OR groups, where R is alkyl or aryl, such as for example, catechol, pyrogallol, resorcinol and the like. The formulation c) of component (2) of the cleaning compositions of this invention may also contain any suitable surfactants, such as for example dimethyl hexynol (Surfynol-61), ethoxylated tetramethyl decynediol (Surfynol-465), polytetrafluoroethylene cetoxypopylbetaine (Zonyl FSK), (Zonyl FSH) and the like.

[0043] Any suitable metal ion-free silicate may be used in the formulation c) of component (2) of the cleaning compositions of this invention. The silicates are preferably quaternary ammonium silicates, such as tetraalkyl ammonium silicate (including hydroxy- and alkoxy-containing alkyl groups generally of from 1 to 4 carbon atoms in the alkyl or alkoxy group). The most preferable metal ion-free silicate component is tetramethyl ammonium silicate. Other suitable metal ion-free silicate sources for this invention may be generated *in-situ* by dissolving any one or more of the following materials in the highly alkaline cleaner. Suitable metal ion-free materials useful for generating silicates in the cleaner are solid silicon wafers, silicic acid, colloidal silica, fumed silica or any other suitable form of silicon or silica. Metal silicates such as sodium metasilicate may be used but are not recommended due to the detrimental effects of metallic contamination on integrated circuits. The silicates may be present in the formulation c) of component (2) of the cleaning compositions of this invention in an amount of from about 0 to 10 wt. %, preferably in an amount of from about 0.1 to about 5 wt. % of the formulation c).

[0044] The formulation c) of component (2) of the cleaning compositions of this invention may also be formulated with suitable metal chelating agents to increase the capacity of the formulation to retain metals in solution and to enhance the dissolution of metallic residues on the wafer substrate. The chelating agent will generally be present in the formulation c) of component (2) of the cleaning compositions of this invention in an amount of from about 0 to 5 wt. %, preferably from an amount of from about 0.1 to 2 wt. % of the formulation c). Typical examples of chelating agents useful for this purpose are the following organic acids and their isomers and salts: (ethylenedinitrilo)tetraacetic acid (EDTA), butylenediaminetetraacetic acid, (1,2-cyclohexylenedinitrilo)tetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DTPA), 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, nitrolotriacetic 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, catechol, gallic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, and cysteine. Preferred chelating agents are aminocarboxylic acids such as EDTA, CyDTA and aminophosphonic acids such as EDTMP.

[0045] The formulation c) of component (2) of the cleaning compositions of this invention may also optionally contain fluoride compounds in the formulation, such as for example, tetramethylammonium fluoride, tetrabutylammonium fluoride, and ammonium fluoride. Other suitable fluorides include, for example fluoroborates, tetrabutylammonium fluoroborates, aluminum hexafluorides, antimony fluoride and the like. The fluoride components will be present in the formulation c) of component (2) of the cleaning compositions of this invention an amount of from 0 to 10 wt. %, preferably from about 0.1 to 5 wt. % of formulation c).

[0046] In the following Tables the following abbreviations are employed to designate the indicated components.

HEP=1-(2-hydroxyethyl)-2-pyrrolidinone

TMAH= 25% tetramethylammonium hydroxide

BT=benzotriazole

DMSO=dimethyl sulfoxide

TEA=triethanolamine

CyDTA=trans-1,2-cyclohexanediamine tetraacetic acid

SFL=sulfolane

EG=ethylene glycol

CAT=catchol

EDTMP=ethylenediamine tetra(methylene phosphonic acid)

DMPD=dimethylpiperidone

TMAF=25% tetramethylammonium fluoride

BSA=benzenesulfonic acid

TMAS=10% tetramethylammonium silicate

[0047] Examples of the types of formulation c) of component (2) of the cleaning compositions of this invention are set forth in the following Tables 14, 15, and 16 in which the amounts of the components are indicated in parts by weight.

TABLE 14
Formulations

Component	A	B	C	D	E	F	G	H
HEP	90							90
H ₂ O		7	8	32	16	12		8
TMAH	10.8	15	16	16	16	24	10	2.7
BT	0.11							0.11
DMSO		16						
TEA		16	16	16		24	10	
CyDTA			0.2	0.2		0.3		
SFL			16	16	24	24	40	
EG								
CAT								
EDTMP								
DMPD								

TABLE 15
FORMULATIONS

Component	I	J	K	L
HEP				
H ₂ O	54	54	32	32
TMAH	45	36	4	16
BT				
DMSO		16		
TEA	36	36	16	16
CyDTA			0.4	
SFL			16	16
EG	54	54	48	
CAT			6	
EDTMP	0.36	0.36		0.4
DMPD				16

In Table 16 there are described variations of Compositions D and F of Table 13 with additional added optional components.

TABLE 16
FORMULATIONS

Component	M	N	O	P	Q	R	S
Composition D	100	100	100				100
Composition F				100	100	100	
TMAF	2.5			2.5			
TMAH		2			2		2
H ₂ O				10	10	10	
BSA			2			2	
H ₂ SO ₄		0.5			0.5		0.5
TMAS							1

5 **[0048]** The formulation d) of component (2) of the cleaning compositions of this invention will comprise one or more of any suitable non-ammonium producing, non-HF producing fluoride salt (non-ammonium, quaternary ammonium fluoride salt) in a suitable solvent. Among the suitable non-ammonia producing, non-HF producing fluoride salts there may be mentioned tetraalkylammonium fluorides of
10 the formula $(R)_4N^+ F^-$, where each R is independently a substituted or unsubstituted alkyl, preferably alkyl of from 1 to 22, and more preferably 1 to 6, carbon atoms ($R \neq H$), such as tetramethylammonium fluoride and tetrabutylammonium fluoride salts; as well as fluoroborates, tetrabutylammonium fluoroborates, aluminum hexafluorides, antimony fluoride and the like.

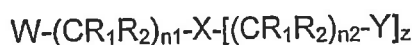
15

20 **[0049]** The non-ammonium producing, non-HF producing fluoride salts show significantly improved compatibility with low- κ dielectrics and copper metallization. Tetraalkylammonium salts, such as tetramethylammonium fluoride (TMAF) can be blended and dissolved in water, certain anhydrous organic solvents, or water and one or more polar, water miscible organic solvents. Selection of a copper/low- κ compatible "friendly" solvent is also advantageous. Any suitable solvent free of

strong nucleophiles, such as unhindered primary or secondary amines, is preferably employed. Preferred solvents do not include unhindered nucleophiles, and include for example, such as dimethyl sulfoxide (DMSO), sulfolane (SFL), dimethyl piperidone, 1-(2-hydroxyethyl)-2-pyrrolidinone (HEP), 1-methyl-2-pyrrolidinone and dimethylacetamide and the like. Polar nitrile-containing solvents, such as acetonitrile, isobutylnitrile and the like, can be especially advantageous.

[0050] Moreover, whereas anhydrous ammonium fluoride is practically insoluble in most organic solvents, in contradistinction, tetraalkylammonium fluoride salts, such as for example tetramethylammonium fluoride (TMAF), can be blended and completely dissolved in organic solvents, such as for example 1-(2-hydroxyethyl)-2-pyrrolidinone (HEP). Thus, a very simple, completely anhydrous, and effective formulation d) of component (2) of the cleaning compositions of this invention for cleaning photoresist and ash residues from substrates having a low- κ dielectric and copper metallization can be readily prepared. An example of such completely anhydrous formulation d) of component (2) of the cleaning compositions of this invention is 50 parts by weight HEP and 0.8 parts by weight TMAF.

[0051] Additionally, while not required by the fluoride salt-containing formulation d) of component (2) of the cleaning compositions of this invention, it may in some instances be desirable to optionally include in the formulation d) one or more "corrosion inhibiting solvent", i.e., a solvent compound that has at least two sites capable of complexing with metal is employed. Preferred as such corrosion inhibiting solvents are compounds having two or more sites capable of complexing with a metal and having one of the two following general formulae:



or



where W and Y are each independently selected from =O, -OR, -O-C(O)-R,
 5 -C(O)-, -C(O)-R, -S, -S(O)-R, -SR, -S-C(O)-R, -S(O)₂-R, -S(O)₂, -N, -NH-R,
 -NR₁R₂, -N-C(O)-R, -NR₁-C(O)-R₂, -P(O), -P(O)-OR and -P(O)-(OR)₂; X is
 alkylene, cycloalkylene or cycloalkylene containing one or more hetero atoms
 selected from O, S, N and P atoms, and arylene or arylene containing one or
 10 more hetero atoms selected from O, S, N and P atoms; each R, R₁ and R₂ are
 each independently selected from hydrogen, alkyl, cycloalkyl or cycloalkyl
 containing one or more hetero atoms selected from O, S, N and P atoms, and
 aryl or aryl containing one or more hetero atoms selected from O, S, N and P
 atoms; each of n₁ and n₂ is independently an integer of from 0 to 6; and z is an
 15 integer of from 1 to 6 when X is alkylene, cycloalkylene or arylene; and z is an
 integer of from 0 to 5 when X is cycloalkylene containing one or more hetero
 atoms selected from O, S, N and P atoms or arylene containing one or more
 hetero atoms selected from O, S, N and P atoms; T is selected from -O, -S, -N
 and -P; Z is selected from hydrogen, -OR₅, -N(R₅)₂, and -SR₅; each of R₃, R₄ and
 20 R₅ are each independently selected from hydrogen, alkyl, cycloalkyl or cycloalkyl
 containing one or more hetero atoms selected from O, S, N and P atoms, and
 aryl or aryl containing one or more hetero atoms selected from O, S, N and P
 atoms; m is an integer of from 0 to 6 and y is an integer of from 1 to 6. Such
 corrosion inhibiting solvents may optionally be present in the formulation d) of
 component (2) of the cleaning compositions of this invention in an amount of from
 25 about 0 to about 80, preferably from about 0 to about 50, and most preferably
 from about 5 to about 40%, by weight of the formulation d).

[0052] In the above definitions alkyl and alkylene are preferably of from 1 to 6
 carbon atoms, more preferably of from 1 to 3 carbon atoms, cycloalkyl and
 30 cycloalkylene preferably contain from 3 to 6 carbon atoms, and aryl and arylene
 preferably contain from about 3 to 14 carbon atoms, more preferably from about

3 to 10 carbon atoms. Alkyl is preferably methyl, ethyl or propyl; alkylene is preferably methylene, ethylene or propylene; aryl is preferably phenyl; arylene is preferably phenylene; hetero-substituted cycloalkyl is preferably dioxyl, morpholinyl and pyrrolidinyl; and hetero-substituted aryl is preferably pyridinyl.

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[0053] Some suitable examples are of such corrosion inhibiting solvents include, for example, but are not limited to ethylene glycol, diethylene glycol, glycerol, diethylene glycol dimethyl ether, monoethanolamine, diethanolamine, triethanolamine, N,N-dimethylethanolamine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 4-(2-hydroxyethyl)morpholine, 2-(methylamino)ethanol, 2-amino-2-methyl-1-propanol, 1-amino-2-propanol, 2-(2-aminoethoxy)-ethanol, N-(2-hydroxyethyl)acetamide, N-(2-hydroxyethyl) succinimide and 3-(diethylamino)-1,2-propanediol.

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[0054] While previous attempts to control or inhibit metal corrosion have involved careful controlling of pH and/or using other corrosion inhibiting compounds, such as benzotriazole (BT), at relatively low concentrations of < 2% by weight, it has been discovered that unexpected, significant improvement in controlling copper metal corrosion can be provided by the formulation d) of component (2) of the cleaning compositions of this invention without the need for such corrosion inhibiting compounds. However, if desired such corrosion inhibiting compounds may optionally be present in the formulation d) of component (2) of the cleaning compositions of this invention. Examples of such other corrosion inhibiting compounds include for example benzotriazole, and aryl compounds containing 2 or more OH or OR groups, where R is alkyl or aryl, such as for example, catechol, pyrogallol, resorcinol and the like. Such other metal corrosion inhibiting compounds may optionally be present in formulation d) of component (2) of the cleaning compositions of this invention an amount of from about 0 to about 40 % by weight of formulation d).

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[0055] The formulation d) of component (2) of the cleaning compositions of this invention may also contain surfactants, such as for example dimethyl hexynol (Surfynol-61), ethoxylated tetramethyl decynediol (Surfynol-465), polytetrafluoroethylene cetoxypopylbetaine (Zonyl FSK), (Zonyl FSH) and the like.

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[0056] Any suitable metal ion-free silicate may be used in the formulation d) of component (2) of the cleaning compositions of this invention. The silicates are preferably quaternary ammonium silicates, such as tetraalkyl ammonium silicate (including hydroxy- and alkoxy-containing alkyl groups generally of from 1 to 4 carbon atoms in the alkyl or alkoxy group). The most preferable metal ion-free silicate component is tetramethyl ammonium silicate. Other suitable metal ion-free silicate sources for this invention may be generated *in-situ* by dissolving any one or more of the following materials in the highly alkaline cleaner. Suitable metal ion-free materials useful for generating silicates in the cleaner are solid silicon wafers, silicic acid, colloidal silica, fumed silica or any other suitable form of silicon or silica. Metal silicates such as sodium metasilicate may be used but are not recommended due to the detrimental effects of metallic contamination on integrated circuits. The silicates may be present in the formulation d) of component (2) of the cleaning compositions of this invention in an amount of from about 0 to 10 wt. %, preferably in an amount of from about 0.1 to about 5 wt. % of formulation d).

[0057] The formulation d) of component (2) of the cleaning compositions of this invention may also be formulated with suitable metal chelating agents to increase the capacity of the formulation to retain metals in solution and to enhance the dissolution of metallic residues on the wafer substrate. The chelating agent will generally be present in the formulation d) of component (2) of the cleaning compositions of this invention in an amount of from about 0 to 5 wt. %, preferably from an amount of from about 0.1 to 2 wt. % of formulation d). Typical examples

of chelating agents useful for this purpose are the following organic acids and their isomers and salts: (ethylenedinitrilo)tetraacetic acid (EDTA), butylenediaminetetraacetic acid, (1,2-cyclohexylenedinitrilo)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, nitrolotriacetic 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, catechol, gallic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, and cysteine. Preferred chelating agents are aminocarboxylic acids such as EDTA, CyDTA and aminophosphonic acids such as EDTMP.

[0058] The formulation d) of component (2) of the cleaning compositions of this invention containing the non-ammonium producing, non-HF producing salts can be formulated into aqueous, semi-aqueous or organic solvent-based compositions. The non-ammonium producing, non-HF producing salts can be used with any suitable stable solvents, preferably one or more polar organic solvents resistant to strong bases and that do not contain unhindered nucleophiles, such as dimethyl sulfoxide (DMSO), sulfolane (SFL), dimethyl piperidone, HEP, 1-methyl-2-pyrrolidinone and dimethylacetamide and the like. Polar nitrile-containing solvents, such as acetonitrile, isobutylnitrile and the like, can be especially advantageous. The formulation d) of component (2) of the cleaning compositions of this invention may also optionally contain organic or inorganic acids, preferably weak organic or inorganic acids, hindered amines, hindered alkanolamines, and hindered hydroxylamines, such as triisopropylamine, and other corrosion inhibitors.

[0059] In the following Table 17 the abbreviations employed to designate the indicated components are as follows.

HEP=1-(2-hydroxyethyl)-2-pyrrolidinone

TMAF= 20% tetramethylammonium fluoride

5 BT=benzotriazole

DMSO=dimethyl sulfoxide

TEA=triethanolamine

TBAF=75% tetrabutylammonium fluoride

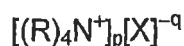
Examples of compositions of this invention are set forth in the following Table 17, in
10 which the amount of the components are indicated in parts by weight of the formulation .

TABLE 17
FORMULATIONS

COMPONENT	A	B	C
HEP	90	45	54
H ₂ O	16	15	
TBAF	5.75		
TMAF		15	
ANHYDROUS TMAF			0.8
BT	0.11	0.4	
DMSO		15	
TEA		15	

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[0060] The formulation e) of component (2) of the cleaning compositions of this invention will comprise one or more of any suitable non-ammonium producing strong base containing non-nucleophilic, positively charged counter ions and one
20 or more of any suitable steric hindered amide solvent stable under strong alkaline conditions. Among the suitable non-ammonia producing strong bases containing non-nucleophilic, positively charged counter ions suitable for use in the formulation e) of component (2) of the cleaning compositions of this invention there may be mentioned tetraalkylammonium hydroxides of the formula:

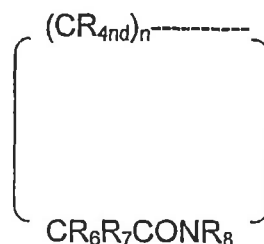


where each R is independently a substituted or unsubstituted alkyl, preferably alkyl or hydroxy alkyl of from 1 to 22, and more preferably 1 to 6, carbon atoms (R≠ H); and X=OH or a suitable salt anion, such as carbonate and the like; and p and q are equal and are integers of 1 to 3. Suitable strong bases also include KOH and NaOH. Formulation e) of component (2) of the cleaning compositions of this invention containing the non-ammonium producing strong bases containing non-nucleophilic, positively charged counter ions show much improved compatibility with low-κ dielectrics and copper metallization. Ammonia-free tetraalkylammonium hydroxides (TAAH) are very strong bases, yet they have been discovered to provide surprisingly improved low-κ compatibility compared to cleaning compositions with ammonium hydroxide. Especially preferred are tetramethylammonium hydroxide, tetrabutylammonium hydroxide, choline hydroxide and tetramethyl ammonium carbonate.

[0061] While previous attempts to control or inhibit metal corrosion have involved careful controlling of pH and/or using corrosion inhibiting compounds, such as benzotriazole (BT), at relatively low concentrations of < 2% by weight, it has been discovered that unexpected, significant improvement in controlling copper metal corrosion can be provided to the formulation e) of component (2) of the cleaning compositions of this invention when one or more steric hindered amide solvent is employed in formulation e). Any suitable steric hindered amide solvent may be employed in the cleaning compositions of this invention. Preferred as such steric hindered amide solvents are hindered acyclic and hindered cyclic amides of the formulae



and



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where n is a numeral of from 1 to 22, preferably 1 to 6; and R₁, R₂, R₃, R₄, R₅, R₆, R₇ and R₈ are each independently selected from H, alkyl (substituted or unsubstituted), preferably alkyl of from 1 to 6 carbon atoms, and aryl (substituted or unsubstituted), preferably aryl of from 3 to 14 carbon atoms, with the proviso the at least one of R₁, R₂, and R₃ and at least one of R₄, R₅, R₆, R₇ and R₈ is not hydrogen.

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[0062] Some suitable examples of such steric hindered amide acyclic solvents include, for example, acetamide, dimethyl formamide (DMF), N,N'-dimethyl acetamide (DMAc), benzamide and the like. Some suitable examples of steric hindered cyclic amides include, for example, N-methyl-2-pyrrolidinone (NMP), 1,5-dimethyl-2-pyrrolidinone, 1,3-dimethyl-2-piperidone, 1-(2-hydroxyethyl)2-pyrrolidinone, 1,5-dimethyl 2-piperidone and the like.

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[0063] The formulation e) of component (2) of the cleaning compositions of this invention containing the non-ammonium producing strong bases can be formulated into aqueous, semi-aqueous or organic solvent-based compositions. The non-ammonium producing, strong bases containing non-nucleophilic, positively charged counter ions can be used with steric hindered amide solvents alone or in combination with other stable solvents, preferably one or more polar organic solvents resistant to strong bases and that do not contain unhindered nucleophiles, such as dimethyl sulfoxide (DMSO), sulfolane (SFL), dimethyl piperidone, diethanolamine, triethanolamine, 2-(methylamino)ethanol, 3-(dimethylamino)-1,2-

propanediol and the like. The formulation e) of component (2) of the cleaning compositions of this invention may also optionally contain organic or inorganic acids, preferably weak organic or inorganic acids, hindered amines, hindered alkanolamines, and hindered hydroxylamines and other corrosion inhibitors, such as benzotriazole, catechol, glycerol, ethylene glycol and the like. The formulation e) of component (2) of the cleaning compositions of this invention may also contain any suitable surfactants, such as for example dimethyl hexynol (Surfynol-61), ethoxylated tetramethyl decynediol (Surfynol-465), polytetrafluoroethylene cetoxypropylbetaine (Zonyl FSK), (Zonyl FSH) and the like.

[0064] Any suitable metal ion-free silicate may be used in the formulation e) of component (2) of the cleaning compositions of this invention. The silicates are preferably quaternary ammonium silicates, such as tetraalkyl ammonium silicate (including hydroxy- and alkoxy-containing alkyl groups generally of from 1 to 4 carbon atoms in the alkyl or alkoxy group). The most preferable metal ion-free silicate component is tetramethyl ammonium silicate. Other suitable metal ion-free silicate sources for this invention may be generated *in-situ* by dissolving any one or more of the following materials in the highly alkaline cleaner. Suitable metal ion-free materials useful for generating silicates in the cleaner are solid silicon wafers, silicic acid, colloidal silica, fumed silica or any other suitable form of silicon or silica. Metal silicates such as sodium metasilicate may be used but are not recommended due to the detrimental effects of metallic contamination on integrated circuits. The silicates may be present in the formulation e) of component (2) of the cleaning compositions of this invention in an amount of from about 0 to 10 wt. %, preferably in an amount of from about 0.1 to about 5 wt. % of formulation e).

[0065] The formulation e) of component (2) of the cleaning compositions of this invention may also be formulated with suitable metal chelating agents to increase

the capacity of the formulation to retain metals in solution and to enhance the dissolution of metallic residues on the wafer substrate. The chelating agent will generally be present in the formulation e) of component (2) of the cleaning compositions of this invention in an amount of from about 0 to 5 wt. %, preferably from an amount of from about 0.1 to 2 wt. % of formulation e). Typical examples of chelating agents useful for this purpose are the following organic acids and their isomers and salts: (ethylenedinitrilo)tetraacetic acid (EDTA), butylenediaminetetraacetic acid, (1,2-cyclohexylenedinitrilo)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, nitrolotriacetic 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, catechol, gallic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, and cysteine. Preferred chelating agents are aminocarboxylic acids such as EDTA, CyDTA and EDTMP.

[0066] The formulation e) of component (2) of the cleaning compositions of this invention may also optionally contain fluoride compounds in formulation, such as for example, tetramethylammonium fluoride, tetrabutylammonium fluoride, and ammonium fluoride. Other suitable fluorides include, for example fluoroborates, tetrabutylammonium fluoroborates, aluminum hexafluorides, antimony fluoride and the like. The fluoride components will be present in formulation e) of component (2) of the cleaning compositions of this invention an amount of from 0 to 10 wt. %, preferably from about 0.1 to 5 wt. % of formulation e).

[0067] Examples of these types of formulations e) of component (2) of the cleaning compositions of this invention are set forth in the following Table 18, in which the amount of the components are indicated in parts by weight of the formulation. In Table 18 the following abbreviations are used to indicate the various components.

DMPD=dimethyl piperidone

TMAH= 25% tetramethylammonium hydroxide

TEA=triethanolamine

CyDTA=trans-1,2-cyclohexanediamine tetraacetic acid

SFL=sulfolane

HEP=1-(2-hydroxyethyl)-2-pyrrolidinone

NMP=N-methyl pyrrolidinone

EDTMP=ethylenediamine tetra(methylene phosphonic acid)

TABLE 18
FORMULATIONS

COMPONENT	A	B	C	D	E	F	G	H
DMPD	32	26	26		20		50	16
H ₂ O	32	32	32					32
TMAH	16	16	16	10	10	10	10	16
TEA		16						15
CyDTA		0.2						
SFL			16		30			
HEP				50				
NMP						50		
EDTMP								0.4

[0068] The aforementioned types of formulations a) through e) employed as component (2) of the nanoelectronic and microelectronic cleaning compositions of this invention can be successfully used as supercritical fluid modifiers/

additives for the main supercritical fluid component (1) of such compositions and provide many benefits, such as:

- A) the ability to form reasonably stable, homogeneous supercritical fluid together with the main supercritical fluid component (1);
- 5 B) good stability (or "minimally reactive") under supercritical pressures and temperatures;
- C) good compatibilities with supercritical construction materials (e.g. stainless steel;
- D) improved cleaning performance and good substrate compatibilities;
- 10 E) superior solvating strength, mass-transfer, with little or no surface tension , and diffusivity over the traditional "non-supercritical" technologies, and are particularly useful for cleaning structures with high aspect ratios or porous materials,
- F) enables lower consumption of main supercritical fluid component (1); and
- 15 G) elimination or minimization of required drying steps.

[0069] The cleaning capabilities of the compositions used in supercritical fluid technologies described above is further illustrated by, but not limited to, the following cleaning examples employing nanoelectronic and microelectronic cleaning compositions of this invention wherein there is cleaned an etched via sample with photoresist/carbon doped oxide (PR/CDO) structure. The results of the cleaning of said structure with the cleaning compositions of this invention are set forth in Table 20. The cleaning process was conducted in a 75-mL cleaning vessel filled with glass beads to fill most voids (space). The cleaning of the etched via sample with photoresist/carbon doped oxide (PR/CDO) structure in the vessel was accomplished by introducing into the vessel separately, but simultaneously, by separate lines, a flow of the component (1) main supercritical fluid (CO₂) and a flow of the component (2) formulation modifier/additive at the flow rates, temperatures,

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and pressures indicated in the process conditions column of Table 20 and wherein:

Formulation #1= 17:26:1.5:0.5 SFL-H₂O-25%TMAH-CyDTA

Formulation #2 = 150:60:17.5:1.8:30 SFL- H₂O-25%TMAH-EDTMP-EG; and

Formulation #3 = 300:35:5:25:3 SFL-H₂O-EG-25%TMAH-CyDTA;

- 5 where CyDTA= trans-1, 2-cyclohexanediamine tetraacetic acid; EDTMP= ethylenediamine tetra (methylene phosphonic acid; SFL= sulfolane; EG = ethylene glycol; TMAH= tetramethylammonium hydroxide and H₂O₂ is hydrogen peroxide.

Table 20.

Compositions and Process Conditions	Cleaning Performance	Substrate Compatibility
Master (Main) solvent: CO ₂ at 12 g/min flow rate; Modifier formulation: [8:1 Formulation #1:30% H ₂ O ₂], at 1.8 g/min flow rate; Pressure: 150 bars; Temperature: 100 °C; Run time: 60 minutes.	Remove all PR (bulk PR and tough "skin") and stubborn via residues (100 %)	No CDO etch
Master (Main) solvent: CO ₂ at 15 g/min flow rate; Modifier: [8:1 Formulation #2:30% H ₂ O ₂], at 2.25 g/min flow rate; Pressure: 188 bars; Temperature: 100 °C; Run time: 60 minutes	Remove all PR (bulk PR and tough "skin") and stubborn via residues (100 %)	No CDO etch
Master (Main) solvent: CO ₂ at 15 g/min flow rate; Modifier: [8:1 Formulation #3:30% H ₂ O ₂], at 2.25 g/min flow rate; Pressure: 200 bars; Temperature: 100 °C; Run time: 60 minutes	Remove all PR (bulk PR and tough "skin") and stubborn via residues (100 %)	No CDO etch

5 **[0070]** While the invention has been described herein with reference to the specific embodiments thereof, it will be appreciated that changes, modification and variations can be made without departing from the spirit and scope of the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modification and variations that fall with the spirit and scope of the appended claims.

Claim:

1. A cleaning composition suitable for cleaning nanoelectronic and microelectronic substrates under supercritical fluid conditions, said composition comprising (1) a supercritical main fluid reaching a supercritical fluid state at a temperature of 250°C or less and a pressure of 600 bars or less (592.2 atm, 8702.3 psi), and (2) as a secondary fluid, a modifier formulation selected from the group consisting of following formulations:
 - a) a formulation comprising:
 - an oxidizing agent;
 - a polar organic solvent selected from the group consisting of sulfones, sulfolenes, and selenones;
 - an alkaline base of the formula $R_4N^+OH^-$ wherein each R is independently a substituted or unsubstituted alkyl group of 1 to 22 carbon atoms;
 - water; and
 - q chelating or metal complexing agent selected from the group consisting of trans-1,2-cyclohexdiaminetetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, ethane-1-hydroxy-1,1-diphosphonate, ethylenediamine tetra (methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), and triethylenetetramine hexa(methylene phosphonic acid);
 - and optionally one or more of the following components:
 - an acid;
 - a corrosion-inhibiting co-solvent;
 - an oxidizer stabilizing agent;
 - a corrosion-inhibiting agent;
 - a metal corrosion inhibitor;
 - a fluoride compound; and
 - a surfactant;
 - b) a silicate free formulation comprising:
 - a polar organic solvent selected from the group consisting of sulfones, sulfolenes and selenones; and
 - a strong alkaline base of the formula $R_4N^+OH^-$ wherein each R is independently a substituted or unsubstituted alkyl group of 1 to 22 carbon atoms;
 - water; and

q chelating or metal complexing agent selected from the group consisting of trans-1,2-cyclohexadiaminetetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, ethane-1-hydroxy-1,1-diphosphonate, ethylenediamine tetra(methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), and triethylenetetramine hexa(methylene phosphonic acid);

and optionally one or more of the following components:

- an acid;
- a corrosion-inhibiting co-solvent;
- an oxidizer stabilizing agent;
- a corrosion-inhibiting agent;
- a metal corrosion inhibitor;
- a fluoride compound; and
- a surfactant;

c) a formulation comprising:

one or more non-ammonium producing strong base of the formula $[(R)_4N^+]_p[X^-]_q$, where each R is independently a substituted or unsubstituted alkyl of from 1 to 22 carbon atoms; and X=OH or a suitable salt anion, and p and q are equal and are integer of from 1 to 3;

one or more corrosion inhibiting solvent compounds, said corrosion inhibiting solvent compound having at least two sites capable of complexing with metals and selected from the group consisting of ethylene glycol, diethylene glycol, glycerol, diethylene glycol dimethyl ether, monoethanolamine, diethanolamine, triethanolamine, N,N-dimethylethanolamine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 4-(2-hydroxyethyl)morpholine, 2-(methylamino)ethanol, 2-amino-2-methyl-1-propanol, 1-amino-2-propanol, 2-(2-aminoethoxy)-ethanol, N-(2-hydroxyethyl)acetamide, N-(2-hydroxyethyl) succinimide and 3-(diethylamino)-1,2-propanediol;

and optionally one or more of the following components:

- water or other organic co-solvent;
- a steric hindered amine or alkanolamine;
- an organic or inorganic acid;
- an other metal corrosion inhibitor compounds;
- a surfactant;

- a metal ion free silicate compound;
 - a metal chelating agent; and
 - a fluoride compound;
- d) a formulation comprising:
- one or more non-ammonium producing, non-HF producing fluoride salt of the formula $(R)_4N^+F^{3-}$, where each R is independently a substituted or unsubstituted alkyl of from 1 to 22 carbon atoms;
 - sulfolane, dimethyl sulfoxide and 1-(2-hydroxyethyl)-2-pyrrolidinone as organic solvents;
 - and optionally one or more of the following components:
 - a metal corrosion inhibiting solvent;
 - a steric hindered amine or alkanolamine;
 - an organic or inorganic acid; from about 0 to 40% by weight of an other metal corrosion inhibitor compound;
 - a surfactant;
 - a metal ion free silicate compound; and from about 0 to 5% by weight of a metal chelating agent; and
- e) a formulation comprising:
- one or more non-ammonium producing strong base of the formula $[(R)_4N^+]_p[X^-]_q$, where each R is independently a substituted or unsubstituted alkyl of from 1 to 22 carbon atoms; and X=OH or a suitable salt anion, and p and q are equal and are integer of from 1 to 3;
 - one or more steric hindered amide, solvents selected from the group consisting of acetamide, dimethyl formamide (DMF), N,N'-dimethyl acetamide (DMAc), benzamide, N-methyl-2-pyrrolidinone (NMP), 1,5-dimethyl-2-pyrrolidinone, 1,3-dimethyl-2-piperidone, 1-(2-hydroxyethyl)-2-pyrrolidinone, and 1,5-dimethyl 2-piperidone;
 - one or more other organic co-solvent selected from the group consisting of dimethyl sulfoxide (DMSO), sulfolane (SFL), and dimethyl piperidone;
 - and optionally one or more of the following components:
 - a steric hindered amine or alkanolamine;
 - an organic or inorganic acid;
 - of an other metal corrosion inhibitor compounds;
 - a surfactant;

a metal ion free silicate compound;
a metal chelating agent; and
a fluoride compound.

2. A cleaning composition of claim 1 wherein the composition comprise from about 5%, to about 20% by weight of the secondary fluid modifier formulation component (2) based on the weight of the supercritical main fluid component (1).
3. A cleaning composition according to claim 1 wherein the supercritical main fluid comprises carbon dioxide.
4. A cleaning composition according to claim 3 wherein the secondary fluid modifier formulation comprises a formulation of sulfolane, water, tetramethylammonium hydroxide, trans-1, 2-cyclohexanediamine tetraacetic acid, and hydrogen peroxide.
5. A cleaning composition according to claim 3 wherein the secondary fluid modifier formulation comprises a formulation of sulfolane, water, ethylene glycol, tetramethylammonium hydroxide, trans-1,2-cyclohexanediamine tetraacetic acid, and hydrogen peroxide.
6. A cleaning composition according to claim 3 wherein the secondary fluid modifier formulation comprises a formulation of sulfolane, water, tetramethylammonium hydroxide, ethylenediamine tetra (methylene phosphonic acid, ethylene glycol, and hydrogen peroxide.
7. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue, the process comprising contacting the substrate for a time and at supercritical fluid conditions with a cleaning composition sufficient to clean the substrate, wherein the cleaning composition comprises (1) a supercritical main fluid reaching a supercritical fluid state at a temperature of 250°C or less and a pressure of 600 bars or less (592.2 atm, 8702.3 psi), and (2) as a secondary fluid, a modifier formulation wherein the second fluid modifier comprises a formulation selected from the group consisting of the following formulations:
 - a) a formulation comprising:

an oxidizing agent;
a polar organic solvent selected from the group consisting of sulfones, sulfolenes, and selenones;
an alkaline base of the formula $R_4N^+OH^-$ wherein each R is independently a substituted or unsubstituted alkyl group of 1 to 22 carbon atoms:

water; and

q chelating or metal complexing agent selected from the group consisting of trans-1,2-cyclohexanediamine tetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, ethane-1-hydroxy-1,1-diphosphonate, ethylenediamine tetra(methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), and triethylenetetramine hexa(methylene phosphonic acid).

and optionally one or more of the following components:

an acid;

a corrosion-inhibiting co-solvent;

an oxidizer stabilizing agent;

a corrosion-inhibiting agent; a metal corrosion inhibitor;

a fluoride compound; and

a surfactant;

b) a silicate free formulation comprising:

a polar organic solvent selected from the group consisting of sulfones, sulfolenes and selenones; and

a strong alkaline base of the formula $R_4N^+OH^-$ wherein each R is independently a substituted or unsubstituted alkyl group of 1 to 22 carbon atoms;

water; and

q chelating or metal complexing agent selected from the group consisting of trans-1,2-cyclohexanediamine tetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, ethane-1-hydroxy-1,1-diphosphonate, ethylenediamine tetra(methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), and triethylenetetramine hexa(methylene phosphonic acid);

and optionally one or more of the following components:

an acid;

a corrosion-inhibiting co-solvent;

an oxidizer stabilizing agent;
a corrosion-inhibiting agent;
a metal corrosion inhibitor;
a fluoride compound; and
a surfactant;

c) a formulation comprising:

one or more non-ammonium producing strong base of the formula $[(R)_4N^+]_p[X^-]_q$, where each R is independently a substituted or unsubstituted alkyl of from 1 to 22 carbon atoms; and X=OH or a suitable salt anion, and p and q are equal and are integer of from 1 to 3;

one or more corrosion inhibiting solvent compounds, said corrosion inhibiting solvent compound having at least two sites capable of complexing with metals and selected from the group consisting of ethylene glycol, diethylene glycol, glycerol, diethylene glycol dimethyl ether, monoethanolamine, diethanolamine, triethanolamine, N,N -dimethylethanolamine, 1-(2-hydroxyethyl)-2-pyrrolidinone, 4-(2-hydroxyethyl)morpholine, 2-(methylamino)ethanol, 2-amino-2-methyl-1-propanol, 1-amino-2-propanol, 2-(2-aminoethoxy)-ethanol, N-(2-hydroxyethyl) acetamide, N-(2-hydroxyethyl) succinimide and 3-(diethylamino)-1,2-propanediol;

and optionally one or more of the following components:

water or other organic co-solvent;
a steric hindered amine or alkanolamine;
an organic or inorganic acid;
an other metal corrosion inhibitor compounds;
a surfactant;
a metal ion free silicate compound;
a metal chelating agent; and
a fluoride compound;

d) a formulation comprising:

one or more non-ammonium producing, non-HF producing fluoride salt of the formula $(R)_4N^+F^{3-}$, where each R is independently a substituted or unsubstituted alkyl of from 1 to 22 carbon atoms;

sulfolane, dimethyl sulfoxide and 1-(2-hydroxyethyl)-2-pyrrolidinone as organic solvents;

and optionally one or more of the following components:

- a metal corrosion inhibiting solvent;
 - a steric hindered amine or alkanolamine;
 - an organic or inorganic acid; from about 0 to 40% by weight of an other metal corrosion inhibitor compound;
 - a surfactant;
 - a metal ion free silicate compound; and from about 0 to 5% by weight of a metal chelating agent; and
- e) a formulation comprising:
- one or more non-ammonium producing strong base of the formula $[(R)_4N^+]_p[X^-]_q$, where each R is independently a substituted or unsubstituted alkyl of from 1 to 22 carbon atoms; and X=OH or a suitable salt anion, and p and q are equal and are integer of from 1 to 3;
 - one or more steric hindered amide solvents selected from the group consisting of acetamide, dimethyl formamide (DMF), N,N'-dimethyl acetamide (DMAc), benzamide, N-methyl-2-pyrrolidinone (NMP), 1,5-dimethyl-2-pyrrolidinone, 1,3-dimethyl-2-piperidone, 1-(2-hydroxyethyl)-2-pyrrolidinone, and 1,5-dimethyl 2-piperidone;
 - one or more other organic co-solvent selected from the group consisting of dimethyl sulfoxide (DMSO), sulfolane (SFL), and dimethyl piperidone;
 - and optionally one or more of the following components:
 - a steric hindered amine or alkanolamine;
 - an organic or inorganic acid;
 - of an other metal corrosion inhibitor compounds;
 - a surfactant.;
 - a metal ion free silicate compound;
 - a metal chelating agent; and
 - a fluoride compound.
8. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue according to claim 7, wherein the composition comprise from about 5%, to about 20% by weight of the secondary fluid modifier formulation component (2) based on the weight of the supercritical main fluid component (1).

9. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue according to claim 7, wherein the supercritical main fluid comprises carbon dioxide.
10. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue according to claim 9, wherein the secondary fluid modifier formulation comprises a formulation of sulfolane, water, tetramethylammonium hydroxide, trans-1,2-cyclohexanediamine tetraacetic acid, and hydrogen peroxide.
11. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue according to claim 9, wherein the secondary fluid modifier formulation comprises a formulation of sulfolane, water, ethylene glycol, tetramethylammonium hydroxide, trans-1,2-cyclohexanediamine tetraacetic acid, and hydrogen peroxide.
12. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue according to claim 9, wherein the secondary fluid modifier formulation comprises a formulation of sulfolane, water, tetramethylammonium hydroxide, ethylenediamine tetra(methylene phosphonic acid, ethylene glycol, and hydrogen peroxide.
13. A cleaning composition according to claim 3 comprising:
tetramethylammonium fluoride, sulfolane, dimethyl sulfoxide and 1-(2-hydroxyethyl)-2-pyrrolidinone.
14. A process for cleaning a nanoelectronic or microelectronic substrate of photoresist or residue according to claim 9, wherein the secondary fluid modifier formulation comprises a formulation of tetramethylammonium fluoride, sulfolane, dimethyl sulfoxide and 1-(2-hydroxyethyl)-2- pyrrolidinone.