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(54) Title: NON-FLUORIDE CONTAINING COMPOSITION FOR THE REMOVAL OF POLYMERS AND OTHER ORGANIC MATERIAL FROM A SURFACE

(57) Abstract: Removal compositions and processes for removing polymers and/or other organic materials from a surface having same thereon. The semi-aqueous composition is substantially devoid of fluoride species.



WO 2010/091045 A2

**NON-FLUORIDE CONTAINING COMPOSITION FOR THE REMOVAL OF POLYMERS
AND OTHER ORGANIC MATERIALS FROM A SURFACE**

FIELD

[0001] The present invention relates generally to removal compositions that are substantially devoid or devoid of fluoride species and that are useful for the removal of polymers and/or other organic materials (e.g., waxes, oils, and paints) from a surface having same thereon.

DESCRIPTION OF THE RELATED ART

[0002] Numerous materials containing polymers are used in the manufacture of electronic devices, such as circuits, disk drives, storage media devices and the like. Such polymeric materials are found in photoresists, solder masks, antireflective coatings, and the like. For example, modern technology utilizes positive-type resist materials for lithographically delineating patterns onto a substrate so that the patterns can be subsequently etched or otherwise defined into the substrate material. The resist material is deposited as a film and the desired pattern is defined by exposing the resist film to energetic radiation. Thereafter the exposed regions are subject to dissolution by a suitable developer liquid. After the pattern has been thus defined in the substrate the resist material must be completely removed from the substrate to avoid adversely affecting or hindering subsequent operations or processing steps.

[0003] It is necessary in such a photolithographic process that the photoresist material, following pattern delineation, be evenly and completely removed from all unexposed areas so as to permit further lithographic operations. Even the partial remains of a resist in an area to be further patterned is undesirable. Further, undesired residue between patterned features can have deleterious effects on subsequent film depositions processes, such as metallization, or cause undesirable surface states and charges leading to reduced device performance.

[0004] The semiconductor industry is moving toward sub-quarter micron geometry features. As the geometry of the features gets smaller and pattern density increases, plasma etching, reactive ion etching, ion milling and the like are required for the lithographic process. During the plasma etch process, hard to remove organometallic polymeric residue forms on the sidewalls of the various features being etched. Furthermore, the photoresist is extensively cross-linked due to the high vacuum and high temperature conditions in the etch chamber.

[0005] Presently, nearly all resist removal compositions include fluoride. Such compositions have the disadvantage of requiring special handling and disposal requirements due to incompatibility with common solvent waste streams, as well as high viscosity which prohibits spray tool processes. In

addition, known stripping compositions have numerous drawbacks including, undesirable flammability, toxicity, volatility, odor, necessity for use at elevated temperatures such as up to 100°C, and high cost due to handling regulated materials. A particular problem with advanced next generation microelectronic devices is that known removal compositions are incompatible with a variety of thin films in such devices, specifically copper and low-k dielectric material present in such devices.

SUMMARY

[0006] The present invention relates to removal compositions useful for removing polymeric and/or other organic materials from a surface.

[0007] In one aspect, a removal composition is described, said removal composition comprising at least one polymer dissolution accelerator, at least one organic solvent, and water, wherein the composition is substantially devoid of fluoride species. In a preferred embodiment, the composition is substantially devoid of amine species as well.

[0008] In another aspect, a removal composition is described, said removal composition consisting essentially of at least one polymer dissolution accelerator, at least one organic solvent, and water, wherein the composition is substantially devoid of fluoride species. In a preferred embodiment, the composition is substantially devoid of amine species as well.

[0009] In still another aspect, a removal composition is described, said removal composition consisting of at least one polymer dissolution accelerator, at least one organic solvent, and water, wherein the composition is substantially devoid of fluoride species. In a preferred embodiment, the composition is substantially devoid of amine species as well.

[0010] In a further aspect, a removal composition is described, said removal composition comprising at least one polymer dissolution accelerator, at least one organic solvent, at least one complexing agent, and water, wherein the composition is substantially devoid of fluoride species. In a preferred embodiment, the composition is substantially devoid of amine species as well.

[0011] Another aspect relates to a removal composition, said removal composition consisting essentially of at least one polymer dissolution accelerator, at least one organic solvent, at least one complexing agent, and water, wherein the composition is substantially devoid of fluoride species. In a preferred embodiment, the composition is substantially devoid of amine species as well.

[0012] Still another aspect relates to a removal composition, said removal composition consisting of at least one polymer dissolution accelerator, at least one organic solvent, at least one complexing agent, and water, wherein the composition is substantially devoid of fluoride species. In a preferred embodiment, the composition is substantially devoid of amine species as well.

[0013] In yet another aspect, a method of removing polymer and/or other organic materials from a surface having same thereon is described, said method comprising contacting the surface with a semi-aqueous removal composition for sufficient time and under sufficient contacting conditions to at least partially remove said polymer and/or other organic materials from the surface, wherein the removal composition includes at least one polymer dissolution accelerator, at least one organic solvent, and water, wherein the composition is substantially devoid of fluoride species.

[0014] In still another aspect, a kit is described, said kit comprising, in one or more containers, one or more of the following reagents for forming a composition, wherein said composition comprises at least one polymer dissolution accelerator, at least one organic solvent, water, and optionally at least one complexing agent, wherein the kit is adapted to form a composition suitable for removing polymeric and/or other organic material from a surface.

[0015] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS THEREOF

[0016] The present invention relates generally to the field of removal of polymeric and/or other organic materials from a surface. More specifically, a removal composition substantially devoid of fluoride is described for the removal of polymers and other organic materials from surfaces including, but not limited to paints, waxes and oils. Even more specifically, the removal compositions are useful for the removal of polymeric material from a microelectronic device, whereby the compositions described herein are compatible with low-k dielectric and metal-containing materials on said device.

[0017] For ease of reference, a “surface” corresponds to any solid material that the polymer or other organic material may be found on including natural or synthetic materials including, but not limited to, microelectronic devices, metals, plastics, fabrics, fibers, soils, wood, paper, glass, leather and other animal hides, cement, concrete, bricks, drywall, asphalt, keratin-containing substances such as hair and nails, rubber, latex, minerals, mineral crystals, amorphous inorganic materials, and combinations thereof.

[0018] “Microelectronic device” corresponds to semiconductor substrates, flat panel displays, phase change memory devices, solar panels and other products including solar substrates, photovoltaics, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, or computer chip applications. It is to be understood that the terms “microelectronic device,” “microelectronic substrate” and “microelectronic device structure” are not meant to be limiting in any way and include any substrate or structure that will eventually become a microelectronic device or microelectronic assembly. The microelectronic device can be patterned, blanketed, a control and/or a test device.

[0019] As described herein, “polymers” and “polymeric material” correspond to any compound, typically of organic origin, having a large number of monomeric units covalently bonded to each other, wherein the monomeric units may be the same as or different from one another. Polymers may be natural or man-made (synthetic), and for the purpose of the invention described herein may include proteins, polysaccharides, polypeptides, polynucleotides, oligomers, copolymers, terpolymers, photoresists, solder masks, antireflective coatings, resist-containing residues, paints, waxes, oils, contaminants, and combinations thereof. For the purpose of the invention described herein, polymers and polymeric material include residues that comprise polymers. Typical synthetic polymer genres include novolacs, polyacrylates, polyamides, polyesters, polycarbonates, polyimides polystyrenes, polybenzocyclobutenes, polynorborenes, and siloxy-functionalized polymers including, but not limited to, phenol formaldehyde resins, polyhydroxystyrenes, polymethylmethacrylates, includes: acrylonitrile butadiene styrene (ABS), polyacrylonitrile (PAN), polybutadiene, poly(butylene terephthalate) (PBT), poly(ether sulfone) (PES, PES/PEES), poly(ether ether ketone)s (PEEK, PES/PEEK), polyethylene (PE), poly(ethylene glycol) (PEG), poly(ethylene terephthalate) (PET), polypropylene (PP), polytetrafluoroethylene (PTFE), styrene-acrylonitrile resin (SAN), poly(trimethylene terephthalate) (PTT), polyurethane (PU), polyvinyl butyral (PVB), polyvinylchloride (PVC), polyvinylidenedifluoride (PVDF), and poly(vinyl pyrrolidone) (PVP). Other polymers for the purposes of this invention include polysiloxanes, polyphosphazenes, and epoxies (polyepoxides).

[0020] As used herein, “residue” corresponds to particles generated during the manufacture of a microelectronic device including, but not limited to, plasma etching, ashing, chemical mechanical polishing, wet etching, and combinations thereof.

[0021] As used herein, “post-CMP residue” corresponds to particles from the polishing slurry, e.g., silica-containing particles, chemicals present in the slurry, reaction by-products of the polishing slurry, carbon-rich particles, polishing pad particles, brush deloading particles, equipment materials of construction particles, copper, copper oxides, copper-containing materials, aluminum, aluminum oxides, aluminum-containing materials, organic residues, and any other materials that are the by-products of the CMP process.

[0022] As defined herein, “post-etch residue” corresponds to material remaining following gas-phase plasma etching processes, e.g., BEOL dual damascene processing. The post-etch residue may be organic, organometallic, organosilicic, or inorganic in nature, for example, silicon-containing material, carbon-based organic material, and etch gas residue such as oxygen and fluorine.

[0023] As defined herein, “post-ash residue,” as used herein, corresponds to material remaining following oxidative or reductive plasma ashing to remove hardened photoresist and/or bottom anti-reflective coating (BARC) materials. The post-ash residue may be organic, organometallic, organosilicic, or inorganic in nature.

[0024] As defined herein, “photoresist” includes undeveloped photoresist, bulk photoresist, and/or hardened photoresist, whether positive or negative. “Bulk photoresist,” as used herein, corresponds to the non-carbonized photoresist on the microelectronic device surface, specifically adjacent and below the hardened photoresist crust. “Hardened photoresist” as used herein includes, but is not limited to: photoresist that has been plasma etched, e.g., during back-end-of-line (BEOL) dual-damascene processing of integrated circuits; ion implanted, e.g., during front-end-of-line (FEOL) processing to implant dopant species in the appropriate layers of the semiconductor wafer; and/or any other methodology whereby a carbonized or highly cross-linked crust forms on the exposed surface of the bulk photoresist. Doping species include, but are not limited to, boron, arsenic, boron difluoride, indium, antimony, germanium, carbon, and/or phosphorous ions.

[0025] As defined herein, “low-k dielectric material” corresponds to any material used as a dielectric material in a layered microelectronic device, wherein the material has a dielectric constant less than about 3.5. Preferably, the low-k dielectric materials include low-polarity materials such as silicon-containing organic polymers, silicon-containing hybrid organic/inorganic materials, organosilicate glass (OSG), TEOS, fluorinated silicate glass (FSG), silicon dioxide, and carbon-doped oxide (CDO) glass. It is to be appreciated that the low-k dielectric materials may have varying densities and varying porosities.

[0026] “Substantially devoid” is defined herein as less than 2 wt. %, preferably less than 1 wt. %, more preferably less than 0.5 wt. %, and most preferably less than 0.1 wt. %. “Devoid” corresponds to 0 wt. %.

[0027] As used herein, “about” is intended to correspond to $\pm 5\%$ of the stated value.

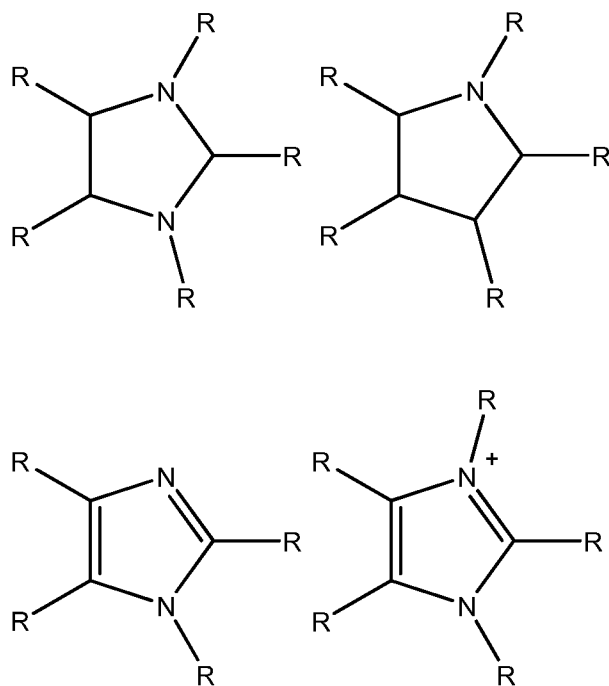
[0028] As used herein, “suitability” for removing polymers and other organic materials from a surface having same thereon corresponds to at least partial removal of said polymers and other organic materials from the surface. Preferably, between 50 and 85% of the polymers and other organic materials are removed from the surface using the compositions described herein, more preferably at least 90%, even more preferably at least 95%, and most preferably at least 99% of the polymers and other organic materials are removed.

[0029] As defined herein, “metals” correspond to: tantalum, tantalum nitride, titanium nitride, titanium, nickel, cobalt, tungsten, and silicides thereof; copper-containing layers; aluminum-containing layers; Al/Cu layers; alloys of Al; alloys of Cu; cobalt-containing layers such as CoWP and CoWBP; gold-containing layers; Au/Pt layers; hafnium oxides; hafnium oxysilicates; zirconium oxides; lanthanide oxides; titanates; nitrogen-doped analogues thereof; ruthenium; iridium; cadmium; lead; indium; selenium; silver; MoTa; and combinations and salts thereof on the microelectronic device.

[0030] As used herein, “fluoride” species correspond to species including an ionic fluoride (F^-) or covalently bonded fluorine. It is to be appreciated that the fluoride species may be included as a fluoride species or generated in situ.

[0031] As defined herein, “amine” species include at least one primary, secondary, or tertiary amine, ammonia, and/or quaternary ammonium hydroxide compounds (e.g., ammonium hydroxide, alkylammonium hydroxide, alkylarylammonium hydroxide, etc.), with the proviso that (i) species including an five-membered heterocyclic ring, wherein at least one member of the ring is a nitrogen atom, and (ii) species including both a carboxylic acid group and an amine group, are not considered amines for the purposes of this invention. Amines for the purposes of this invention include, but are not limited to: aliphatic primary, secondary, or tertiary amines; 4, 6, 7, 8, 9 or 10-membered saturated or unsaturated amine rings; alkylammonium hydroxide compounds having the general formula $R_1R_2R_3R_4NOH$ where R_1 , R_2 , R_3 and R_4 are the same as or different from one another and are hydrogen and C_1 - C_6 alkyl groups (e.g., methyl, ethyl, propyl, butyl, pentyl or hexyl); alkylarylammonium hydroxide compounds have the general formula $R_1R_2R_3R_4NOH$ where R_1 , R_2 , R_3 and R_4 are the same as or different from one another and are hydrogen, C_1 - C_6 alkyl groups (e.g., methyl, ethyl, propyl, butyl, pentyl or hexyl) and substituted or unsubstituted C_6 - C_{10} aryl groups (e.g., benzyl); and alkanolamines.

[0032] Five-membered heterocyclic rings having at least one member of the ring being a nitrogen atom are best described by referring to the following structures:



where R may be the same as or different from one another and are selected from the group consisting of hydrogen, C_1 - C_6 alkyls (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl), C_1 - C_6 alcohols (e.g.,

methanol, ethanol, propanol, butanol, pentanol, hexanol), C₁-C₆ primary amines, C₁-C₆ secondary amines, and carbonyl groups.

[0033] As defined herein, “complexing agent” includes those compounds that are understood by one skilled in the art to be complexing agents, chelating agents, sequestering agents, and combinations thereof. Complexing agents will chemically combine with or physically hold the metal atom and/or metal ion to be removed using the compositions described herein.

[0034] As defined herein, “other organic materials” correspond to paints, waxes, oils and contaminants.

[0035] As used herein, “contaminants” correspond to chemicals, excluding residue and the components of the removal compositions, present on the surface of the microelectronic device subsequent to the plasma etching, ashing, wet etching, or chemical mechanical polishing process, reaction and chemical by-products, and any other materials that are the by-products of said processes. Typically, contaminants will be organic in nature.

[0036] In this application, the term “paint” will be understood to refer to coatings such as epoxies, enamels, latexes, primers, basecoats, clearcoats, lacquers, varnishes, shellacs and polyurethane finishes which are used to protect and/or beautify surfaces. “Paints” may be fresh, dried, and/or aged. As used in this application, the term “paint removal” refers to compositions which remove or facilitate the removal of paint from a surface.

[0037] “Waxes” are defined as substances that are plastic solids at ambient temperatures and, on being subjected to moderately elevated temperatures, become low viscosity liquids. One type of wax, “paraffin wax,” is a petroleum wax which occurs naturally in many types of crude oil around the world. Chemically, paraffins, and by extension paraffin waxes occurring naturally in petroleum, are usually mixtures of straight carbon chain alkanes. The physical properties of the paraffin waxes, including melting point, congealing point, and plastic flow properties, vary with the “carbon chain length” of the wax or waxes present in the petroleum.

[0038] “Oil” includes non-polar compounds that are viscous at room temperature and are immiscible with water. Oils may be classified as mineral oils, originating from biomass, or organic oils, which are produced by plants, animals and other organisms through organic processes. Organic oils include, but are not limited to, lipids such as oils, fats, waxes, cholesterol and other oily substances found in living things.

[0039] As used herein, the term “semi-aqueous” refers to a mixture of water and organic components.

[0040] Compositions may be embodied in a wide variety of specific formulations, as hereinafter more fully described. In all such compositions, wherein specific components of the composition are discussed in reference to weight percentage ranges including a zero lower limit, it will be understood that such components may be present or absent in various specific embodiments of the composition,

and that in instances where such components are present, they may be present at concentrations as low as 0.001 weight percent, based on the total weight of the composition in which such components are employed.

[0041] In general, the semi-aqueous compositions include at least one polymer dissolution accelerator, at least one organic solvent, water, and optionally at least one complexing agent, wherein the composition is useful for the removal of polymers and other organic materials from a surface having same thereon. The compositions are preferably substantially devoid of fluoride species.

[0042] In one aspect, a composition comprising, consisting of or consisting essentially of at least one organic solvent, at least one polymer dissolution accelerator, and water is described, wherein the composition is substantially devoid of fluoride and amine species and wherein the composition is useful for the removal of polymer and other organic material from a surface having same thereon. In another aspect, a composition comprising, consisting of or consisting essentially of at least one complexing agent, at least one organic solvent, at least one polymer dissolution accelerator, and water is described, wherein the composition is substantially devoid of fluoride and amine species. In yet another aspect, a composition comprising, consisting of or consisting essentially of at least one organic solvent, at least one imidazole compound, and water is described, wherein the composition is substantially devoid of fluoride and amine species. In yet another aspect, a composition comprising, consisting of or consisting essentially of at least one complexing agent, at least one organic solvent, at least one imidazole compound, and water is described, wherein the composition is substantially devoid of fluoride species and amine species. In general, the specific proportions and amounts of components, in relation to each other, may be suitably varied to provide the desired removal action of the composition for polymer, other organic materials and/or processing equipment, as readily determinable within the skill of the art without undue effort. The water is preferably deionized.

[0043] The complexing agents preferably have a high affinity for aluminum-containing residues. Complexing agents contemplated include, but are not limited to, aminocarboxylic acids, organic acids and derivatives thereof, phosphonic acids and derivatives thereof, and combinations thereof including: (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, 1,5,9-triazacyclododecane-N,N',N''-tris(methylenephosphonic acid) (DOTRP), 1,4,7,10-tetraazacyclododecane-N,N',N'',N'''-tetrakis(methylenephosphonic acid) (DOTP), nitrilotris(methylene)triphosphonic acid, diethylenetriaminepenta(methylenephosphonic acid) (DETAP), aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), bis(hexamethylene)triamine phosphonic acid,

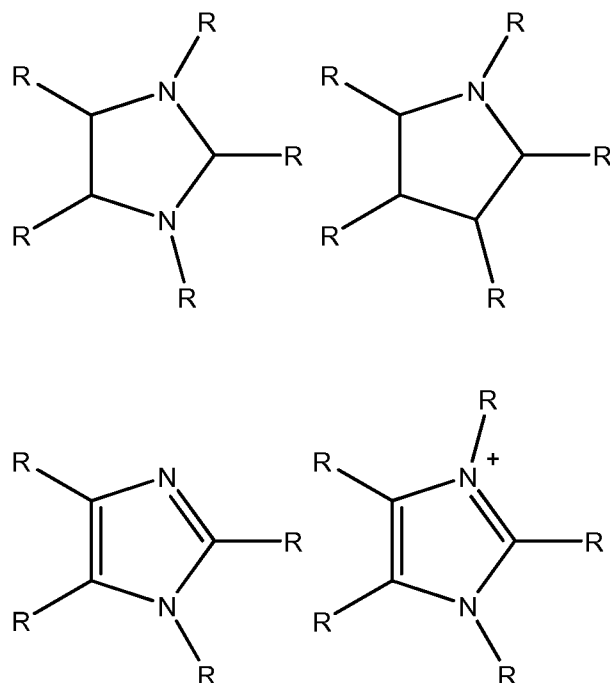
1,4,7-triazacyclononane-N,N',N''-tris(methylenephosphonic acid (NOTP), 2-phosphonobutane-1,2,4-tricarboxylic acid, nitrilotriacetic acid (NTA), citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, oxalic acid, phthalic acid, maleic acid, mandelic acid, malonic acid, lactic acid, o-, m-, or p-salicylic acid and derivatives thereof, dihydroxybenzoic acid, 5-sulfosalicylic acid, catechol, gallic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, cysteine, acetic acid, dihydroxysalicylic acid, iminodiacetic acid, glyphosphate, N-(Phosphonomethyl)-iminodiacetic acid, formic acid, propanoic acid, butanoic acid, sulfate ions, N-(2-Hydroxyethyl)-iminodiacetic acid, pyridine-2,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, 7-Iodo-8-hydroxyquinoline-5-sulfonic acid, 2-amino-2-propylphosphonic acid, 1,2-dihydroxybenzene-4-sulfonic acid, 4,5-dihydroxy-1,3-benzene disulfonic acid (Tiron), solochrome violet R, 3-hydroxy-2-naphthoic acid, chromotropic acid, nitroacetic acid, oxydiacetic acid, thiodiacetic acid, 8-hydroxy-7-(aryloxy)-quinoline-5-sulfonic acid, 2-oxobutanoic acid, acetoacetic acid, phenylserine, L-ascorbic acid, squaric acid, acetohydroxamic acid, 3-hydroxy-5,7-disulfo-2-naphthoic acid, 2,3-dihydroxynaphthalene-6-sulfonic acid, sulfoxine, oxine, succinic acid, 3,4-dihydroxybenzoic acid, 2-(3,4-dihydroxyphenyl)-2-(1,1-benzopyran)-3,5,7-triol, 3-hydroxy-7-sulfo-2-naphthoic acid, 1,2-dihydroxynaphthalene-4-sulfonic acid, N,N-bis(2-hydroxyethyl)glycine, N-(phosphonomethyl)-iminodiacetic acid, iminobis(methylenephosphonic acid), D-gluconic acid, tartaric acid, 1-oxopropane-1,2-dicarboxylic acid, propane-1,2,3-tricarboxylic acid, N,N',N''-tris[2-(N-hydroxycarbamoyl)ethyl]-1,3,5-benzenetricarboxamide (BAMTPH), desferrioxamine-B, 1,7-dihydroxy-4-sulfo-2-naphthanoic acid, aspartic acid, glutamic acid, pyridoxal-5-(dihydrogenphosphate), pyridoxal, amino(phenyl)methylene-diphosphoric acid, ethylene glycol tetraacetic acid (EGTA), 1,2 cyclohexanediaminetetraacetic acid (CDTA), ethylenebis(imino-(2-hydroxyphenyl)methylene(methyl)-phosphonic acid)), N-(2-hydroxyethyl)-ethylenedinitrilo-N,N',N'-triacetic acid, trimethylenedinitrilotetracetic acid, (2-dihydroxytrimethylene)-dinitrilotetracetic acid, xylenol orange, methylthymol blue, 3-hydroxyglutamic acid, L-phosphoserine, DL-amino-3-phosphopropanoic acid, and combinations thereof.

[0044] Preferred complexing agents include phosphonic acid and derivatives thereof, salicylic acid and derivatives thereof, and aminocarboxylic acids, other agents having an aluminum complexing power substantially similar to that of salicylic acid ($K = 13$), and combinations thereof. Most preferably, the complexing agents have solubility in water (in a solution including just the complexing agent and water) greater than or equal to about 0.5 wt.%, based on the total weight of the composition. Particularly preferred complexing agents include 2,3-hydroxybenzoic acid, salicylic acid, sulfosalicylic acid, HEDP, and combinations thereof. Even more preferred complexing agents include salicylic acid, sulfosalicylic acid, or combinations of salicylic acid and sulfosalicylic acid.

[0045] The organic solvents that may be added to the compositions of this aspect include, but are not limited to, sulfones, lactones, tetrahydrofurans and esters including, but not limited to, dimethylsulfoxide (DMSO), tetramethylene sulfone (sulfolane), dimethyl sulfone, diethyl sulfone, bis(2-hydroxyethyl) sulfone, methyl sulfolane, ethyl sulfolane, gamma-butyrolactone, delta-

valerolactone, epsilon-caprolactone, alpha-acetylbutyrolactone, tetrahydro-2-furanmethanol, tetrahydro-2-furoic acid, 3-hydroxytetrahydrofuran, tetrahydro-2-furanamine, dibasic esters (e.g., dimethyl succinate, dimethyl adipate, dimethyl glutarate, diisobutyl succinate, diisobutyl adipate, diisobutyl glutarate), alkyl carbonates (e.g., ethyl carbonate, propyl carbonate, butyl carbonate, glycerol), ethyl-3-ethoxypropionate, derivatives of any of the aforementioned compounds, and combinations thereof. Particularly preferred organic solvents include DMSO, gamma-butyrolactone or combinations of DMSO and gamma-butyrolactone.

[0046] The polymer dissolution accelerators include five-membered heterocyclic rings having at least one member of the ring being a nitrogen atom are best described by referring to the following structures:



where R may be the same as or different from one another and are selected from the group consisting of hydrogen, C₁-C₆ alkyls (e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl), C₁-C₆ alcohols (e.g., methanol, ethanol, propanol, butanol, pentanol, hexanol), C₁-C₆ primary amines, C₁-C₆ secondary amines, and carbonyl groups. Examples include, but are not limited to, 1-(3-aminopropyl)-imidazole (API), imidazole, 1,2-hydroxyethylimidazole (HEI), histamine (neutral or protonated), hydantoin, 1,3-dimethyl-2-imidazolidinone, N-methylpyrrolidinone, 1-ethyl-3-methylimidazolium salt (e.g., halide or methane sulfonate), 1-ethyl-2,3-dimethylimidazolium salt (e.g., halide), and combinations thereof. Particularly preferred polymer dissolution accelerators include HEI, API, or a combination of HEI and API. The presence of the polymer dissolution accelerator does not preclude the possibility that the polymer and/or other organic materials will delaminate from the surface and subsequently dissolve in the composition.

[0047] The compositions described herein have pH in a range from about 1 to about 14, and preferably about 6 to about 8. Favored compositions are initially substantially devoid of fluoride, amines (with the proviso that (i) species including an five-membered heterocyclic ring, wherein at least one member of the ring is a nitrogen atom, and (ii) species including both a carboxylic acid group and an amine group, are not considered amines for the purposes of this invention), abrasive material, oxidants such as H₂O₂, vinyl imidazole (and polyvinyl imidazole), antibacterial additives, copper, mannanase enzymes, fluorinated solvents, catalysts having at least one imine linkage and combinations thereof. The compositions must be in one distinct phase (i.e., all of the components are miscible) and the compositions must not be polymerizable (e.g., the composition should be substantially devoid of monomers and resins that are typically found in polymer-deposition solutions). As defined herein, "initially devoid" corresponds to a composition that has not yet been in contact with a surface having polymer and other organic materials thereon.

[0048] In a preferred embodiment, the composition has a pH in a range from about 10 to about 14, wherein the composition comprises, consists of or consists essentially of at least one organic solvent, at least one polymer dissolution accelerator, and water. Preferably, the amount of organic solvent is about 20 to about 80 wt%, the amount of polymer dissolution accelerator in about 1 to about 20 wt% and the amount of water is in a range from about 10 to about 70 wt%, based on the total weight of the composition.

[0049] In another preferred embodiment, the composition has a pH in a range from about 6 to about 8, wherein the composition comprises, consists of or consists essentially of at least one complexing agent, at least one organic solvent, at least one polymer dissolution accelerator, and water. Preferably, the amount of organic solvent is about 20 to about 80 wt%, the amount of polymer dissolution accelerator in about 1 to about 20 wt%, the amount of complexing agent is about 1 to about 15 wt%, and the amount of water is in a range from about 10 to about 70 wt%, based on the total weight of the composition.

[0050] In various preferred embodiments, the compositions are formulated in the following Formulations A-L and wherein all percentages are by weight, based on the total weight of the formulation:

Formulation A: 20-80 wt% DMSO, 1-20 wt% API, 10-70 wt% water

Formulation B: 20-80 wt% gamma-butyrolactone, 1-20 wt% API, 10-70 wt% water

Formulation C: 20-80 wt% DMSO, 1-20 wt% API, 1-15 wt% salicylic acid, 10-70 wt% water

Formulation D: 20-80 wt% gamma-butyrolactone, 1-20 wt% API, 1-15 wt% salicylic acid, 10-70 wt% water

Formulation E: 20-80 wt% DMSO, 1-20 wt% HEI, 1-15 wt% salicylic acid, 10-70 wt% water

Formulation F: 20-80 wt% gamma-butyrolactone, 1-20 wt% HEI, 1-15 wt% salicylic acid, 10-70 wt% water

Formulation G: 20-80 wt% DMSO, 1-20 wt% API, 1-15 wt% sulfosalicylic acid, 10-70 wt% water

Formulation H: 20-80 wt% gamma-butyrolactone, 1-20 wt% API, 1-15 wt% sulfosalicylic acid, 10-70 wt% water

Formulation I: 20-80 wt% DMSO, 1-20 wt% HEI, 1-15 wt% sulfosalicylic acid, 10-70 wt% water

Formulation J: 20-80 wt% gamma-butyrolactone, 1-20 wt% HEI, 1-15 wt% sulfosalicylic acid, 10-70 wt% water

Formulation K: 72 wt% gamma-butyrolactone, 6 wt% API, 5 wt% sulfosalicylic acid, 17 wt% water

Formulation L: 80 wt% DMSO, 10 wt% API, 10 wt% water

For example, the removal composition can comprise, consist of or consist essentially of: DMSO, salicylic acid or a salicylic acid derivative and water; gamma-butyrolactone, salicylic acid or a salicylic acid derivative and water; DMSO, API, salicylic acid or a salicylic acid derivative and water; or DMSO, HEI, salicylic acid or a salicylic acid derivative and water.

[0051] In another embodiment, the aforementioned compositions further include polymeric and/or other organic materials. For example, the composition may include at least one complexing agent, at least one organic solvent, at least one polymer dissolution accelerator, water and polymeric and/or organic material. In another embodiment, the composition may include at least one organic solvent, at least one polymer dissolution accelerator, water, and polymeric and/or organic material. The polymeric and/or organic material may be dissolved and/or suspended in the removal composition described herein.

[0052] The compositions described herein are compatible with low-k dielectric and metal-containing materials on the surface. For example, when polymeric and/or other organic materials are removed from a microelectronic device, low-k dielectrics and metals are not damaged using the removal compositions described herein. Furthermore, the compositions are water soluble, non-corrosive, non-flammable and of low toxicity. When used to remove polymers and/or other organic materials from microelectronic devices, the compositions described herein may be used in single wafer (as well as batch wafer) tool sets which is a significant advance over the amine-containing cleaners in the art.

[0053] The compositions described herein are easily formulated by simple addition of the respective ingredients and mixing to homogeneous condition. Furthermore, the compositions may be readily formulated as single-package formulations or multi-part formulations that are mixed at or before the point of use, e.g., the individual parts of the multi-part formulation may be mixed at the tool or in a storage tank upstream of the tool. The concentrations of the respective ingredients may be widely varied in specific multiples of the composition, i.e., more dilute or more concentrated, and it will be

appreciated that the compositions described herein can variously and alternatively comprise, consist or consist essentially of any combination of ingredients consistent with the disclosure herein.

[0054] Accordingly, another aspect relates to a kit including, in one or more containers, one or more components adapted to form the compositions described herein. The kit may include, in one or more containers, at least one complexing agent, at least one organic solvent, at least one polymer dissolution accelerator and optionally water, for combining with additional solvent, e.g., water and/or organic solvent, at the fab or the point of use. Alternatively, the kit may include, in one or more containers, at least one organic solvent, at least one polymer dissolution accelerator, and optionally water, for combining with additional solvent, e.g., water and/or organic solvent, at the fab or the point of use.

[0055] In another aspect, a method of removing polymer and/or other organic materials from a surface is described, wherein said method includes contacting a removal composition with the surface having the polymer and/or other organic materials thereon, under sufficient contacting conditions to remove the polymer and/or other organic materials from the surface. The surface corresponds to any solid material that the polymer or other organic material may be found on including, but not limited to, microelectronic devices, metals, plastics, fabrics, fibers, soils, wood, paper, glass, leather and other animal hides, cement, concrete, bricks, drywall, asphalt, keratin-containing substances such as hair and nails, rubber, latex, and combinations thereof. For example, in one embodiment, photoresist and/or resist-containing residues (e.g., post-etch and/or post-ash) may be removed. In another embodiment, paint may be removed. In still another embodiment, wax may be removed. In yet another embodiment, oils may be removed.

[0056] For example, traditionally, paint is removed from a surface by either mechanical methods such as abrasives or, in more recent years, using various chemicals. Unfortunately, the mechanical methods developed to remove paint from a surface do not allow for all of the paint to be removed, and the abrasives and abrasive techniques often used may also damage the surface. Moreover, removing paint mechanically from a surface is made more difficult if the surface has many crevices and grooves. In fact, it may be impossible to mechanically remove all of the paint from the surface. The removal compositions and methods of use described herein overcome the deficiencies of the prior art.

[0057] In a removal application, a removal composition as described herein is contacted in any suitable manner to the surface having polymer and/or other organic material thereon, e.g., by spraying a removal composition on the surface, by dipping (in a volume of a removal composition) of the surface including the polymeric/organic material, by contacting the surface with another material, e.g., a pad, or fibrous sorbent applicator element, that has a removal composition absorbed thereon, by contacting the surface including the polymeric/organic material to be removed with a recirculating removal composition, or by any other suitable means, manner or technique, by which a removal composition is brought into removal contact with the material(s) to be removed. The removal process

using a removal composition may include a static clean, a dynamic clean, or sequential processing steps including dynamic cleaning, followed by static cleaning of the surface in a removal composition, with the respective dynamic and static steps being carried out alternately and repetitively, in a cycle of such alternating steps.

[0058] The compositions described herein have particular utility in applications including, but not limited to, photoresist removal, post-etch residue removal, post-ash residue removal, surface preparation, post-plating cleaning, post-CMP residue removal, contaminant removal, anti-reflective coating removal, and combinations thereof.

[0059] As applied to microelectronic manufacturing operations, the compositions described herein are usefully employed to remove polymers and/or other organic materials from the surface of the microelectronic device. Preferably, the compositions do not damage low-k dielectric materials or corrode metal interconnects on the device surface. Preferably the compositions remove at least 85 % of the polymers and/or other organic materials present on the device prior to removal, more preferably at least 90 %, even more preferably at least 95 %, and most preferably at least 99%.

[0060] In use of the compositions described herein for removing polymers and/or other organic materials from surfaces having same thereon, the composition typically is contacted with the surface for a time of from about 5 sec to about 60 minutes, preferably about 1 min to 30 min, at temperature in a range of from about 20°C to about 60°C. Such contacting times and temperatures are illustrative, and any other suitable time and temperature conditions may be employed that are efficacious to at least partially clean the polymers and/or other organic materials from the surface. “At least partially clean” and “substantial removal” both correspond to at removal of at least 85 % of the polymer and/or other organic materials present on the surface prior to polymer/organic material removal, more preferably at least 90 %, even more preferably at least 95 %, and most preferred at least 99 %.

[0061] Following the achievement of the desired cleaning action, the composition may be readily removed from the device to which it has previously been applied, as may be desired and efficacious in a given end use application of the compositions described herein. Preferably, the rinse solution includes deionized water and optionally further includes at least one corrosion inhibitor. Thereafter, the device may be dried using nitrogen or a spin-dry cycle. Preferred corrosion inhibitors include, but are not limited to, ascorbic acid, adenosine, L(+)-ascorbic acid, isoascorbic acid, ascorbic acid derivatives, benzotriazole (BTA), citric acid, ethylenediamine, gallic acid, oxalic acid, tannic acid, ethylenediaminetetraacetic acid (EDTA), uric acid, 1,2,4-triazole (TAZ), tolyltriazole, 5-phenyl-benzotriazole, 5-nitro-benzotriazole, 3-amino-5-mercapto-1,2,4-triazole, 1-amino-1,2,4-triazole, hydroxybenzotriazole, 2-(5-amino-pentyl)-benzotriazole, 1-amino-1,2,3-triazole, 1-amino-5-methyl-1,2,3-triazole, 3-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 3-isopropyl-1,2,4-triazole, 5-phenylthiol-benzotriazole, halo-benzotriazoles (halo = F, Cl, Br or I), naphthotriazole, 2-mercaptobenzimidazole (MBI), 2-mercaptobenzothiazole, 4-methyl-2-phenylimidazole, 2-

mercaptothiazoline, 5-aminotetrazole, 5-amino-1,3,4-thiadiazole-2-thiol, 2,4-diamino-6-methyl-1,3,5-triazine, thiazole, triazine, methyltetrazole, 1,3-dimethyl-2-imidazolidinone, 1,5-pentamethylenetetrazole, 1-phenyl-5-mercaptotetrazole, diaminomethyltriazine, imidazoline thione, mercaptobenzimidazole, 4-methyl-4H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiadiazole-2-thiol, benzothiazole, tritoyl phosphate, imidazole, indiazole, benzoic acid, boric acid, malonic acid, ammonium benzoate, catechol, pyrogallol, resorcinol, hydroquinone, cyanuric acid, barbituric acid and derivatives such as 1,2-dimethylbarbituric acid, alpha-keto acids such as pyruvic acid, adenine, purine, phosphonic acid and derivatives thereof, glycine/ascorbic acid, Dequest 2000, Dequest 7000, p-tolylthiourea, succinic acid, phosphonobutane tricarboxylic acid (PBTCA), and combinations thereof. Most preferably, the corrosion inhibitor comprises PBTCA.

[0062] Yet another aspect relates to the improved microelectronic devices made according to the methods described herein and to products containing such microelectronic devices.

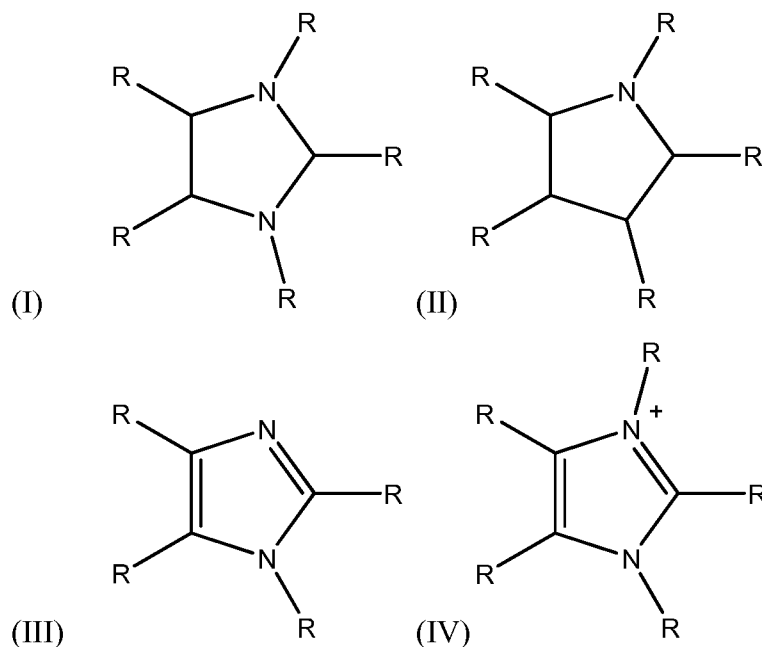
[0063] A still further aspect relates to methods of manufacturing an article comprising a microelectronic device, said method comprising contacting the microelectronic device with a composition for sufficient time to remove polymers and/or other organic materials from the microelectronic device having said polymers and/or other organic thereon, and incorporating said microelectronic device into said article.

[0064] Although the invention has been variously disclosed herein with reference to illustrative embodiments and features, it will be appreciated that the embodiments and features described hereinabove are not intended to limit the invention, and that other variations, modifications and other embodiments will suggest themselves to those of ordinary skill in the art, based on the disclosure herein. The invention therefore is to be broadly construed, as encompassing all such variations, modifications and alternative embodiments within the spirit and scope of the claims hereafter set forth.

THE CLAIMS

What is claimed is:

1. A removal composition comprising at least one polymer dissolution accelerator, at least one organic solvent, and water, wherein the composition is substantially devoid of fluoride species.
2. The removal composition of claim 1, wherein the pH of the composition is about 10 to about 14.
3. The removal composition of claim 1, further comprising at least one complexing agent.
4. The removal composition of claim 3, wherein the pH of the composition is about 6 to about 8.
5. The removal composition of any of the preceding claims, wherein the at least one organic solvent includes a compound selected from the group consisting of sulfones, lactones, tetrahydrofurans, dibasic esters, and combinations thereof.
6. The removal composition of any of the preceding claims, wherein the at least one organic solvent includes a compound selected from the group consisting of dimethylsulfoxide, tetramethylene sulfone, dimethyl sulfone, diethyl sulfone, bis(2-hydroxyethyl) sulfone, methyl sulfolane, ethyl sulfolane, gamma-butyrolactone, delta-valerolactone, epsilon-caprolactone, alpha-acetylbutyrolactone, tetrahydro-2-furanmethanol, tetrahydro-2-furoic acid, 3-hydroxytetrahydrofuran, tetrahydro-2-furanamine, dimethyl succinate, dimethyl adipate, dimethyl glutarate, diisobutyl succinate, diisobutyl adipate, diisobutyl glutarate, ethyl carbonate, propyl carbonate, butyl carbonate, glycerol, ethyl-3-ethoxypropionate, derivatives of any of the aforementioned compounds, and combinations thereof.
7. The removal composition of any of the preceding claims, wherein the at least one organic solvent comprises DMSO, gamma-butyrolactone, or a combination of DMSO and gamma-butyrolactone.
8. The removal composition of any of the preceding claims, wherein the at least one polymer dissolution accelerator comprises a five-membered heterocyclic ring having at least one member of the ring being a nitrogen atom.
9. The removal composition of claim 8, wherein the at least one polymer dissolution accelerator comprises a compound having a structure selected from the group consisting of (I), (II), (III), and (IV):



where R may be the same as or different from one another and are selected from the group consisting of hydrogen, C₁-C₆ alkyls, C₁-C₆ alcohols, C₁-C₆ primary amines, C₁-C₆ secondary amines, and carbonyl groups.

10. The remover composition of any of the preceding claims, wherein the at least one polymer dissolution accelerator comprises a compound selected from the group consisting of 1-(3-aminopropyl)-imidazole (API), imidazole, 1,2-hydroxyethylimidazole (HEI), histamine, hydantoin, 1,3-dimethyl-2-imidazolidinone, N-methylpyrrolidinone, 1-ethyl-3-methylimidazolium salt, 1-ethyl-2,3-dimethylimidazolium salt, and combinations thereof.

11. The removal compositions of any of the preceding claims, wherein the at least one polymer dissolution accelerator comprises 1-(3-aminopropyl)-imidazole (API), 1,2-hydroxyethylimidazole (HEI), or a combination API and HEI.

12. The removal composition of any of claims 3-11, wherein the at least one complexing agent comprises a compound selected from the group consisting of aminocarboxylic acids, organic acids and derivatives thereof, phosphonic acids and derivatives thereof, and combinations thereof.

13. The removal composition of any of claims 3-11, wherein the at least one complexing agent comprises species selected from the group consisting of salicylic acid, 5-sulfosalicylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), and combinations thereof.

14. The removal composition of any of claims 3-11, wherein the at least one complexing agent comprises salicylic acid, 5-sulfosalicylic acid, or the combination of salicylic acid and sulfosalicylic acid.
15. The removal composition of any of the preceding claims, wherein the composition is substantially devoid of amines, with the proviso that (i) the polymer dissolution accelerators, and (ii) species including both a carboxylic acid group and an amine group are not considered amines.
16. The removal composition of any of the preceding claims, wherein the composition is substantially devoid of at least one of: abrasive material; oxidants; vinyl imidazole; antibacterial additives; copper; mannanase enzymes; fluorinated solvents; catalysts having at least one imine linkage; and combinations thereof.
17. The removal composition of any of the preceding claims, wherein the removal composition is in one distinct phase and/or is not polymerizable.
18. The removal composition of any of the preceding claims, wherein said composition further comprises polymeric material and/or other organic material.
19. A method of removing polymer and/or other organic materials from a surface having same thereon, said method comprising contacting the surface with a semi-aqueous removal composition for sufficient time and under sufficient contacting conditions to at least partially remove said polymer and/or other organic materials from the surface, wherein the removal composition includes at least one polymer dissolution accelerator, at least one organic solvent, and water, wherein the composition is substantially devoid of fluoride species.
20. The method of claim 19, wherein the removal composition further comprises at least one complexing agent.
21. The method of any of claims 19-20, wherein said contacting comprises conditions selected from the group consisting of: time of from about 5 sec to about 60 minutes; temperature in a range of from about 20°C to about 60; and combinations thereof.
22. The method of any of claims 19-21, further comprising rinsing the surface with a rinsing solution following contact with the composition, wherein the rinsing solution comprises water.

23. The method of claim 22, wherein the rinsing solution further comprises at least one corrosion inhibitor.