

TITLE OF THE INVENTION:

Eco-Friendly Biocides for
Chemical Mechanical Planarization (CMP) Polishing Compositions

CROSS REFERENCE TO RELATED PATENT APPLICATIONS

[0001] The application claims the benefit of U.S. Application No. 63/601,467 filed on November 21, 2023. The disclosure of the application is hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] This invention relates to Chemical Mechanical Planarization (CMP) polishing compositions. More specifically, the invention relates to the protection of Chemical Mechanical Planarization (CMP) polishing compositions using eco-friendly biocides for inhibiting microbe (bacteria and/or fungi) growth in the composition.

[0003] The problem of bacterial and fungal growth in polishing composition is known in the art.

[0004] US3,336,236 addressed the issue using sodium chlorite in an amount sufficient to inhibit growth and reproduction of the bacteria; US 3,816,330 addressed the issue using about 10-1000 parts per million of hexachlorophene; US 3,860,431 and US 2,823,186 addressed the issue using polyhydric alcohols; US2,801,216 and 3,046,234 addressed the issue using dialdehydes; US3,377,275 and 3,148,110 addressed the issue using formaldehyde; however, the aforementioned methods have unacceptable polishing rates. Thus, US 4,169,337; US 4,462,188; US 4,588,421; and US 4,892,612 taught the use of various polishing rate accelerator to boost the polishing rates.

[0005] US 5,230,833 found that increased microbiological growth is observed during recirculation and dilution of the slurry which did not have microbiological growths. The microbiological growths were promoted when organic rate accelerators are used.

[0006] US 5,230,833 addressed the issue with the use of bactericides and fungicides; such as tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, alkylbenzyltrimethylammonium chloride, and

alkylbenzyltrimethylammonium hydroxide, wherein the alkyl chain ranges from 1 to about 20 carbon atoms. The preferred biocide is sodium chlorite or sodium hypochlorite; and the preferred fungicide is sodium OMADINE® (pyrithione).

[0007] WO200160940 indicated that the above chemicals used for inhibiting the microbiological growth are not always compatible with abrasive slurries used for chemical-mechanical polishing (CMP) of semiconductor wafers and with abrasive free slurries used with fixed abrasive polishing pads for semiconductor wafer polishing. WO200160940 disclosed the use of a five membered organic ring compound containing both a sulfur and a nitrogen in the ring which provides biocide protection of CMP slurries without affecting polishing performance. Examples of such compounds are 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT) and 2-methyl-4-isothiazolin-3-one (MIT) which have been widely adopted to use as the biocides. US 8,999,193 disclosed the use of MIP and CMIP as the biocides in tungsten CMP polishing composition; US10,600,655 disclosed the use of MIP and CMIP as the biocides in STI CMP polishing composition; and 11,718,767 disclosed the use of MIP and CMIP as the biocides in SiN CMP polishing composition.

[0008] The commonly used biocide in CMP polishing compositions are containing 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT), 2-methyl-4-isothiazolin-3-one (MIT), or 2-n-Octyl-4-isothiazolin-3-one(OIT).

[0009] However, those heterocyclic organic compounds are known to be hazardous for the environment: wastewater treatment system, human health, highly toxic to the aquatic life, and worst, the long lasting effects.

[0010] Furthermore, the CMP composition needs biological growth inhibitors or preservatives to prevent microbe (bacterial and fungal) growth during the storage.

[0011] It should be readily apparent from the foregoing that there remains a need within the art for highly desirable environmentally friendly or eco-friendly chemicals as alternative biocides in CMP polishing compositions, especially in CMP composition during the storage.

BRIEF SUMMARY OF THE INVENTION

[0012] The present invention satisfies the need by providing desirable environmentally friendly or eco-friendly chemicals as alternative biocides to replace commonly used MIP, CMIP, OIT biocides in CMP polishing compositions.

[0013] More specifically, the present invention discloses the use of FDA approved food preservatives and additives as the effective biocides in CMP polishing compositions.

[0014] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a chemical additive;

a biocide; and

water-soluble solvent; and

optionally at least one of

abrasive;

a pH adjusting agent;

an oxidizer;

an activator;

a surfactant;

a corrosion inhibitor;

where pH of the composition ranges from 2 to 9, 2 to 8, 2 to 7, or 2 to 6.

[0015] The chemical additive can be any additive that promotes microbiological growth in a CMP polishing composition. The chemical additive includes but is not limited to any chemicals that perform a function in a CMP polishing composition as a dishing reducer, a removal rate suppressor, a removal rate accelerator, a surfactant, a corrosion inhibitor, an erosion reducer, defect reducer, dispersion agent, chelating agent, stabilizer, and combinations thereof in a CMP polishing composition. Those functions have their commonly acceptable meanings in the art and should be readily understood by a person of ordinary skill in the art. For instance, a dishing reducer reduces the dishing during polishing; an organic rate accelerator/suppressor enhances/suppresses polishing rate of a material to be polished.

[0016] The biocide is an eco-friendly chemical includes but is not limited to FDA approved food additives and/or preservatives. For example, the biocide includes but is not limited to sorbic acid, its derivatives or salts thereof; and benzoic acid, its derivatives or salts thereof.

[0017] The optional abrasive includes but is not limited to inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof.

[0018] The optional pH adjusting agent includes but is not limited to (a)nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty

acids, various polycarboxylic acids, and mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH.

[0019] The optional oxidizer includes but is not limited to peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, and ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, KClO_4 , KBrO_4 , and KMnO_4 ; and combinations thereof.

[0020] The optional activator includes but is not limited to (1) inorganic oxide particle with transition metal coated onto its surface; wherein the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2) soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate, ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate, and combinations thereof; (3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V, and combinations thereof; and combinations thereof.

[0021] The optional surfactant can be any surfactant includes but is not limited to non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and mixtures thereof.

[0022] The optional corrosion inhibitor can be any corrosion inhibitor which includes but is not limited to nitrogenous cyclic compounds.

[0023] In another aspect (Aspect 2), there is provided a CMP polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing at least one material, comprising the steps of:
contacting the at least one surface with a polishing pad;
delivering the CMP polishing composition of Aspect 1;
polishing the at least one surface containing the at least one material with the CMP polishing composition.

[0024] In yet another aspect (Aspect 3), there is provided a CMP polishing system, comprising:

a semiconductor substrate comprising at least one surface containing at least one material;
a polishing pad; and
the CMP polishing composition of Aspect 1;
wherein the at least one surface containing the at least one material is in contact with the polishing pad and the CMP polishing composition.

[0025] The at least one material refers to any materials used in the semiconductor substrate or pattern wafer; includes metals or metal alloys such as W, Cu, Co, Al, Ni, Mn, and their alloys; novel metals such as Ru; barrier layer materials such as Ta, TaN, Ti, TiN, and Co; dielectric materials such as SiO₂, SiN, and SiC; and low-k and ultra-low-k materials, such as Black Diamond.

[0026] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

[0027] The embodiments of the invention can be used alone or in combinations with each other.

DETAILED DESCRIPTION OF THE INVENTION

[0028] It is the object of this invention to provide biocides which are eco-friendly.

[0029] The present invention satisfies the need by providing desirable environmentally friendly or eco-friendly chemicals as alternative biocides in CMP polishing compositions; as well as in the systems, and methods of using the CMP polishing composition or slurry. The CMP polishing composition or CMP polishing slurry are exchangeable.

[0030] More specifically, the invention discloses the eco-friendly biocides which prohibit microbiological growth in a CMP polishing composition that contains chemical additives that promote microbiological growth. The eco-friendly biocides include but are not limited to some of FDA approved food additives and preservatives.

[0031] The CMP polishing composition can be abrasive free CMP polishing compositions which is used with fixed abrasive polishing pads for semiconductor wafer polishing.

[0032] The CMP polishing composition can also contain more than one part, such as two parts: the chemical package and the abrasive package wherein the two packages will be mixed together at the point of use. The chemical package usually contains the chemical additives that promote microbiological growth, and thus the chemical package

usually contains the biocide. The packages can also be concentrated and will be diluted at the point of use. The abrasive package usually also contains the biocide to prevent microbiological growth to enhance its storage shelf times.

[0033] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:

a chemical additive;

a biocide; and

water-soluble solvent; and

optionally at least one of

abrasive;

a pH adjusting agent;

an oxidizer;

an activator;

a surfactant;

a corrosion inhibitor;

wherein pH of the polishing composition ranges from 2 to 9, 2 to 8, 2 to 7, or 2 to 6.

[0034] The chemical additive can be any additive that promotes microbiological growth in a CMP polishing composition. The chemical additive includes but is not limited to any chemicals that perform a function in a CMP polishing composition as a dishing reducer, a removal rate suppressor, a removal rate accelerator, a surfactant, a corrosion inhibitor, an erosion reducer, defect reducer, dispersion agent, chelating agent, stabilizer, and combinations thereof in a CMP polishing composition. Those functions have their commonly acceptable meanings in the art and should be readily understood by a person of ordinary skill in the art. For instance, a dishing reducer reduces the dishing during polishing; an organic rate accelerator/suppressor enhances/suppresses polishing rate of a material to be polished.

[0035] For example, the chemical additive can be a dishing reducer such as (a) a polyol includes but is not limited to maltitol, lactitol, maltotritol, ribitol, D-sorbitol, mannitol, dulcitol, iditol, D-(–)-Fructose, sorbitan, sucrose, ribose, Inositol, glucose, D-arabinose, L-arabinose, D-mannose, L-mannose, meso-erythritol, beta-lactose, arabinose, fructose, xylitol, and combinations thereof, as disclosed in US11,078,417 for STI polishing composition; (b) 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU), and/or 2-aminobenzoimidazole for W polishing composition as disclosed in US20200040256; and

(c) 1,2,4-triazole, 1,2,3-triazole, and benzotriazole for Cu polishing composition as disclosed in US11,401,441.

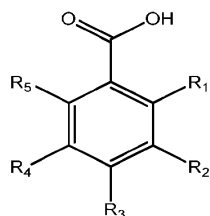
[0036] The chemical additive can also be a removal rate accelerator such as (a) organic sulfonic acid, organic aromatic sulfonic acid such as benzene sulfonic acid, piperazine, organic phosphonic acid, for STI polishing composition as disclosed in US2020004,551; (b) organic carboxylic acids for W polishing composition as disclosed in US20200040256; and (c) various amino acids, such as glycine and alanine, amino acid derivatives, and organic amines for Cu polishing composition as disclosed in US9,978,609.

[0037] The chemical additive can also be a polymer or co-polymer includes but is not limited to polyacrylic acid, polymethylacrylic acid, polyamide, polystyrene sulfonic acid, polyamine, polyethyleneimine, polyethylene oxide, polypropylene oxide, polyethylene glycol, polyglycerin, polyoxyethylene, polyglyceryl ether, polyoxypropylene, polyglyceryl ether, polyacrylamide, poly(acrylic acid-co-maleic acid), poly(acrylamide-co-acrylic acid), poly(methyl vinyl ether), poly(propylene glycol), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate), polyvinyl sulfonic acid, polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl pyridine-N-oxide, Poly(acrylamide-acrylic acid), poly(4-styrenesulfonic acid-co-maleic acid), poly acrylamide-co-diallyldimethylammonium chloride, poly(ethylene-co-methacrylic acid), and polyvinyl ether, poly(4-Vinylpyridine, poly(4-vinylpyridine-co-butylmethacrylate), poly(diallyldimethylammonium chloride), poly(N-isopropylacrylamide), poly(vinylphosphonic acid), polyglykol, polyoxyethylene sorbitan tetraoleate, polysorbate 20, polysorbate 40, polysorbate 80, poly(vinyl acetate), poly(styrene-co-allyl alcohol), poly(4-vinylphenol), and poly(2-ethyl-2-oxazoline).

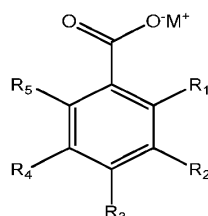
[0038] The concentration (or amount) of chemical additive ranges from 0.01 wt.% to 20.0 wt.%, 0.05 wt.% to 15 wt.%, or 0.1 wt.% to 10 wt.%. The weight percent is relative to the composition.

[0039] The biocide is an eco-friendly chemical includes but is not limited to FDA approved food additives and/or a preservatives. For example, the biocide includes but is not limited to sorbic acid, it's derivatives or salts thereof; and benzoic acid, it's derivatives or salts thereof.

[0040] The benzoic acid, its derivatives, and their salts include but are not limited to the ones have a general molecular structure of:



(a),



(b),

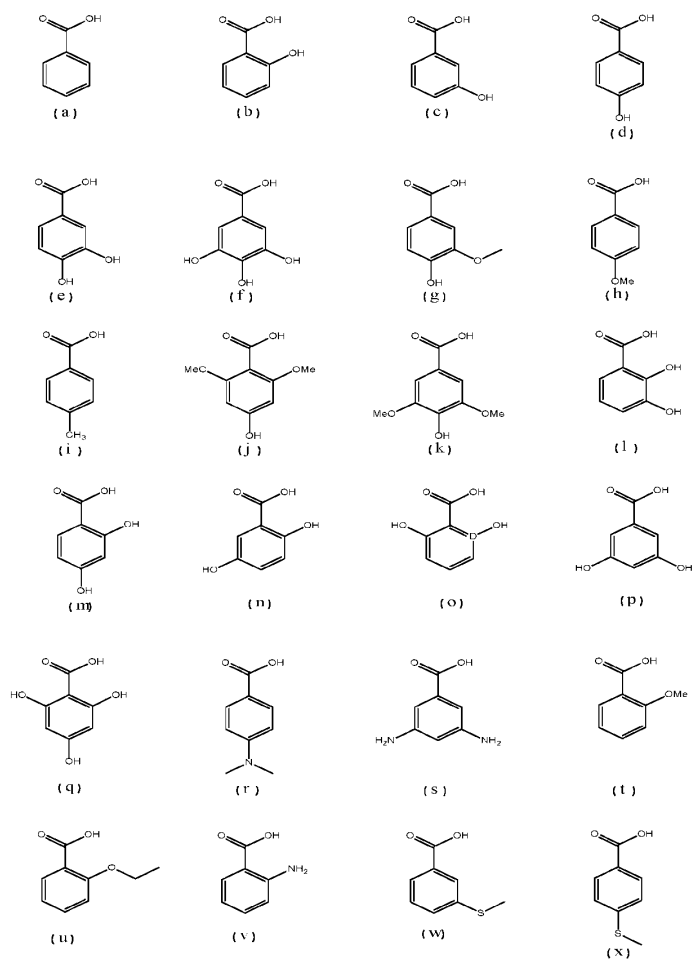
and combinations thereof.

[0041] Each of R1, R2, R3, R4, and R5 is independently selected from the group consisting of hydrogen, hydroxyl group, alkyl group, alkoxy group, amino group, dialkylamino group, alkylthio group, and combinations thereof.

[0042] R1, R2, R3, R4, and R5 can all be hydrogen atoms resulting in benzoic acid or its salts. Some of R1, R2, R3, R4, and R5 can be hydrogen atoms and others can be different functional groups connected to the -2, -3, -4, -5 or -6 position in benzoic acid derivatives. These functional groups include, but are not limited to, hydroxyl group, alkyl group, alkoxy group, amino group, dialkylamino group, and alkylthio group. These functional groups can be attached to the benzoic acid ring in mono-, bis-, or tris form.

[0043] M⁺ is a metal ion which includes but is not limited to potassium ion, ammonium ion, and sodium ion. Potassium salt of benzoic acid and ammonium salt of benzoic acid are preferred.

[0044] Examples of benzoic acid and benzoic acid derivative are listed below with the molecular structures:



[0045] The structures are benzoic acid (a), 2-hydroxybenzoic acid (salicylic acid) (b), 3-hydroxybenzoic acid (c), 4-hydroxybenzoic acid (d), 3,4-dihydroxybenzoic acid (e), 3,4,5-trihydroxybenzoic acid (f), 3-methoxy-4-hydroxybenzoic acid (g), 4-methoxybenzoic acid (h), 4-methylbenzoic acid (i), 2,6-dimethoxy-4-hydroxybenzoic acid (j), 3,5-dimethoxy-4-hydroxybenzoic acid (k), 2,3-dihydroxybenzoic acid (l), 2,4-dihydroxybenzoic acid (m), 2,5-dihydroxybenzoic acid (n), 2,6-dihydroxybenzoic acid (o), 3,5-dihydroxybenzoic acid (p), 2,4,6-trihydroxybenzoic acid (q), 4-(dimethylamino)benzoic acid (r), 3,5-diaminobenzoic acid (s), 2-methoxybenzoic acid (t), 2-ethoxybenzoic acid (u), 2-aminobenzoic acid (v), 3-methylthiobenzoic acid (w), and 4-methylthiobenzoic acid (x).

[0046] The biocide can also be sorbic acid, its derivatives and their salts, such as potassium salt of sorbic acid, ammonium salt of sorbic acid, sodium salt of sorbic acid, sorbohydroxamic acid, and sorbic aldehyde.

[0047] The amount of the biocide can range from about 0.005 wt.% to 1.0 wt.%, about 0.01 wt.% to 0.75 wt.%, or about 0.05 wt.% to 0.5 wt.%. The weight percent is relative to the composition.

[0048] The water-soluble solvent includes but is not limited to deionized (DI) water, distilled water, and alcoholic organic solvents.

[0049] The optional abrasive includes but is not limited to inorganic oxide particles including but not limited to fumed silica, colloidal silica, high purity colloidal silica, fumed alumina, colloidal alumina, cerium oxide, titanium dioxide, zirconium oxide; metal oxide-coated inorganic oxide particles including but not limited to ceria-coated inorganic oxide particles; organic polymer particles; metal oxide-coated organic polymer particles; and combinations thereof.

[0050] The amount of the abrasive can range from about 0.01 wt.% to 30 wt.%, about 0.05 wt.% to 20 wt.%, about 0.01 to 10 wt.%, or about 0.1 wt.% to 5 wt.%. The weight percent is relative to the composition.

[0051] The abrasive particles have mean particle sizes (measured by Dynamic Light Scattering DLS technology) ranging from about 2nm to 1,000nm, 10nm to 500nm, or 20nm to 250nm; or 2 nm to 160 nm, 2 nm to 100 nm, 2 nm to 80 nm, 2 nm to 60 nm, 3 nm to 50 nm, 3 nm to 40 nm, 4 nm to 30 nm, or 5 nm to 20 nm.

[0052] The optional oxidizer includes but is not limited to peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, and ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, KClO_4 , KBrO_4 , and KMnO_4 ; and combinations thereof.

[0053] The amount of the oxidizer can range from about 0.01 wt.% to 30 wt.%, about 0.1 wt.% to 20 wt.%, or about 0.5 wt.% to about 10 wt.%. The weight percent is relative to the composition.

[0054] The optional activator includes but is not limited to (1) inorganic oxide particle with transition metal coated onto its surface; wherein the transition metal is selected from

the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2) soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate, ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate, and combinations thereof; (3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V, and combinations thereof; and combinations thereof.

[0055] The amount of the activator can range from about 0.00001 wt.% to 5 wt.%, about 0.0001 wt. % to 2.0 wt. %, about 0.0005 wt. % to 1.0 wt.%; or about 0.001 wt. % to 0.5 wt.%.

[0056] The optional surfactant can be any surfactant includes but is not limited to non-ionic surfactant, anionic surfactant, cationic surfactant, ampholytic surfactant, and mixtures thereof.

[0057] Non-ionic surfactants may be chosen from a range of chemical types including but not limited to long chain alcohols, ethoxylated alcohols, ethoxylated acetylenic diol surfactants, polyethylene glycol alkyl ethers, propylene glycol alkyl ethers, glucoside alkyl ethers, polyethylene glycol octylphenyl ethers, polyethylene glycol alkylphenyl ethers, glycerol alkyl esters, polyoxyethylene glycol sorbiton alkyl esters, sorbiton alkyl esters, cocamide monoethanol amine, cocamide diethanol amine dodecyl dimethylamine oxide, block copolymers of polyethylene glycol and polypropylene glycol, polyethoxylated tallow amines, and fluorosurfactants. Polymer molecular weight of surfactant may range from several hundreds to over 1 million. The viscosities of these materials also possess a broad distribution.

[0058] Anionic surfactants include, but are not limited to salts with suitable hydrophobic tails, such as alkyl carboxylate, alkyl polyacrylic salt, alkyl sulfate, alkyl phosphate, alkyl bicarboxylate, alkyl bisulfate, alkyl biphosphate, such as alkoxy carboxylate, alkoxy sulfate, alkoxy phosphate, alkoxy bicarboxylate, alkoxy bisulfate, alkoxy biphosphate, such as substituted aryl carboxylate, substituted aryl sulfate, substituted aryl phosphate, substituted aryl bicarboxylate, substituted aryl bisulfate, and substituted aryl biphosphate etc. The counter ions for this type of surfactants include, but are not limited to potassium, ammonium and other positive ions. The molecular weights of these anionic surface wetting agents range from several hundred to several hundred thousand.

[0059] Cationic surfactants possess the positive net charge on major part of molecular frame. Cationic surfactants are typically halides of molecules comprising hydrophobic chain and cationic charge centers such as amines, quaternary ammonium, benzyalkonium, and alkylpyridinium ions.

[0060] In another aspect, the surfactant can be an ampholytic surfactant, which possess both positive (cationic) and negative (anionic) charges on the main molecular chains and with their relative counter ions. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates, as in the sultaines CHAPS (3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate) and cocamidopropyl hydroxysultaine. Betaines such as cocamidopropyl betaine have a carboxylate with the ammonium. Some of the ampholytic surfactants may have a phosphate anion with an amine or ammonium, such as the phospholipids phosphatidylserine, phosphatidylethanolamine, phosphatidylcholine, and sphingomyelins.

[0061] The amount of the surfactant can range from 0.0001 wt.% to 10 wt. %, 0.01wt.% and 3 wt.%, or 0.05 wt.% and 1 wt.%.

[0062] The optional corrosion inhibitor can be any corrosion inhibitor, includes but is not limited to nitrogenous cyclic compounds; such as 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, benzothiazoles such as 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate such as 1,3,5-tris(2-hydroxyethyl), and mixtures thereof. Preferred inhibitors are 1,2,4-triazole, 5 amino triazole and 1,3,5-tris(2-hydroxyethyl)isocyanurate.

[0063] The amount of the corrosion inhibitor can range from less than 1.0 wt.%, less than 0.5 wt.%, or less than 0.25 wt.%.

[0064] In another aspect (Aspect 2), there is provided a CMP polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing at least one material, comprising the steps of:
contacting the at least one surface with a polishing pad;
delivering the CMP polishing composition of Aspect 1;
polishing the at least one surface containing the at least one material with the CMP polishing composition.

[0065] In yet another aspect (Aspect 3), there is provided a CMP polishing system, comprising:
a semiconductor substrate comprising at least one surface containing at least one material;
a polishing pad; and
the CMP polishing composition of Aspect 1;
wherein the at least one surface containing the at least one material is in contact with the polishing pad and the CMP polishing composition.

[0066] The at least one material refers to any materials used in the semiconductor substrate or patten wafer; includes metals or metal alloys such as W, Cu, Co, Al, Ni, Mn, and their alloys; novel metals such as Ru; barrier layer materials such as Ta, TaN, Ti, and TiN; dielectric materials such as SiO₂, SiN, and SiC; and low-k and ultra-low-k materials, such as Black Diamond.

[0067] The following non-limiting examples are presented to further illustrate the present invention.

Biocide Efficacy Testing

[0068] Ceria-coated Silica particles have a mean particle size (MPS) or primary particle size (measured by DLS) of 20 nanometers (nm) to 500 nanometers (nm) were supplied by JGCC Inc. in Japan.

[0069] Chemicals, such as D-Sorbitol, sorbic acid, benzoic acid, and all other chemical raw materials were supplied by Millipore Sigma, St. Louis, MO.

[0070] An abrasive free CMP polishing composition, or a chemical package composition used in a two-package CMP polishing composition was prepared using D-sorbitol as the chemical additive.

[0071] Biocide Efficacy Testing was performed with the intentional additions of microbe (bacteria and fungi). All tests were done at a temperature of 30°C.

Example 1

[0072] The reference sample (Ref.) had 15 wt.% D-sorbitol, pH adjusting agent, deionized water.

[0073] All working samples (WS) had 15 wt.% D-sorbitol, pH adjusting agent and deionized water, and benzoic acid or one of its derivatives.

[0074] WS #1 had 0.1 wt.% benzoic acid (a), WS #2 had 0.1 wt.% 4-hydroxybenzoic acid (d), WS #3 had 0.1 wt.% 3,4,5-trihydroxybenzoic acid (f), WS #4 had 0.1 wt.% 4-hydroxyl-3-methoxy benzoic acid (g), WS #5 had 0.1 wt.% 4-methoxy benzoic acid (h), WS #6 had 0.1 wt.% 4-methylbenzoic acid (i), WS #7 had 0.1 wt.% 2,3-dihydroxybenzoic acid (l), WS #8 had 0.1 wt.% 3,5-diaminobenzoic acid (s), respectively as biocide. All working samples were adjusted to have a pH at 2.15.

[0075] The testing results were listed in the Table 1 below.

Table 1. Biocide Efficacy Testing Result Comparison

Sample	Contaminant Reading at Day 0 (cfu/ml*)	Contaminant Reading at Day 7 (cfu/ml)
Ref. 1	2.6×10^6	$>1.4 \times 10^7$
WS# 1	$>1.4 \times 10^7$	$<3.0 \times 10^{-1}$
WS# 2	2.5×10^5	9.0×10^1
WS# 3	$>1.4 \times 10^7$	1.1×10^3
WS# 4	$>1.4 \times 10^7$	2.5×10^2
WS# 5	$>1.4 \times 10^7$	4.0×10^3
WS# 6	$>1.4 \times 10^7$	4.0×10^3
WS# 7	2.5×10^5	4.0×10^2
WS# 8	$>1.4 \times 10^7$	2.0×10^3

*Colony Forming Unit per mL(cfu/ml)

[0076] As the testing results shown in Table 1, the contaminant reading at Day 7 for the Ref was higher than the contaminant reading at Day zero (0) indicating microbiological growth without using a biocide.

[0077] The contaminant readings at Day 7 for all working samples were significantly lower than the contaminant reading at Day 0 . Thus, benzoic acid and derivatives demonstrated the ability for preventing the microbiological growth in the compositions.

Example 2

[0078] The effect of the benzoic acid concentrations on the biocide efficacy was evaluated.

[0079] All compositions had 15 wt.% D-sorbitol, deionized water, and pH adjusting agent. The compositions were adjusted to have a very acidic pH around 2.1.

[0080] Three working samples 9 (WS #9), 10 (WS#10) and 11 (WS#11) used benzoic acid at concentrations of 0.001wt.%, 0.01wt.% and 0.1wt.% respectively.

[0081] The testing results were listed in Table 2 below.

Table 2. Benzoic Acid Concentration Test

Sample	Contaminant Reading at Day 0 (cfu/ml)	Contaminant Reading at Day 7 (cfu/ml)
WS#9	$>1.0 \times 10^7$	$>1.0 \times 10^7$
WS#10	$>1.0 \times 10^7$	$\sim 1.0 \times 10^4$
WS#11	$>1.0 \times 10^7$	$<3.0 \times 10^{-1}$

[0082] 0.001wt.% benzoic acid (WS#9) in the composition did not effectively prevent the microbiological growth in the composition.

[0083] The contaminant reading at Day 7 for WS #10 and WS #11 were significantly lower than the contaminant reading at Day 0. The microbiological growth was effectively prevented with the use of 0.01and 0.1 wt.% benzoic acid in the composition.

Example 3

[0084] In this Example, all compositions had 15 wt.% D-sorbitol, 0.1 wt.% sorbic acid, pH adjusting agent and deionized water. Sorbic acid was used as the alternative biocide.

[0085] Working example 12 (WS #12) had a pH adjusted to 4.0.

[0086] Working example 13 (WS #13) had a pH adjusted to 5.0.

[0087] The biocide efficacy testing results were listed in Table 3.

Table 3. Sorbic Acid Concentration Biocide Efficacy Testing Results

Sample	Contaminant Reading at Day 0	Contaminant Reading at Day 7
WS#12	1.4×10^7	9.0×10^{-1}
WS#13	1.4×10^7	9.0×10^0

[0088] As the testing results shown in Table 3, 0.1 wt.% sorbic acid had shown very effective biocide efficacy to prevent the growth of bacteria at both pH 4.0 and 5.0.

Polishing Experiments

PARAMETERS:

Å: angstrom(s) – a unit of length

BP: back pressure, in psi units

CMP: chemical mechanical planarization = chemical mechanical polishing

CS: carrier speed

DF: Down force: pressure applied during CMP, unit: psi

min: minute(s)

ml: milliliter(s)

mV: millivolt(s)

psi: pounds per square inch

PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)

SF: polishing composition flow, ml/min

TEOS: silicon oxide films by Chemical Vapor Deposition (CVD) using tetraethyl orthosilicate as the precursor

Wt.%: weight percentage (of a listed component)

Removal Rate (RR) = (film thickness before polishing - film thickness after polishing)/polish time.

Removal Rates and Selectivity

Tungsten Removal Rates: Measured tungsten removal rate at 2.5 psi down pressure of the CMP tool.

TEOS Removal Rates: Measured TEOS removal rate at a given down pressure. The down pressure of the CMP tool was 2.5 psi.

SiN Removal Rates: Measured SiN removal rate at a given down pressure. The down pressure of the CMP tool was 2.5 psi.

Polishing pad, IC1010 and other pads were used during CMP, supplied by DOW, Inc.

Metrology

[0089] Films were measured with a ResMap CDE, model 168, manufactured by Creative Design Engineering, Inc, 20565 Alves Dr., Cupertino, CA, 95014. The ResMap tool is a four-point probe sheet resistance tool. Forty-nine-point diameter scan at 5mm edge exclusion for film was taken.

CMP Tool

[0090] The CMP tool that was used is a 200mm Mirra, or 300mm Reflexion manufactured by Applied Materials, 3050 Boweres Avenue, Santa Clara, California, 95054. An IC1010 pad supplied by DOW, Inc, 451 Bellevue Rd., Newark, DE 19713 was used on platen 1 for blanket and pattern wafer studies.

[0091] The IC1010 pad or other pad was broken in by conditioning the pad for 18 mins. At 7 lbs. down force on the conditioner. To qualify the tool settings and the pad break-in four TEOS monitors were polished with Versum® STI2305 composition, supplied by Versum Materials Inc. at baseline conditions.

Wafers

[0092] Polishing experiments were conducted using PECVD or LECVD or HD TEOS wafers, and SiN wafers, the patterned wafer are MIT864 oxide patterned wafer. These blanket and patterned wafers were purchased from Silicon Valley Microelectronics, 2985 Kifer Rd., Santa Clara, CA 95051.

[0093] In blanket wafer studies, oxide blanket wafers, and SiN blanket wafers were polished at baseline conditions. The tool baseline conditions were: table speed; 87 rpm, head speed: 93 rpm, membrane pressure; 3.1 psi, composition flow; 200 ml/min., Saesol E4 disk was used for 100% in-situ conditioning.

[0094] These polished patterned wafers (MIT864) wafers were measured on the Veeco VX300 profiler/AFM instrument.

Example 4

[0095] In CMP polishing example 4, removal rates of different films were measured, and RR Selectivity were calculated.

[0096] The reference polishing composition 1 (Ref. 1) contained 0.5 wt.% ceria-coated silica abrasive, 0.15 wt.% D-sorbitol, 18.6 ppm bioban 425 (2-octyl-2H-isothiazole-3-one, OIT biocide) as biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[0097] The reference polishing composition 2 (Ref. 2) contained 0.5 wt.% ceria-coated silica abrasive, 0.15 wt.% D-sorbitol, pH adjusting agent, deionized water, and no biocide. The pH was adjusted to 5.35.

[0098] The working polishing composition (Working Sample) contained 0.5 wt.% ceria-coated silica abrasive, 0.15 wt.% D-sorbitol, 10.0 ppm benzoic acid as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[0099] The blanket film polishing results were shown in Table 4.

Table 4. Effects of Eco-Friendly Biocide on Film RR & Oxide: SiN Selectivity

Sample	TEOS RR (Å/min.)	HDP RR (Å/min.)	SiN RR (Å/min.)	TEOS: SiN Selectivity	HDP: SiN Selectivity
Ref. 1	4995	4703	92	54	51
Ref. 2	5023	4911	103	49	48
Working Sample	5239	5002	98	53	51

[00100] As the results shown in Table 4, there was little difference in CMP polishing performance among the three polishing compositions.

[00101] Furthermore, using a biocide (either the eco-friendly biocide or the traditional OIT biocide) in the polishing composition did not affect the CMP polishing performance.

Example 5

[00102] In CMP polishing example 5, the oxide trench pitch dishing on different size features vs different over polishing times were obtained from two reference samples and the working samples. The results were listed in Table 5.

Table 5. Effects of Eco-Friendly Biocide on Oxide Trench Dishing vs OP Times (Sec.)

Compositions	OP Times (Sec.)	100 μ m pitch dishing	200 μ m pitch dishing
Ref. 1	60	245	396
	120	396	561
Ref. 2	60	371	403
	120	518	559
Working Sample	60	234	340
	120	418	547

[00103] As the results shown in Table 5, while using eco-friendly biocide benzoic acid to replace traditional OIT biocide, similar oxide trench dishing vs different over polishing times on two different sized features were obtained.

[00104] The oxide patterned wafer polishing results obtained from two reference samples and the working sample on oxide trench dishing rates on different size features were compared and listed in Table 6.

Table 6. Effects of Eco-Friendly Biocide on Oxide Trench Dishing Rates

Compositions	P100 Dishing Rate ($\text{\AA}/\text{sec.}$)	P200 Dishing Rate ($\text{\AA}/\text{sec.}$)
Ref. 1	2.3	2.7
Ref. 2	2.0	2.8
Working Sample	1.9	2.6

[00105] As the results shown in Table 6, while using eco-friendly biocide benzoic acid to replace traditional OIT biocide, the similar or slightly lower oxide trench dishing rates

on 100µm or 200µm features were obtained vs the oxide trench dishing rates on different sized oxide trench features.

[00106] As the results shown above, the disclosed eco-friendly biocides have demonstrated the same CMP polishing performance as the traditionally used biocides.

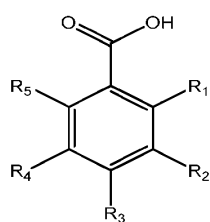
[00107] The embodiments of this invention listed above, including the working example, are exemplary of numerous embodiments that may be made of this invention. It is contemplated that numerous other configurations of the process may be used, and the materials used in the process may be elected from numerous materials other than those specifically disclosed.

Claims

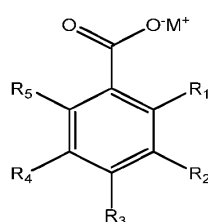
1. A Chemical Mechanical Planarization polishing composition comprising, consisting essentially of, or consisting of:
 - a chemical additive;
 - a biocide; and
 - water-soluble solvent; and
 - optionally at least one of
 - abrasive;
 - a pH adjusting agent;
 - an oxidizer;
 - an activator;
 - a surfactant;
 - a corrosion inhibitor;wherein
the biocide is selected from the group consisting of sorbic acid, it's derivatives or salts thereof; benzoic acid, it's derivatives or salts thereof; and combinations thereof; and
pH of the composition ranges from 2 to 9, 2 to 8, 2 to 7, or 2 to 6.
2. The Chemical Mechanical Planarization polishing composition of Claim 1, wherein the chemical additive promotes microbiological growth in the polishing composition.
3. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 2, wherein the chemical additive is selected from the group consisting of (a) maltitol, lactitol, maltotritol, ribitol, D-sorbitol, mannitol, dulcitol, iditol, D-(–)-Fructose, sorbitan, sucrose, ribose, Inositol, glucose, D-arabinose, L-arabinose, D-mannose, L-mannose, meso-erythritol, beta-lactose, arabinose, fructose, xylitol, and combinations thereof; (b) 2-aminobenzoimidazole, 1,8-Diazabicyclo(5.4.0)undec-7-ene, and combinations thereof; (c) organic sulfonic acid, organic aromatic sulfonic acid, piperazine, organic phosphonic acid, and combinations thereof; (d) organic carboxylic acid; (e) amino acid or amine; (f) polymer or co-polymer selected from the group consisting of polyacrylic acid, polymethylacrylic acid, polyamide, polystyrene sulfonic acid, polyamine, polyethyleneimine, polyethylene oxide, polypropylene oxide, polyethylene glycol, polyglycerin, polyoxyethylene, polyglyceryl ether,

polyoxypropylene, polyglyceryl ether, polyacrylamide, poly(acrylic acid-co-maleic acid), poly(acrylamide-co-acrylic acid), poly(methyl vinyl ether), poly(propylene glycol), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate), polyvinyl sulfonic acid, polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl pyrdine-N-oxide, Poly(acrylamide-acrylic acid), poly(4-styrenesulfonic acid-co-maleic acid), poly acrylamide-co-diallyldimethylammonium chloride, poly(ethylene-co-methacrylic acid), and polyvinyl ether, poly(4-Vinylpyridine, poly(4-vinylpyridine-co-butylmethacrylate), poly(diallyldimethylammonium chloride), poly(N-isopropylacrylamide), poly(vinylphosphonic acid), polyglykol, polyoxyethylene sorbitan tetraoleate, polysorbate 20, polysorbate 40, polysorbate 80, poly(vinyl acetate), poly(styrene-co-allyl alcohol), poly(4-vinylphenol), and poly(2-ethyl-2-oxazoline), and combinations thereof; (g) 1,2,4-triazole, 1,2,3-triazole, benzotriazole, and combinations thereof; (f) and combinations of (a) to (g).

4. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 3, wherein concentration of the chemical additive ranges from 0.01 wt.% to 20.0 wt.%, 0.05 wt.% to 15 wt.%, or 0.1 wt.% to 10 wt.%.
5. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 4, wherein the benzoic acid, it's derivatives or salts thereof have a general molecular structure selected from the group consisting of:



(a),



(b),

and combinations thereof;

wherein

each of R1, R2, R3, R4, and R5 is independently selected from the group consisting of hydrogen, hydroxyl group, alkyl group, alkoxy group, amino group, dialkylamino

group, alkylthio group, and combinations thereof; and each of them can be connected to -2, -3, -4, -5 or -6 position in the benzene ring; and

M⁺ is a metal ion selected from the group consisting of potassium ion, ammonium ion, and sodium ion.

6. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 5, wherein the biocide is selected from the group consisting of benzoic acid, potassium salt of benzoic acid, ammonium salt of benzoic acid, sodium salt of benzoic acid, potassium salt of sorbic acid, ammonium salt of sorbic acid, sodium salt of sorbic acid, potassium salt of sorbic acid, sorbohydroxamic acid, sorbic aldehyde, and combinations thereof.
7. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 6, wherein the biocide is selected from the group consisting of potassium salt of benzoic acid, ammonium salt of benzoic acid, and combinations thereof.
8. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 7, wherein the biocide is selected from the group consisting of benzoic acid, 2-hydroxybenzoic acid (salicylic acid), 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid, 3-methoxy-4-hydroxybenzoic acid, 4-methoxybenzoic acid, 4-methylbenzoic acid, 2,6-dimethoxy-4-hydroxybenzoic acid, 3,5-dimethoxy-4-hydroxybenzoic acid, 2,3-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 2,4,6-trihydroxybenzoic acid, 4-(dimethylamino)benzoic acid, 3,5-diaminobenzoic acid, 2-methoxybenzoic acid, 2-ethoxybenzoic acid, 2-aminobenzoic acid, 3-methylthiobenzoic acid, 4-methylthiobenzoic acid, and combinations thereof.
9. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 8, wherein concentration of the biocide ranges from 0.005 wt.% to 1.0 wt.%, about 0.01 wt.% to 0.75 wt.%, or about 0.05 wt.% to 0.5 wt.%
10. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 9, wherein the Chemical Mechanical Planarization polishing

composition comprises the abrasive selected from the group consisting of fumed silica, colloidal silica, fumed alumina, colloidal alumina, cerium oxide, titanium dioxide, zirconium oxide; metal oxide-coated inorganic oxide particles; organic polymer particles; metal oxide-coated organic polymer particles; and combinations thereof.

11. The Chemical Mechanical Planarization polishing composition according to Claim 10, wherein concentration of the abrasive ranges from 0.01 wt.% to 30 wt.%, about 0.05 wt.% to 20 wt.%, about 0.01 to about 10 wt.%, or about 0.1 wt.% to 5 wt.%.
12. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 11, wherein the Chemical Mechanical Planarization polishing composition comprises the oxidizer selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, and ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, KClO_4 , KBrO_4 , and KMnO_4 ; and combinations thereof.
13. The Chemical Mechanical Planarization polishing composition according to Claim 12, wherein concentration of the oxidizer ranges from about 0.01 wt.% to 30 wt.%, about 0.1 wt.% to 20 wt.%, or about 0.5 wt.% to about 10 wt.%.
14. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 13, wherein the Chemical Mechanical Planarization polishing composition comprises the activator selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface, wherein the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2) soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate, ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate, and combinations thereof; (3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe,

Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V, and combinations thereof; and combinations thereof.

15. The Chemical Mechanical Planarization polishing composition according to Claim 14, wherein concentration of the activator ranges from about 0.00001 wt.% to 5 wt.%, about 0.0001 wt. % to 2.0 wt. %, about 0.0005 wt. % to 1.0 wt.%; or about 0.001 wt. % to 0.5 wt.%.
16. A Chemical Mechanical Planarization polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing at least one material, comprising the steps of:
contacting the at least one surface with a polishing pad;
delivering the Chemical Mechanical Planarization polishing composition of any one of claims 1 to 15; and
polishing the at least one surface containing the at least one material with the chemical mechanical planarization composition;
wherein the at least one material is selected from the group consisting of metal, metal alloy, novel metal, barrier layer material, dielectric material, low-k and ultra-low-k material, and combinations thereof.
17. The Chemical Mechanical Planarization polishing method of claim 16, wherein the at least one material is selected from the group consisting of W, Cu, Co, Al, Ni, Mn, Ru, Ta, TaN, Ti, TiN, SiO₂, SiN, SiC, Black Dimond, and combinations thereof.
18. A Chemical Mechanical Planarization polishing system, comprising:
a semiconductor substrate comprising at least one surface containing at least one material;
a polishing pad; and
the Chemical Mechanical Planarization polishing composition of any one of claims 1 to 15;
wherein the at least one surface containing the at least one material is in contact with the polishing pad and the chemical mechanical planarization composition; and

wherein the at least one material is selected from the group consisting of metal, metal alloy, novel metal, barrier layer material, dielectric material, low-k and ultra-low-k material, and combinations thereof.

19. The Chemical Mechanical Planarization polishing system of claim 18, wherein the at least one material is selected from the group consisting of W, Cu, Co, Al, Ni, Mn, Ru, Ta, TaN, Ti, TiN, SiO₂, SiN, SiC, Black Dimond, and combinations thereof.