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(54) **Title:** BIOCIDES FOR CHEMICAL MECHANICAL PLANARIZATION (CMP) POLISHING COMPOSITIONS

(57) **Abstract:** Present invention provides biocides for inhibiting microbe (bacteria and/or fungi) growth in Chemical Mechanical Planarization (CMP) polishing compositions. The biocide includes organic compounds with at least one diol functional group at one end of the compound, and with at least one organic alkyl ether group at the other end of the compound.

TITLE OF THE INVENTION:

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. 63/602,001 filed on November 22, 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 biocides for inhibiting microbiological growth (bacteria and/or fungi) 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, alkylbenzyldimethylammonium chloride, and alkylbenzyldimethylammonium 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® (pyrithone).

[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 Shallow Trench Isolation (STI) CMP polishing composition; and 11,718,767 disclosed the use of MIP and CMIP as the biocides in SiN CMP polishing composition.

[0008] 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.

[0009] For instance, Environmental Working Group(EWG) combines three separate ratings - nutrition, ingredient concerns and processing - into a single EWG score. EWG Scores range from 1 (best) to 10 (worst). EWG lists EWG score for MIT as 7, CMIT as 6, and OIT as $^{+}$D and states it is very highly toxic to aquatic life.

[0010] It should be readily apparent from the foregoing that there remains a need within the art for highly desirable to use more friendly chemicals as alternative biocides in CMP polishing compositions, especially in CMP composition during the storage.

BRIEF SUMMARY OF THE INVENTION

[0011] The present invention satisfies the need by providing more friendly chemicals as alternative biocides in CMP polishing compositions.

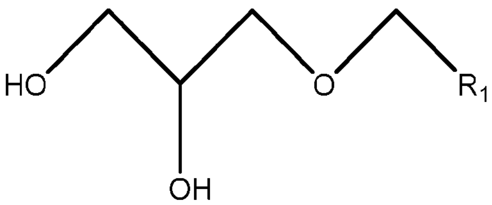
[0012] More specifically, the present invention discloses the use of chemicals that are much more environmentally friendly as the effective biocides in CMP polishing compositions.

[0013] For example, ethylhexylglycerin has EWG score of 2; and caprylyl glyceryl ether, and caprylyl glyceryl ether has EWG score of 1. Those chemicals are much more environmental-friendly than the commonly used biocides containing MIT, CMIT and OIT in CMP polishing compositions.

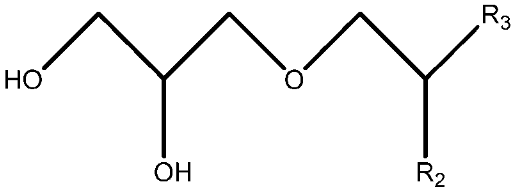
[0014] In one aspect (Aspect 1), there is provided a CMP polishing composition comprising, consisting essentially of, or consisting of:
a chemical additive;
a biocide; and
water-soluble solvent; and
optionally at least one of
abrasive;
a pH adjusting agent;
an oxidizer;
an activator;
a surfactant; and
a corrosion inhibitor;
wherein the biocide comprises an organic compound with at least one diol functional group at one end of the organic compound and with at least one organic alkyl ether group at the other end of the organic compound; wherein the organic alkyl ether group has at least one straight or branched alkyl chain connecting to the oxygen atom in the organic alkyl ether group;
pH of the polishing composition ranges from 2 to 9, 2 to 8, 2 to 7, or 2 to 6.

[0015] The chemical additive can be any additives that promote 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 includes but is not limited to an organic compound having a general molecular structure of:



(a),



(b),

and combinations thereof;

where each of R_1, R_2, and R_3 is independently an organic alkyl group with $-(CH_2)_n-CH_3$ moieties with n ranging from 1 to 12.

[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 which 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 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, 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] The present invention satisfies the need by providing desirable 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. Herein, composition and slurry are exchangeable.

[0029] More specifically, the invention discloses the biocides which prohibit microbiological growth in a CMP polishing composition that contains chemical additives promoting microbiological growth.

[0030] The CMP polishing composition can be abrasive free CMP polishing compositions which is used with fixed abrasive polishing pads for semiconductor wafer polishing.

[0031] 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.

[0032] 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; and

a corrosion inhibitor;

wherein the biocide comprises an organic compound with at least one diol functional group at one end of the organic compound and with at least one organic alkyl ether group at the other end of the organic compound; wherein the organic alkyl ether group has at least one straight or branched alkyl chain connecting to the oxygen atom in the organic alkyl ether group;

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

[0033] The chemical additive can be any additive that promote microbiological growth. 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.

[0034] 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.

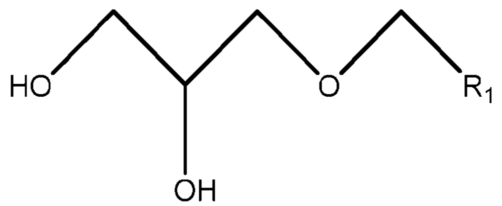
[0035] The chemical additive can also be a removal rate accelerator such as (a) organic sulfonic acid, organic aromatic sulfonic acid such as benzene sulfonic acid, piperazine, organic phosphonic acid, for STI polishing composition as disclosed in US2020004,551; (b)organic carboxylic acids for W polishing 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.

[0036] The chemical additive can also be a polymer or co-polymer includes but is not limited to polyacrylic acid, polymethylcrylic 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-diallydimethylyammonium chloride, poly(ethylene-co-methacrylic acid), and polyvinyl ether, poly(4-Vinylpyridine, poly(4-vinylpyridine-co-butylmethacrylate), poly(diallydimethylammonium cholride), 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).

[0037] 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.

[0038] The biocide includes but is not limited to an organic compound with at least one diol functional group at one end of the organic compound and with at least one organic alkyl ether group at the other end of the organic compound; wherein the organic alkyl ether group has at least one straight or branched alkyl chain connecting to the oxygen atom in the organic alkyl ether group;

[0039] The biocide can have a general molecular structure including but not being limited to:



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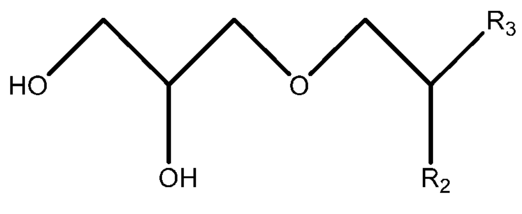
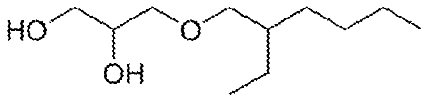


(b),

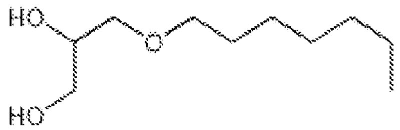
and combinations thereof;

wherein each of R1, R2 and R3 is independently an organic alkyl group with $-(CH_2)_n-CH_3$ moieties having n ranging from 1 to 12.

[0040] Specific examples are ethylhexylglyceirn which has the general molecular structure (b) having R2 as ethyl group and R3 as butyl group; heptylglyceryl ether and caprylyl glyceryl ether which have the general molecular structure (a) having R1 as hexyl group and heptyl group respectively:



ethylhexylglycerin,



heptylglyceryl ether , and

caprylyl glyceryl ether.

[0041] Ethylhexylglycerin, heptylglyceryl ether and caprylyl glyceryl ether are widely used in skincare products which are more friendly for human skin. For example, they are the main ingredients for Saksine™ 50 (main ingredient: ethylhexylglycerin), Saksine™ 70 (main ingredient: heptylglyceryl ether), and Saksine™ 80 (main ingredient: caprylyl glyceryl ether) of Saskine™ products from SACHEM, Inc..

[0042] The concentration of the biocide can range from about 0.005 wt.% to 2.0 wt.%, about 0.01 wt.% to 1.5 wt.%, 0.05 to 1.0 wt.%; or 0.075 to 0.5 wt.%. The weight percent is relative to the composition.

[0043] The water-soluble solvent includes but is not limited to deionized (DI) water, distilled water, and alcoholic organic solvents.

[0044] The optional abrasive includes but is not limited to inorganic oxide particles including but not being 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 being limited to ceria-coated inorganic oxide particles; organic polymer particles; metal oxide-coated organic polymer particles; and combinations thereof.

[0045] The concentration of the abrasive can range from about 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.%. The weight percent is relative to the composition.

[0046] The abrasive particles have mean particle sizes (measured by Dynamic Light Scattering DLS technology) ranging from about 2 nm to 1,000 nm, 10 nm to 500 nm, or 20 nm to 250 nm; 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.

[0047] 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.

[0048] The oxidizer concentration 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.

[0049] 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.

[0050] 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.%.

[0051] 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.

[0052] 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, proplylene glycol alkyl ethers, glucoside alkyl ethers, polyethylene glycol octylphenyl ethers, polyethylene glycol alkylpgenyl 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, fluorosurfactants, and combinations thereof. Polymers can have a molecular weight ranging from several hundreds to over 1 million. The viscosities of these materials also possess a broad distribution.

[0053] 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.

[0054] 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.

[0055] 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.

[0056] 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.%.

[0057] 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.

[0058] 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.%.

[0059] 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.

[0060] 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.

[0061] 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, TiN, Co, and combinations thereof; dielectric materials such as SiO2, SiN, SiC, and combinations thereof; and low-k and ultra-low-k materials, such as Black Diamond.

[0062] The following non-limiting examples are presented to further illustrate the present invention.

GLOSSARY

COMPONENTS

[0063] Ceria-coated Silica: used as abrasive having a particle size of approximately 20 nanometers (nm) to 500 nanometers (nm);

[0064] Ceria-coated Silica particles (with varied sizes) were supplied by JGCC Inc. in Japan.

[0065] Chemicals, such as D-Sorbitol, and other chemical raw materials were supplied by MilliporeSigma, St. Louis, MO. Chemicals Saskine™ 50, Saskine™ 70, and Saskine™ 80 were supplied by Sachem Inc located in Austin, Texas.

Biocide Efficacy Testing

[0066] Biocide Efficacy Testing was performed with the intentional additions of microbe (bacteria and fungi). All tests were done at a temperature of 30⁰C.

Example 1

[0067] The first reference (Ref. 1) contained 15 wt.% D-sorbitol, pH adjusting agent, deionized water and no biocide with pH being adjusted to 2.15.

[0068] The working samples #1, #2 and #3 added 0.1 wt.% Saskine™ 50, Saskine™ 70, and Saskine™ 80 as the alternative biocide in Ref. 1 respectively. The pH was adjusted to about 2.1.

[0069] The biocide efficacy testing results at about pH 2.1 were listed in the Table 1 below:

Table 1. Biocide Efficacy Testing Result Comparison at pH about 2.1

Sample	Contaminant Reading at Day 0 (cfu/ml*)	Contaminant Reading at Day 7 (cfu/ml)
Ref. 1	2.6×10^6	1.4×10^7
#1	4.0×10^4	0.0×10^0
#2	1.4×10^7	2.0×10^1
#3	1.4×10^7	7.0×10^{-1}

*Colony Forming Unit per mL(cfu/ml)

[0070] As the testing results shown in Table 1, the contaminant reading at Day 7 for Ref.1 (no biocide) was higher than the contaminant reading at Day 0(zero) indicating the fungal and/or bacteria growth.

[0071] When Saskine™ 50, Saskine™ 70, and Saskine™ 80 which have Ethylhexylglycerin, heptylglyceryl ether and caprylyl glyceryl ether as the main ingredients respectively were used, the contaminant readings were significantly reduced from day 0 to day 7. Thus, results indicate that ethylhexylglycerin, heptylglyceryl ether and caprylyl glyceryl ether can be used as biocide in CMP product to effectively prevent the growth of fungal and/or bacteria.

Example 2

[0072] The effect of pH on the biocide efficacy was evaluated at pH 7.0.

[0073] The second reference (Ref. 2) contained 15 wt.% D-sorbitol, pH adjusting agent, deionized water and no biocide with pH being adjusted to 7.0.

[0074] The working samples #4, #5, and # 6 used 15 wt.% D-Sorbitol, 0.1 wt.% Saskine™ 50, Saskine™ 70, and Saskine™ 80 respectively as the alternative biocide, and deionized water with pH being adjusted to 7.0.

[0075] The biocide efficacy testing results at pH 7.0 was listed in the Table 2 below:

Table 2. Biocide Efficacy Testing Result Comparison at pH 7.0

Sample	Contaminant Reading at Day 0 (cfu/ml*)	Contaminant Reading at Day 7 (cfu/ml)
Ref.2	>1.4 x 10^7	>1.4 x 10^7
#4	1.4 x 10^7	4.0 x 10^2
#5	1.4 x 10^7	4.5 x 10^4
#6	1.4 x 10^7	4.0 x 10^3

[0076] As the results shown in Table 2, without using any biocide in Reference 2, the contaminant reading (cfu/ml*) remained high. When Saskine™ 50, Saskine™ 70, or Saskine™ 80 was used, the contaminant reading was significantly reduced from Day 0 to Day 7 indicating that Saskine™ compounds are effective biocides to prevent the microbiological growth in the compositions at pH 7.0.

Example 3

[0077] The working samples contained 15 wt.% D-sorbitol, pH adjusting agent, deionized water, and different concentrations of alternative biocides Saskine™ 70 and Saskine™ 80 : working samples #7, #8 and #9 having 0.01 wt. %, 0.05 wt. % and 0.1 wt. % of Saskine™ 70 respectively; and working samples #10, #11 and #12 having 0.01 wt. %, 0.05 wt. % and 0.1 wt. % of Saskine™ 80, respectively.

[0078] The working samples all had a pH about 7.0.

[0079] The biocide efficacy testing results were listed in Table 3.

Table 3. Effects of Conc. On Biocide Efficacy% at pH 7.0

Sample	Contaminant Reading at Day 0 (cfu/ml*)	Contaminant Reading at Day 7 (cfu/ml)
#7	1.4 x 10^7	1.4 x 10^7
#8	1.4 x 10^7	4.5 x 10^4
#9	1.4 x 10^7	1.0 x 10^0

#10	1.4 x 10^7	1.4 x 10^7
#11	1.4 x 10^7	4.3 x 10^3
#12	9.0 x 10^3	9.0 x 10^0

[0080] As the results shown in Table 3, there was no biocide effect from Saskine™ 70 and Saskine ™ 80 at a concentration of 100 ppm at pH 7.0. However, at a concentration of 500 ppm or 1000 ppm, Saskine™ compounds are effective biocides to prevent the microbiological growth in the compositions at pH 7.0.

Example 4

[0081] The biocide efficacy testing of using Saksine™ 50 (ethylhexylglycerin) or Saksine™ 80 (caprylyl glyceryl ether) as the alternative biocide was conducted at pH 5.74. All samples had a pH at 5.74.

[0082] Reference 3 (Ref. 3) was composed of 17.5 wt.% calcined ceria particles, 0.875 wt.% polyacrylic acid, pH adjusting agent and deionized water. No biocide was used.

[0083] The working polishing composition #13 was composed of the 17.5 wt.% calcined ceria particles and 0.875 wt.% polyacrylic acid, pH adjusting agent, deionized water and 0.1 wt.% Saskine™ 50 (ethylhexylglycerin).

[0084] The working polishing composition #14 was composed of the 17.5 wt.% calcined ceria particles and 0.875 wt.% polyacrylic acid, pH adjusting agent, deionized water and 0.1 wt.% Saskine™ 80 (caprylyl glyceryl ether).

[0085] The biocide efficacy testing results are listed in Table 4.

Table 4. Ethylhexylglycerin and Caprylyl Glyceryl Ether at pH 5.74

Sample (wt.%)	Contaminant Reading at Day 0 (cfu/ml*)	Contaminant Reading at Day 7 (cfu/ml)
Ref. 3	1.4 x 10^7	2.0 x 10^6
#13	2.5 x 10^6	4.0 x 10^4
#14	9.0 x 10^2	0.0 x 10^0

[0086] As the testing results shown in Table 4, Ref. 3 had a small decreased contaminant reading at Day 7 vs at Day 0(zero).

[0087] When 0.1 wt.% Saskine™ 50(ethylhexylglycerin) or 0.1 wt.% Saskine™ 80 (caprylyl glyceryl ether) was used as alternative biocide, the contaminant reading at Day 7 was significantly lower than the contaminant reading at Dat 0(zero) which has shown that Saskine™ compounds are effective biocides to prevent the microbiological growth in the compositions at pH 5.74.

[0088] The biocide efficacy test results proved that more friendly type of biocides can be used in the pH range of 2 to 7 in the CMP polishing compositions as the effective biocide and can be used directly to replace the commonly used MIT, CMIT or OIT type of biocide in CMP polishing compositions.

Polishing Experiments

CMP Methodology

PARAMETERS

General

[0089] Å or A: angstrom(s) – a unit of length

[0090] BP: back pressure, in psi units

[0091] CMP: chemical mechanical planarization = chemical mechanical polishing

[0092] CS: carrier speed

[0093] DF: Down force: pressure applied during CMP, unit: psi

[0094] min: minute(s)

[0095] ml: milliliter(s)

[0096] mV: millivolt(s)

[0097] mM: millimolar

[0098] psi: pounds per square inch

[0099] PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)

[00100] SF: composition flow, ml/min

[00101] Wt. %: weight percentage (of a listed component)

[00102] TEOS: SiN Selectivity: (removal rate of TEOS)/ (removal rate of SiN)

[00103] HDP: high density plasma deposited TEOS

[00104] TEOS or HDP Removal Rates: Measured TEOS or HDP removal rate at a given down pressure. The down pressure of the CMP tool was 2.0, 3.0 or 4.0 psi in the examples.

[00105] SiN Removal Rates: Measured SiN removal rate at a given down pressure. The down pressure of the CMP tool was 3.0 psi in the examples listed.

Metrology

[00106] 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

[00107] 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.

[00108] 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

[00109] 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.

[00110] 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.

[00111] These polished patterned wafers (MIT864) wafers were measured on the Veeco VX300 profiler/AFM instrument.

Example 5

[00112] In CMP polishing example 5, one set of removal rates of different films, oxide trench pitch dishing on different size features vs different over polishing times and oxide trench dishing rates on different size features were measured. RR Selectivity were also calculated.

[00113] The reference polishing composition number one (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.

[00114] The reference polishing composition number two (Ref. 2) contained 0.5 wt.% ceria-coated silica abrasive, 0.15 wt.% D-sorbitol, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00115] The working polishing composition 1(Sample# 1) contained 0.5 wt.% ceria-coated silica abrasive, 0.15 wt.% D-sorbitol, 25.0 ppm Saskine™ 50 (ethylhexylglycerin) as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00116] The working polishing composition 2(Sample# 2) contained 0.5 wt.% ceria-coated silica abrasive, 0.15 wt.% D-sorbitol, 50.0 ppm Saskine™ 50 (ethylhexylglycerin) as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00117] The blanket film polishing results were measured, TEOS: SiN selectivity, and HDP: SiN selectivity were calculated and listed in Table 5.

Table 5. 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
Sample# 1	5164	4968	98	53	51
Sample# 2	5184	4947	96	53	51

[00118] As the results shown in Table 5, there was little difference in CMP polishing performance among the polishing compositions.

[00119] 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.

[00120] 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 6.

Table 6. Effects of Eco-Friendly Biocide on Oxide Trench Dishing vs OP Times (Sec.)

Compositions	OP Times (Sec.)	100µm pitch dishing	200µm pitch dishing
Ref. 1	60	245	396
	120	396	561
Ref. 2	60	371	403
	120	518	559
Sample# 1	60	247	363
	120	411	529
Sample# 2	60	244	369
	120	376	519

[00121] As the results shown in Table 6, using eco-friendly Saskine™ 50 (ethylhexylglycerin) to replace traditional OIT biocide, similar oxide trench dishing vs different over polishing times on two different sized features were obtained.

[00122] The oxide trench dishing rates on different size features were obtained from two reference samples and the working samples. The results were listed in Table 7.

Table 7. Effects of Eco-Friendly Biocide on Oxide Trench Dishing Rates

Compositions	P100 Dishing Rate (Å/sec.)	P200 Dishing Rate (Å/sec.)
Ref. 1	2.8	3.4
Ref. 2	3.3	3.4
Sample# 1	2.8	3.0
Sample# 2	2.3	2.6

[00123] As the results shown in Table 7, using eco-friendly Saskine™ 50 (ethylhexylglycerin) to replace traditional OIT biocide, the similar or slightly lower oxide trench dishing rates were obtained.

[00124] SiN trench loss rates from patterned wafer polishing were obtained from two reference samples and the working samples on different size features. The results were listed in Table 8.

Table 8. Effects of Eco-Friendly Biocide on SiN Trench Loss Rates

Compositions	P100 SiN Loss Rate (Å/sec.)	P200 SiN Loss Rate (Å/sec.)
Ref. 1	1.2	1.2
Ref. 2	1.7	1.3
Sample# 1	1.3	1.1
Sample# 2	1.2	1.1

[00125] As the results shown in Table 8, using eco-friendly and alternative biocide Saskine™ 50 (ethylhexylglycerin) to replace traditional OIT biocide, the similar SiN trench loss rates on 100µm or 200µm features were obtained.

Example 6

[00126] In CMP polishing example 6, another set of removal rates of different films, oxide trench pitch dishing on different size features vs different over polishing times and oxide trench dishing rates on different size features were measured. RR Selectivity were also calculated.

[00127] The reference polishing composition number 3 (Ref. 3) contained 0.5 wt.% calcined ceria abrasive, and 0.05 wt.% polyacrylic acid, 7.5ppm neolone M10 (methyl isothiazolinone MIT based biocide) as biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00128] The reference polishing composition number 4 (Ref. 4) contained 0.5 wt.% calcined ceria abrasive, 0.05 wt.% polyacrylic acid, and no biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00129] The working polishing composition 3(Sample# 3) contained 0.5 wt.% calcined ceria abrasive, 0.05 wt.% polyacrylic acid, 7.15ppm Saskine™ 50 (ethylhexylglycerin) as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00130] The working polishing composition 4 (Sample# 4) contained 0.5 wt.% calcined ceria abrasive, 0.05 wt.% polyacrylic acid, 14.3ppm Saskine™ 50 (ethylhexylglycerin) as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00131] The working polishing composition 5(Sample# 5) contained 0.5 wt.% calcined ceria abrasive, 0.05 wt.% polyacrylic acid, 21.4ppm Saskine™ 50 (ethylhexylglycerin) as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00132] The working polishing composition 6(Sample# 6) contained 0.5 wt.% calcined ceria abrasive, 0.05 wt.% polyacrylic acid, and 28.6ppm Saskine™ 50 (ethylhexylglycerin) as eco-friendly biocide, pH adjusting agent, and deionized water. The pH was adjusted to 5.35.

[00133] The removal rates of different films, and the calculated RR Selectivity were listed in Table 9.

Table 9. 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. 3	2161	2120	87	25	24
Ref. 4	2149	2082	86	25	24
Sample# 3	2093	2062	85	25	24
Sample# 4	2056	1990	82	25	24
Sample# 5	2116	2055	82	26	25
Sample# 6	2197	2093	87	25	24

[00134] As the results shown in Table 9, there was little difference in CMP polishing performance among the polishing compositions.

[00135] The oxide trench dishing on different size features vs different over polishing times were listed in Table 10.

Table 10. Effects of Eco-Friendly Biocide on Oxide Trench Dishing vs OP Times (Sec.)

Compositions	OP Times (Sec.)	100µm pitch dishing	200µm pitch dishing
Ref. 3	60	146	259
	120	209	309
Ref. 4	60	145	256
	120	211	327
Sample# 3	60	177	295
	120	242	413
Sample# 4	60	123	234
	120	178	316
Sample# 5	60	127	292
	120	198	368
Sample# 6	60	147	280
	120	227	370

[00136] As the results shown in Table 10, there was little difference in CMP polishing performance among the polishing compositions.

[00137] The oxide patterned wafer polishing results obtained from two reference samples and the working samples on oxide trench dishing rates on different size features were listed in Table 11.

Table 11. Effects of Eco-Friendly Biocide on Oxide Trench Dishing Rates

Compositions	P100 Dishing Rate (Å/sec.)	P200 Dishing Rate (Å/sec.)
Ref. 3	1.1	1.2
Ref. 4	0.7	1.6
Sample# 3	0.9	2.0
Sample# 4	0.6	0.6
Sample# 5	1.1	1.2
Sample# 6	1.5	2.2

[00138] As the results shown in Table 11, the similar oxide trench dishing rates on 100µm and 200µm features were obtained.

[00139] The oxide patterned wafer polishing results obtained from two reference samples and the working samples on SiN trench loss rates on different size features were listed in Table 12.

Table 12. Effects of Eco-Friendly Biocide on SiN Trench Loss Rates

Compositions	P100 SiN Loss Rate (Å/sec.)	P200 SiN Loss Rate (Å/sec.)
Ref. 3	1.0	1.0
Ref. 4	1.0	1.0
Sample# 3	1.1	1.2
Sample# 4	0.9	1.0
Sample# 5	0.9	1.0
Sample# 6	1.0	1.1

[00140] As the results shown in Table 12, the similar SiN trench loss rates on 100µm or 200µm features were obtained.

[00141] As the results shown above, the disclosed eco-friendly biocides have demonstrated the same CMP polishing performance as the traditionally used biocides.

[00142] 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; and
   a corrosion inhibitor;
   wherein the biocide comprises an organic compound with at least one diol functional group at one end of the organic compound and with at least one organic alkyl ether group at other end of the organic compound; wherein the organic alkyl ether group has at least one straight or branched alkyl chain connecting to the oxygen atom in the organic alkyl ether group;
   and
   pH of the polishing 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 CMP polishing composition.

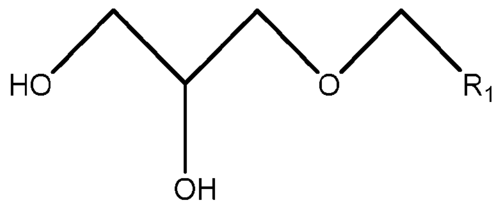
3. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 2, wherein the chemical additive is selected from the group consisting of (a) maltitol, lactitol, maltotritol, ribitol, D-sorbitol, mannitol, dulcitol, iditol, D-(−)-Fructose, sorbitan, sucrose, ribose, 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, polymethylcrylic 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-diallydimethylyammonium chloride, poly(ethylene-co-methacrylic acid), and polyvinyl ether, poly(4-Vinylpyridine, poly(4-vinylpyridine-co-butylmethacrylate), poly(diallydimethylammonium cholride), 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).

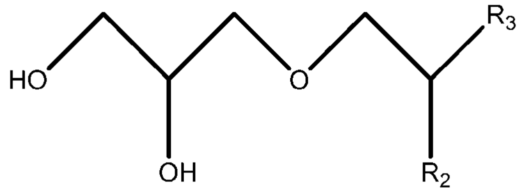
4. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 3, wherein the chemical additive is selected from the group consisting of organic sulfonic acid, organic aromatic sulfonic acid, piperazine, organic phosphonic acid, organic carboxylic acid, amino acid, amine, and combinations thereof.

5. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 4, 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.%.

6. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 5, wherein the biocide is an organic compound having a general molecular structure selected from the group consisting of



(a),



(b),

and

combinations of (a) and (b);

wherein each of R1, R2 and R3 is independently an organic alkyl group with $-(CH_2)_n-CH_3$ moieties having n ranging from 1 to 12.

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 ethylhexylglycerin, heptylglyceryl ether and caprylyl glyceryl ether, and combinations thereof.

8. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 7, wherein concentration of the biocide ranges from about 0.005 wt.% to 2.0 wt.%, about 0.01 wt.% to 1.5 wt.%, 0.05 to 1.0 wt.%; or 0.075 to 0.5 wt.%.

9. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 8, wherein 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.

10. The Chemical Mechanical Planarization polishing composition according to Claim 9, 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.%.

11. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 10, wherein 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; non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, and $KMnO_4$; and combinations thereof.

12. The Chemical Mechanical Planarization polishing composition according to Claim 11, 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.%.

13. The Chemical Mechanical Planarization polishing composition according to any one of Claims 1 to 12, 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.

14. The Chemical Mechanical Planarization polishing composition according to of Claim 13, 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.%.

15. 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 according to any one of claims 1 to 14; and
polishing the at least one surface containing the at least one material with the Chemical Mechanical Planarization polishing 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.

16. The Chemical Mechanical Planarization polishing method of claim 15, wherein the at least one material is selected from the group consisting of W, Cu, Co, Al, Ni, Mn, Ru, Ta, TaN, Ti, TiN, SiO_2, SiN, SiC, Black Diamond, and combinations thereof.

17. 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 14;
wherein the at least one surface containing the at least one material is in contact with the polishing pad and the chemical mechanical planarization polishing 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.

18. The Chemical Mechanical Planarization polishing system of claim 17, wherein the at least one material is selected from the group consisting of W, Cu, Co, Al, Ni, Mn, Ru, Ta, TaN, Ti, TiN, SiO_2, SiN, SiC, Black Diamond, and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/054665

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09G1/02 C09K3/14
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09G C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2019 104797 A (KAO CORP) 27 June 2019 (2019-06-27) paragraphs [0036], [0037], [0045]; claims 1-8; examples 1-4, 6, 7; table 1	1-18
X	JP 2001 085374 A (KAO CORP) 30 March 2001 (2001-03-30) paragraphs [0016], [0019] - [0025], [0033] - [0047], [0054], [0055], [0058] - [0061]; claims 1-6; examples 2,7,11,12,14; tables 1,2	1-18
X	US 2023/287243 A1 (TADA MASAKI [JP] ET AL) 14 September 2023 (2023-09-14) paragraphs [0036] - [0044], [0054], [0057] - [0079], [0085], [0086]; claims 1-9; examples 1-18	1-18

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 111 423 819 A (SHENZHEN LONA ABRASIVE MAT CO LTD) 17 July 2020 (2020-07-17) claim 6	1-18

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/054665

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