METHODS AND COMPOSITIONS FOR POLISHING SILICON-CONTAINING SUBSTRATES

FIELD OF THE INVENTION

[0001] This invention pertains to chemical-mechanical polishing compositions and methods for polishing a silicon-containing substrate. More particularly, this application relates to chemical-mechanical polishing compositions containing a ceria abrasive, a polishing additive and a surfactant, and methods of their use.

BACKGROUND OF THE INVENTION

[0002] Chemical-mechanical planarization, or chemical-mechanical polishing (CMP), is a well known technique used to planarize substrates. CMP utilizes a chemical composition, known as a CMP composition (which also is referred to as a CMP slurry) for removal of material from the substrate. Polishing compositions typically are applied to a substrate by contacting the surface with a polishing pad (e.g., polishing cloth or polishing disk) saturated with the polishing composition. The polishing of the substrate typically is further aided by the chemical activity of the polishing composition and/or the mechanical activity of an abrasive suspended in the polishing composition or incorporated into the polishing pad (e.g., fixed abrasive polishing pad).

[0003] Conventional CMP compositions and methods typically are not entirely satisfactory at planarizing substrates. In particular, CMP polishing compositions and methods can result in less than desirable polishing rates and high surface defectivity when applied to a substrate. Because the performance of many substrates is directly associated with obtaining a planar and defect free surface, it is crucial to use a CMP composition and method that results in a high polishing efficiency, selectivity, uniformity, and removal rate and leaves a high quality polish with minimal surface defects.

[0004] Polishing slurries that provide high polishing rates on silicon metal oxides and low polishing rates on polysilicon, also know as "reverse poly" or "oxide stop on poly" slurries, are desired. Such slurries are needed in the processing of various integration schemes including floating gate electrodes. The difficulty in achieving high oxide-to-polysilicon selectivity is believed to be due to the very facile removal of polysilicon in typical dielectric slurries (for example: high pH silica-based slurries).

[0005] In conventional polishing slurries containing ceria, the use of low levels (below 0.5 wt. %) of ceria can lead to local areas of overly high removal. This is demonstrated in FIG 1 wherein, on wafer (2), features (1) represent examples of local areas of high removal and each contour line represents a 10 nm topography change into the wafer. These isolated regions of

overly high removal are sometimes called "pitting", "staining", "spots" or "hot spots". These spots are depressions in the surface that typically are on the order of 0.001 to 10 mm^2 in area, and are typically 2 to 200 nm in depth.

[0006] Accordingly, there is a need for methods and compositions, which enable the reliable use of low solids ceria slurries for polishing silicon-containing substrates in reverse poly applications, while also providing good surface uniformity.

BRIEF SUMMARY

[0007] The present disclosure provides a chemical-mechanical polishing (CMP) method and composition for polishing a silicon-containing substrate, the method comprising, consisting essentially of or consisting of the steps of contacting a silicon-containing substrate with a polishing pad and a CMP composition, and causing relative motion between the polishing pad and the substrate while maintaining a portion of the CMP composition in contact with the surface of the substrate to abrade at least a portion of the surface of the substrate, thereby polishing the substrate. The CMP composition has a pH of 7 or less, and comprises, consists essentially of, or consists of an aqueous carrier containing a ceria abrasive, a polishing additive bearing a functional group with a pK_a of 4 to 9, and a nonionic surfactant with a hydrophilic portion and a lipophilic portion. The hydrophilic portion of the nonionic surfactant has a number average molecular weight of at least 500 g/mol.

[0007a] In an aspect, there is provided a CMP composition having a pH of about 5.5 or less and comprising an aqueous carrier containing a ceria abrasive in a concentration of about 0.005 wt. % to about 0.5 wt. %, wherein the ceria has an average primary particle size of between about 40 nm to about 120 nm, a polishing additive bearing a functional group having a pKa of about 4 to about 9, and a non ionic surfactant comprising a hydrophilic portion and a lipophilic portion wherein the hydrophilic portion has a number average molecular weight of 500 g/mol or higher.

BRIEF DESCRIPTION OF THE DRAWING

[0008] FIG. **1** is a topographical representation of local areas of high removal on a silicon-containing wafer.

[0009] FIG. **2** is a graph of the removal rate (Å /min) versus the measurement point across the diagonal on a 200 mm diameter silicon dioxide containing wafer with local areas of high removal, and on a 200 mm diameter silicon dioxide containing wafer with no local areas of high removal.

[0010] FIG. **3** is a graph of the thickness (Å) versus the measurement point across the diagonal on a 200 mm diameter polysilicon containing wafer polished with a composition containing no surfactant, a composition containing 150 ppm of a polyoxyethylene alkylphenyl ether nonionic surfactant, and a composition containing 400 ppm of the polyoxyethylene alkylphenyl ether nonionic surfactant.

[0011] FIG. **4** is a graph of removal rate (Å/min) versus the molecular weight (g/mol) of the hydrophilic portion of nonionic polyoxyethylene alkylphenyl ether surfactants in a composition used for polishing a polysilicon containing wafer.

[0012] FIG. 5 is a graph of removal rate (Å/min) versus the molecular weight (g/mol) of the hydrophilic portion of nonionic, polyoxyethylene-polyoxypropylene copolymer surfactants in a composition used for polishing a polysilicon containing wafer.

[0013] FIG. 6 is a graph of removal rate (Å/min) versus the molecular weight (g/mol) of the hydrophilic portion of nonionic, ethoxylated polydimethicone copolymer surfactants in a composition used for polishing a polysilicon containing wafer.

DETAILED DESCRIPTION OF THE INVENTION

[0014] The present invention provides a chemical-mechanical polishing (CMP) method for polishing a silicon-containing substrate, the method comprising, consisting essentially of or consisting of the steps of contacting a silicon-containing substrate with a polishing pad and a CMP composition, and causing relative motion between the polishing pad and the substrate while maintaining a portion of the CMP composition in contact with the surface between the pad and the substrate for a time period sufficient to abrade at least a portion of the surface of the substrate. The CMP composition comprises an aqueous carrier containing a ceria abrasive, a polishing additive bearing a functional group with a pK_a of 4 to 9, and a non ionic surfactant including an hydrophilic portion and a lipophilic portion wherein the hydrophilic portion has a number average molecular weight of at least 500 g/mol. The pH of the composition is 7 or less.

[0015] The present invention provides methods and compositions for polishing silicon-containing substrates, which lower and preferably eliminate local areas of higher removal on the substrate (e.g., provides low levels of pitting, staining, spotting, and the like).

[0016] The present invention is particularly useful for reducing local areas of high removal, even when the ceria concentration in the CMP slurry is less than 0.5 weight percent of the composition (wt.%) (e.g., less than 0.2 wt. % or less than 0.1 wt. %) ceria. The concentration of ceria used is typically greater than 0.005 wt. % (e.g., greater than 0.01 wt. %). Preferably, the ceria is in a concentration of 0.005 wt. % to 0.5 wt. % (e.g. 0.01 wt. % to 0.1 wt.%).

[0017] The ceria abrasive can have any suitable primary particle size. The primary particle size desirably is measured by a laser diffraction technique. Typically, the abrasive has an average primary particle size of 200 nm or less, preferably 180 nm or less (e.g., 160 nm or less, 140 nm or less, or 120 nm or less). Typically the abrasive has an average primary particle size of at least 10 nm, preferably at least 20 nm (e.g., at least 40 nm, at least 60 nm, or at least 80 nm). Typically the ceria abrasive has an average primary particle size of between about10 nm and 180 nm (e.g. 40 nm to 120 nm).

[0018] The CMP composition preferably is resistant to particle agglomeration, such that the average agglomerate particle size is 300 nm or less (e.g., 250 nm or less, or even 200 nm or

less). The absence of agglomeration is also reflected in the overall width of the particle size distribution, which typically is ± 35% (e.g., ± 25%, or even ± 15%) of the average primary particle size.

[0019] The polishing additive is included in the polishing composition to modify the surface properties of the silicon-containing dielectric layer being polished so as to make the surface more receptive to interaction with abrasive particles. The pH of the polishing composition plays an important role in determining the interactions between the polishing additives and the surface of the silicon-containing dielectric layer. The polishing composition typically has a pH of 7 or less, preferably 6.5 or less (e.g., 5.5 or less). The polishing composition typically has a pH of at least 2, preferably at least 3 (e.g., at least 3.5). In order for the polishing additive to interact with the silicon-containing dielectric layers within this pH range, the polishing additive desirably bears a functional group having a pK_a (in water) of 4 to 9, preferably 4 to 7 (e.g., 4 to 6). Moreover, it is desirable that the polishing additive has an overall net charge that is more positive than about -1 (e.g., a net charge = 0, +1, +2, etc.). The net charge is determined to be the charge of the polishing additive when the functional group having a pK_a in the range of 4 to 9 is protonated.

[0020] The functional group of the polishing additive can be any suitable functional group, and typically is selected from amines, carboxylic acids, alcohols, thiols, sulfonamides, imides, hydroxamic acids, barbituric acids, hydrazines, amidoxines, salts thereof, and combinations thereof. Polishing additives bearing these functional groups and having a pK_a of 4 to 9 include one or more compounds selected from the group, consisting of an arylamine, an aminoalcohol, an aliphatic amines, a heterocyclic amine, a hydroxamic acid, an aminocarboxylic acid, a cyclic monocarboxylic acid, an unsaturated monocarboxylic acid, a substituted phenol, a sulfonamide, a thiol, and a combination thereof. Preferably, the polishing additive comprises one or more compounds selected from the group consisting of an arylamine, a heterocyclic amine, an aminocarboxylic acid, and a combination thereof. Any of the foregoing polishing additives may exist in the form of a salt, for example a salt selected from the group consisting of hydrochloride salts, hydrobromide salts, sulfate salts, sulfonate salts, trifluoromethanesulfonate salts, acetate salts, trifluoroacetate salts, picrate salts, perfluorobutyrate salts, sodium salts, potassium salts, ammonium salts, halide salts, or the like.

[0021] The arylamine can be any suitable arylamine having a pK_a of 4 to 9. Preferably, the arylamine is a primary arylamine. The arylamine optionally can be substituted with one or more substituents selected from the group consisting of C_{1-12} alkyl, C_{1-12} alkoxy, C_{6-12} aryl, carboxylic acid, sulfonic acid, phosphonic acid, hydroxyl, thiol, sulfonamide, acetamide, salts thereof, and

combinations thereof. For example, the arylamine can be aniline, 4-chloroaniline, 3-methoxyaniline, N-methylaniline, 4-methoxyaniline, p-toluidine, anthranilic acid, 3-amino-4-hydroxybenzene sulfonic acid, an aminobenzyl alcohol, an aminobenzyl amine, 1-(2-aminophenyl)pyrrole, 1-(3-aminophenyl)ethanol, 2-aminophenylether, 2,5-bis-(4-aminophenyl)-1,3,4-oxadiazole, 2-(2-aminophenyl)-1H-1,3,4-triazole, 2-aminophenol, 3-aminophenol, 4-aminophenol, a dimethylaminophenol, 2-aminothiolphenol, 3-aminothiolphenol, 4-aminothiolphenol, 4-aminophenyl methyl sulfide, 2-aminobenzenesulfonamide, orthanilic acid, 3-aminobenzene boronic acid, 5-aminoisophthalic acid, sulfacetamide, sulfanilic acid, o-arsanilic, p-arsanilic acid, (3R)-3-(4-trifluoromethylphenylamino)pentanoic acid amide, salts thereof, and combinations thereof.

[0022] The aminoalcohol can be any suitable aminoalcohol having a pK_a of 4 to 9. For example aminoalcohol can be selected from the group consisting of triethanolamine, benzyldiethanolamine, tris(hydroxymethyl)aminomethane, hydroxylamine, tetracycline, salts thereof, and combinations thereof. Preferably, the aminoalcohol is a tertiary aminoalcohol.

[0023] The aliphatic amine can be any suitable aliphatic amine having a pK_a of 4 to 9. Suitable aliphatic amines include methoxyamine, hydroxylamine, N-methylhydroxylamine, N,O-dimethylhydroxylamine, β-difluoroethylamine, ethylenediamine, triethylenediamine, diethyl butylamino-(2-hydroxyphenyl)methyl)phosphonate, an iminoethane, an iminobutane, triallylamine, a cyanoamine (e.g., aminoacetonitrile, diethylaminoacetonitrile, 2-amino-2-cyanopropane, an (isopropylamino)propionitrile, a (diethylamino)propionitrile, an aminopropionitrile, dicyanodiethylamine, 3-(dimethylamino)propionitrile, salts thereof, and a combination thereof. The aliphatic amine can also be a hydrazine. Preferably, the hydrazine comprises one or more compounds selected from the group consisting of hydrazine, methylhydrazine, tetramethylhydrazine, N,N-diethylhydrazine, phenylhydrazine, N,N-dimethylhydrazine, trimethylhydrazine, ethylhydrazine, salts thereof (e.g., hydrochloride salts), and a combination thereof.

[0024] The heterocyclic amine can be any suitable heterocyclic amine having a pK_a of 4 to 9, including monocyclic, bicyclic, and tricyclic amines. Typically, the cyclic amine is a 3-, 4-, 5- or 6-membered cyclic structure comprising one or more nitrogen atoms and one or more other atoms such as carbon, carbon and oxygen, carbon and sulfur, and the like. Preferably, the cyclic amine is a 5- or 6-membered cyclic structure. The heterocyclic amine optionally is substituted by one or more substituents selected from the group consisting of H, OH, COOH, SO_3H, PO_3H, Br, Cl, I, F, NO_2, hydrazine, a C_{1-8} alkyl (optionally substituted with OH, COOH, Br, Cl, I, or NO_2), a C_{6-12} aryl (optionally substituted with OH, COOH, Br, I, or NO_2), C(O)H, C(O)R (where

R is a C_{1-8} alkyl or a C_{6-12} aryl), and a C_{1-8} alkenyl. Desirably, the heterocyclic amine contains at least one unsubstituted heterocyclic nitrogen. For example, the heterocyclic amine can be imidazole, 1-methylimidazole, 2-methylimidazole, 2-ethylimidazole, 2-hydroxymethylimidazole, 1-methyl-2-hydroxymethylimidazole, benzimidazole, quinoline, isoquinoline, hydroxyquinoline, melamine, pyridine, bipyridine, 2-methylpyridine, 4-methylpyridine, 2-aminopyridine, 3-aminopyridine, 2,3-pyridinedicarboxylic acid, 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid, 5-butyl-2-pyridinecarboxylic acid, 4-hydroxy-2-pyridinecarboxylic acid, 3-hydroxy-2-pyridinecarboxylic acid, 2-pyridinecarboxylic acid, 3-benzoyl-2-pyridinecarboxylic acid, 6-methyl-2-pyridinecarboxylic acid, 3-methyl-2-pyridinecarboxylic acid, 6-bromo-2-pyridinecarboxylic acid, 6-chloro-2-pyridinecarboxylic acid, 3,6-dichloro-2-pyridinecarboxylic acid, 4-hydrazino-3,5,6-trichloro-2-pyridinecarboxylic acid, quinoline, isoquinoline, 2-quinolinecarboxylic acid, 4-methoxy-2-quinolinecarboxylic acid, 8-hydroxy-2-quinolinecarboxylic acid, 4,8-dihydroxy-2-quinolinecarboxylic acid, 7-chloro-4-hydroxy-2-quinolinecarboxylic acid, 5,7-dichloro-4-hydroxy-2-quinolinecarboxylic acid, 5-nitro-2-quinolinecarboxylic-acid, 1-isoquinolinecarboxylic acid, 3-isoquinolinecarboxylic acid, acridine, benzoquinoline, benzacridine, clonidine, anabasine, nomicotine, triazolopyridine, pyridoxine, serotonin, histamine, benzodiazepine, aziridine, morpholine, 1,8-diazabicyclo[5,4,0]undecene-7 (DABCO), hexamethylenetetramine, piperazine, N-benzoylpiperazine, 1-tosylpiperazine, N-carbethoxypiperazine, 1,2,3-triazole, 1,2,4-triazole, 2-aminothiazole, pyrrole, pyrrole-2-carboxylic acid and alkyl, halo, or carboxylic acid-substituted derivatives thereof, 3-pyrroline-2-carboxylic acid, ethylpyrroline, benzylpyrroline, cyclohexylpyrroline, tolylpyrroline, tetrazole, 5-cyclopropyltetrazole, 5-methyltetrazole, 5-hydroxytetrazole, 5-phenoxytetrazole, 5-phenyltetrazole, salts thereof, and combinations thereof. The heterocyclic amine also can be an imide, an aminidine, or a barbituric acid compound. For example, suitable imides include fluorouracil, methylthiouracil, 5,5-diphenylhydantoin, 5,5-dimethyl-2,4-oxazolidinedione, phthalimide, succinimide, 3,3-methylphenylglutarimide, 3,3-dimethylsuccinimide, salts thereof, and combinations thereof. Suitable aminidines include imidazo[2,3-b]thioxazole, hydroxyimidazo[2,3-a]isoindole, salts thereof, and combinations thereof. Suitable barbituric acids include 5,5-methylphenylbarbituric acid, 1,5,5-trimethylbarbituric acid, hexobarbital, 5,5-dimethylbarbituric acid, 1,5-dimethyl-5-phenylbarbituric acid, salts thereof, and combinations thereof.

[0025] The hydroxamic acid can be any suitable hydroxamic acid having a pK_a of 4 to 9. Suitable hydroxamic acids include formohydroxamic acid, acetohydroxamic acid, benzohydroxamic acid, salicylhydroxamic acid, 2-aminobenzohydroxamic acids, 2-

chlorobenzohydroxamic acid, 2-fluorobenzohydroxamic acid, 2-nitrobenzohydroxamic acid, 3-nitrobenzohydroxamic acid, 4-aminobenzohydroxamic acid, 4-chlorobenzohydroxamic acid, 4-fluorobenzohydroxamic acid, 4-nitrobenzohydroxamic acid, 4-hydroxybenzohydroxamic acid, salts thereof, and combinations thereof.

[0026] The aminocarboxylic acid can be any suitable aminocarboxylic acid having a pK_a of 4 to 9. Certain common aminocarboxylic acid compounds such as proline, glycine, phenylglycine, and the like have a pK_a of 2-2.5 for the carboxylic acid moiety and 9-10 for the amino moiety, and are not suitable for use in the context of the invention. Contrastingly, aminocarboxylic acids such as glutamic acid, beta-hydroxyglutamic acid, aspartic acid, asparagine, azaserine, cysteine, histidine, 3-methylhistidine, cytosine, 7-aminocephalosporanic acid, and camosine each contain a functional group having a pK_a of in the range of 4 to 9.

[0027] The cyclic monocarboxylic acid can be any suitable cyclic monocarboxylic acid having a pK_a of 4 to 9. Di- and poly-carboxylic acids previously suggested for use in polishing silicon-containing dielectric layers can have a pK_a in the desired range, but have a total charge that leads to undesirable agglomeration, adhesion, and/or rapid settling of the inorganic abrasive particles. Desirably, the cyclic carboxylic acid compound comprises a C_{4-12} cyclic alkyl or C_{6-12} aryl group. The cyclic carboxylic acid compound optionally is substituted by one or more substituents selected from H, OH, COOH, Br, Cl, I, F, NO_2, hydrazine, a C_{1-8} alkyl (optionally substituted with OH, COOH, Br, Cl, I, or NO_2), a C_{6-12} aryl (optionally substituted with OH, COOH, Br, I, or NO_2), C(O)H, C(O)R (where R is a C_{1-8} alkyl or a C_{6-12} aryl), and C_{1-8} alkenyl. Preferably, the cyclic carboxylic acid compound is not a di- or poly-hydroxybenzoic acid. Suitable cyclic monocarboxylic acid, compounds include benzoic acid, C_{1-12}-alkyl-substituted benzoic acids, C_{1-12}-alkoxy-substituted benzoic acids, naphthalene 2-carboxylic acid, cyclohexane carboxylic acid, cyclohexyl acetic acid, 2-phenylacetic acid, 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 2-piperidinecarboxylic acid, cyclopropanecarboxylic acids (e.g., cis- and trans-2-methylcyclopropanecarboxylic acid), salts thereof, and combinations thereof. Especially preferred polishing additives are 4-hydroxybenzoic acid, cyclohexane carboxylic acid, benzoic acid, salts thereof, and combinations thereof.

[0028] The unsaturated monocarboxylic acid can be any suitable unsaturated monocarboxylic acid (e.g., alkenecarboxylic acid) having a pK_a of 4 to 9. Typically, the unsaturated monocarboxylic acid is a C_{3-6}-alk-2-enoic acid. Preferably, the unsaturated monocarboxylic acid comprises one or more compounds selected from the group consisting of a cinnamic acid, a propenoic acid (e.g., acrylic acid, 3-chloroprop-2-enecarboxylic acid), a butenoic acid (e.g., crotonic acid, 3-chlorobut-2-enecarboxylic acid, 4-chlorobut-2-

enecarboxylic acid), pentenoic acids (e.g., cis- or trans-2-pentenoic acid, 2-methyl-2-pentenoic acid), a hexenoic acid (e.g., 2-hexenoic acid, 3-ethyl-2-hexenoic acid), salts thereof, and a combinationthereof.

[0029] The substituted phenol can be any suitable substituted phenol having a pK_a of 4 to 9. Preferably, the substituted phenol contains a substituent selected from nitro, chloro, bromo, fluoro, cyano, alkoxycarbonyl, alkanoyl, acyl, alkylsulfonyl, and combinations thereof. Suitable nitrophenols include nitrophenol, 2,6-dihalo-4-nitrophenols, 2,6-di-C_{1-12}-alkyl-4-nitrophenols, 2,4-dinitrophenol, 2,6-dinitrophenol, 3,4-dinitrophenol, 2-C_{1-12}-alkyl-4,6-dinitrophenols, 2-halo-4,6-dinitrophenols, dinitro-o-cresol, trinitrophenols such as picric acid, salts thereof, and combinations thereof.

[0030] The sulfonamide can be any suitable sulfonamide having a pK_a of 4 to 9. Suitable sulfonamides include N-chlorotolylsulfonamide, dichlorophenamide, mafenide, nimesulide, sulfamethizole, sulfaperin, sulfacetamide, sulfadiazine, sulfadimethoxine, sulfamethazine, sulfapyridine, sulfaquinoxaline, salts thereof, and combinations thereof.

[0031] The thiol can be any suitable thiol having a pK_a of 4 to 9. Suitable thiols include hydrogen sulfide, cysteamine, cysteinylcysteine, methyl cysteine, thiophenol, p-cholorthiophenol, o-aminothiophenol, o-mercaptophenylacetic acid, p-nitrobenzenethiol, 2-mercaptoethanesulfonate, N-dimethylcysteamine, dipropylcysteamine, diethylcysteamine, mercaptoethylmorpholine, methylthioglycolate, mercaptoethylamine, N-trimethylcysteine, glutathione, mercaptoethylepiperidine, diethylaminopropanethiol, salts thereof, and combinations thereof.

[0032] When the polishing additive is an arylamine, the polishing additive preferably comprises one or more compounds selected from the group consisting of aniline, anthranilic acid, an aminophenol, orthanilic acid, salts thereof, and combinations thereof. When the polishing additive is a heterocyclic amine compound, the polishing additive preferably comprises one or more compounds selected from the group consisting of imidazole, quinoline, pyridine, 2-methylpyridine, 2-pyridinecarboxylic acid, a pyridinedicarboxylic acid, 2-quinolinecarboxylic acid, morpholine, piperazine, a triazole, pyrrole, pyrrole-2-carboxylic acid, a tetrazole, salts thereof, and combinations thereof. When the polishing additive is an aminocarboxylic acid compound, the polishing additive preferably comprises one or more compounds selected from the group consisting of glutamic acid, aspartic acid, cysteine, histidine, salts thereof, and a combination thereof. When the polishing additive is a cyclic mono-carboxylic acid compound, the polishing additive preferably comprises one or more compounds

selected from the group consisting of benzoic acid, cyclohexane carboxylic acid, cyclohexylacetic acid, 2-phenylacetic acid, a salt thereof, and a combination thereof.

[0033] The polishing composition typically comprises 5 wt. % or less polishing additive (e.g., 2 wt. % or less) polishing additive. The polishing composition desirably comprises 0.005 wt. % or more (e.g., 0.01 wt. % or more) polishing additive. Preferably, the polishing composition comprises 1 wt. % or less (e.g., 0.5 wt. % or less, 0.2 wt. % or less) polishing additive. Preferably the additive comprises one or more compounds selected from the group consisting of an arylamine, an aminoalcohol, an aliphatic amine, a heterocyclic amine, a hydroxamic acid, an aminocarboxylic acid, a cyclic monocarboxylic acid, an unsaturated monocarboxylic acid, a substituted phenol, a sulfonamide, a thiol, a salt thereof, and a combination thereof.

[0034] The hydrophilic portion of the surfactant comprises, consists essentially of, or consists of oxyethylene (-O-CH_2-CH_2-) repeat units, vinyl alchohol [-CH_2-CH_2(OH)-] repeat units, a sorbitan group, highly substituted saturated or partially unsaturated C_{6-30} alkyls, or a combination thereof (e.g., polyoxyethylenesorbitan). The highly substituted saturated or partially unsaturated C_{6-30} alkyls preferably are substituted with one or more hydrophilic functional groups, for example a hydroxyl group. The hydrophilic portion of the nonionic surfactant typically has a molecular weight of at least 500 g/mol (e.g., 1000 g/mol or more, 1500 g/mol or more, or 3000 g/mol or more). For polymeric or oligomeric hydrophilic materials, the molecular weight preferably is a number average molecular weight. Compounds having a very high number average molecular weight may afford a viscosity increase that is detrimental to the slurry handling, polishing performance and slurry stability. It is therefore preferable to use a surfactant having a hydrophilic portion with a number average molecular weight below 1,000,000 g/mol (i.e., below 100,000 g/mol, below 50,000 g/mol or below 10,000 g/mol).

[0035] The lipophilic portion of the surfactant can be a silicone-free fragment containing a hydrocarbon moiety where there are 6 to 30 hydrocarbon units (e.g., 10 to 20 hydrocarbon units). Preferably, the hydrocarbon moiety is an alkyl group, an alkyl substituted aryl group, an alkoxy-substituted aryl group, and an aryl-substituted alkyl group or an aryl group.

[0036] In addition, the surfactant can comprise any acetylenic glycol surfactant comprising, consisting essentially of, or consisting of a tetraalkyldecyne head group and an oxyethylene tail group, such as 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate. The surfactant also can be an amphiphilic nonionic surfactant such as a polyoxyethylene alkyl ether and a polyoxyethylene alkanoic acid ester, wherein the alkyl portion thereof is a C_{6-30} alkyl, which can be saturated or partially unsaturated, and is optionally branched. For example, the amphiphilic nonionic

surfactant can comprise a polyoxyethylene lauryl ether, a polyoxyethylene cetyl ether, a polyoxyethylene stearyl ether, a polyoxyethylene oleyl ether, a polyoxyethylene monolaurate, a polyoxyethylene monostearate, a polyoxyethylene distearate, or a polyoxyethylene monooleate. Similarly, the surfactant can be a polyoxyethylene alkylphenyl ether or polyoxyethylene alkylcyclohexyl ether, wherein the alkyl group thereof is a C_{6-30} alkyl, can be saturated or partially unsaturated, and can be optionally branched, such as a polyoxyethylene octylphenyl ether, a polyoxyethylene nonylphenyl ether, or a polyoxyethylene dinonyphenyl ether.

[0037] The amphiphilic nonionic surfactant can also comprise a sorbitan alkanoic acid ester or a polyoxyethylenesorbitan alkanoic acid ester, wherein the alkyl portion thereof is a C_{6-30} alkyl, which can be saturated or partially unsaturated, and can be optionally branched. For example, the amphiphilic nonionic surfactant can comprise sorbitan monolaurate, sorbitan monooleate, sorbitan monopalmitate, sorbitan monostearate, sorbitan sequioleate, sorbitan trioleate, or sorbitan tristearate, as well as a polyoxyethylenesorbitan monolaurate, a polyoxyethylenesorbitane monopalmitate, a polyoxyethylene sorbitan monostearate, a polyoxyethylene sorbitan tristearate, a polyoxyethylenesorbitan monooleate, a polyoxyethylenesorbitan triooleate, or a polyoxyethylenesorbitan tetraoleate.

[0038] Alternatively, the surfactant can comprise a polydimethicone block or graft copolymers comprising, consisting essentially of, or consisting of a polydimethicone portion and a hydrophilic oxygen-containing portion (e.g., polyoxyethylene, polyoxyethylene and polyoxypropylene, or polyoxyethylene and polyethylene, or an alkyl polyglucose, an ethoxylated ester or diester of an alkyl glucose). The block or graft copolymer can comprise combinations of the above hydrophilic portions, for example a polydimethicone portion bound to a polyoxyethylene and a polyoxypropylene copolymer, and the like.

[0039] The surfactant preferably is hydrophilic, as can be determined by the surfactant's Hydrophilic-Lipophilic Balance (HLB) value. The HLB value is an indication of the solubility of a surfactant in water and, thus, is related to the wt.% amount of the hydrophilic portion of the surfactant (e.g., the wt.% amount of ethylene oxide). The surfactant HLB value can be approximated, in some cases, for nonionic surfactants containing an ethylene oxide group as being equal to the weight percent (wt.%) amount of the ethylene oxide groups in the surfactant multiplied by 20, giving a value between 0 and 20. A low HLB value indicates a lipophilic surfactant (i.e., having a small amount of hydrophilic groups), and a high HLB value indicates a hydrophilic surfactant (having a high amount of hydrophobic groups). Nonionic surfactants having an HLB of 10 or greater have been classified to as being "hydrophilic" nonionic surfactants, whereas nonionic surfactants having an HLB of less than 10 have been classified as

being "lipophilic" (see e.g., *The HLB System*, published by ICI United States, Inc., 1976). In a preferred embodiment, the nonionic surfactant is a hydrophilic nonionic surfactant and thus has an HLB not less than 10 (e.g., not less than 12). In a preferred embodiment, the nonionic surfactant is a hydrophilic surfactant with an HLB less than 19 (e.g. less than 18).

[0040] Preferred surfactants include polyoxyethylene nonylphenyl ethers and polyoxyetheylene dinonylphenyl ethers (e.g., IGEPAL® surfactants from Rhone-Poulenc, ICANOL® surfactants from BASF and LEUTENSOL® surfactants from BASF), polyoxyethylene-polyoxypropylene copolymers (e.g., PLURONIC® surfactants from BASF) and polydimethicone compolymers (e.g., SILWET® surfactants from GE Silicons).

[0041] Typically the surfactant is present in the polishing composition at a concentration of not less than 10 ppm, preferably not less than 20 ppm (e.g., not less than 50 ppm, not less than about100 ppm, not less than 150 ppm. or not less than 200 ppm). Typically the surfactant is present in a concentration not more than 10,000 ppm, preferably not more than 1000 ppm (e.g., not more than 750 ppm, or not more than 500 ppm).

[0042] The polishing composition described herein optionally further comprises one or more components such as an anti-foaming agent and a biocide. The anti-foaming agents and biocides can be any suitable anti-foaming and antimicrobial agents, respectively, that are suitable for use in CMP slurries.

[0043] The concentration of biocide used in the polishing composition is typically in the range of 1 to 50 ppm, preferably in the range of 10 to 20 ppm, based on the liquid carrier and any components dissolved or suspended therein. Examples of suitable biocides include an isothiazolinone biocide.

[0044] The concentration of anti-foaming agent present in the polishing composition typically is in the range of 5 to 140 ppm based on the liquid carrier and any components dissolved or suspended therein. Suitable antifoaming agents include polydimethysiloxane polymers (polydimethicones), and the like.

[0045] The polishing composition described herein also optionally comprises one or more metal complexing or sequestering agents. For example these may comprise mono-, di-, tri- and poly-carboxylic acids (e.g., EDTA and citric acid); mono-, di-, tri-, and poly-phosphonic acids (e.g., DEQUEST® phosphonic acids, and the like), as well as mono-, di-, tri- and poly-amines.

[0046] The present invention provides methods and compositions for polishing silicon-containing dielectric materials at a higher removal rate relative to silicon-containing semiconductor materials. Typical silicon-containing dielectric materials include, for example, silicon dioxide, boron silicates, phosphorous silicates, borophosphosilicate glass (BPSG),

undoped silicate glass (USG) and combinations thereof, as well as silicon nitrides and silicon oxynitrides. Typical silicon-containing semiconductor materials include for example, polysilicon, single crystal silicon, p-doped silicon, and n-doped silicon. Semiconductor materials also include such materials as the so-called III-V materials (e.g., gallium arsenide and aluminum phosphide). Typically, the present invention provides a selectivity for removal of silicon-containing dielectric materials relative to removal of silicon-containing semiconductor materials of greater than 5 to 1 (e.g., greater than or equal to 10 to 1, greater than or equal to 20 to 1, or greater than or equal to 30 to 1). Rates of polishing below 100 Å/min and close to 0 Å/min can be achieved on a silicon-containing semiconductor substrate (e.g., below 80 Å/min, below 60 Å/min or below 40 Å/min). Rates of polishing greater than 1000 Å/min can be achieved on the silicon-containing dielectric materials (e.g., greater than 2000 Å/min, greater than 3000 Å/min or greater than 4000 Å/min).

[0047] The compositions and methods of the invention are useful for polishing any suitable substrate. Preferably, the substrate comprises at least one silicon-containing layer comprising silicon dioxide (e.g., PETEOS), single crystal silicon, polycrystalline silicon (e.g., polysilicon), doped silicon (e.g., nitrogen and phosphorous doped polysilicon), low-k dielectric materials having a dielectric constant 3.5 or less (e.g., 1 to 3), silicon nitrides, silicon borides, and silicon. Without limitation, the compositions and methods of the present invention are also particularly useful for polishing substrates comprising germanium.

[0048] Any method of determining the quality of the surface uniformity may be used. For the purposes of describing the present invention the following measurements will be used, without limitation. A diagonal removal rate profile is the removal rate profile measured diagonally across the wafer and can usually be described by a polynomial equation of order 5 and lower as shown in FIG. 2. For example the removal rate of a film can be calculated from the difference of the thickness before and after polishing using ellipsometry. If there are many events of local areas of high removal, the polynomial fit is poor as evident by a low least square correlation (R^2). The presence of fewer local areas of high removal improves the correlation. Thus, the square of the correlation coefficient, R^2, for a 5th order or lower least-square fit of the diagonal removal profile can be used as a convenient tool to evaluate the surface quality of a polished wafer. In particular, an R^2 value of 0.5 (50%) or greater, preferably at least 0.6 (60%) or more, and preferably at least 0.7 (70%), indicates that the surface of the polished wafer is relatively free from local areas of overly high removal (e.g., pits, spots, stains, and the like).

[0049] Another effect of local areas of high removal is to increase the within-wafer non-uniformity; however, this parameter could be largely due to global phenomena such as low

overall edge polish to center differences in polishing rate. The non-uniformity can be calculated by taking the standard deviation of the thickness difference between the pre-polished wafer and the post-polished wafer for each measurement point. The magnitude of this standard deviation compared to the total average thickness difference expressed as a percentage, is referred to herein as within-wafer non-uniformity.

[0050] Local areas of high removal can also be described by a "dishing number". The dishing number is the difference between an average high area and an average lower area on a substrate over a given distance (profile). Typically this dishing number is used to describe depressions (dishing) between two areas of different materials, such as between a silicon oxide and a copper/silicon oxide array. As used herein, the dishing number refers to the difference between a high area and low area of the same material.

[0051] When used with the above described substrates, the methods and compositions of the present invention provide within-wafer non-uniformity values preferably lower than 20% (e.g. lower than 15% or lower than 10%). Additionally, a dishing number of less than 80 nm, on a profile of 1 to 5 mm, (e.g., less than 50 nm, less than 25 nm or less than 10 nm) is obtained when the methods and compositions of the present invention are used.

EXAMPLES

[0052] The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

[0053] This example demonstrates the effectiveness of compositions of the present invention for reducing local areas of high removal on PETEOS and polysilicon wafers. In the present example

[0054] PETEOS (silicon oxide) and polysilicon (poly) wafers (200 mm diameter) were polished with several CMP compositions of the invention using a conventional CMP apparatus. The CMP slurries that were evaluated contained 0.1% ceria (100 nm diameter, mean particle size), 1600 ppm of 2-pyridinecarboxylic acid (polishing additive), and ammonium hydroxide to adjust the pH to 5. Each slurry also contained a surfactant in the amount shown in Table 1 or Table 2. A slurry that contained no surfactant was also utilized for comparison purposes. The polishing parameters used to polish the wafers were as follows: down force pressure in the range of 20.2 kPa (2.95 psi) to 21.0 kPa (3.05 psi), platen speed 110 rpm, carrier speed 101 rpm, and flow rate 200 mL/min. An EPIC® D100 (Cabot Microelectronics Corporation, Aurora, IL) concentrically grooved pad and *in situ* conditioning were used on the polishing tool for polishing the wafers. The wafers were polished for 120 seconds each. The thickness of each wafer was

measured at 49 equally-spaced points across the diameter of the wafer, pre- and post-polishing, and the standard deviation of the difference in total thickness for each wafer, pre- and post-polishing was determined. The percentage of the determined standard deviation compared to the total thickness difference was then calculated as a measure of polishing uniformity. Because, local areas of high removal appear as spots due to the refraction of light through silicon oxide, a visual inspection of the PETEOS wafers was also made. In contrast, local areas of high removal are more difficult to observe with the unaided eye on polysilicon. Therefore for polysilicon, visual inspection was done using an optical microscope at 5X magnification. The results of the thickness determinations and visual inspections are summarized in Table 2.

Table 1: PETEOS and Polysilicon Defectivity Data

Surfactant	Wafer	% STD DEV	Visual Inspection
None (comparative)	PETEOS	23.8	Spots
150ppm IGEPAL® CO-890 (Invention)	PETEOS	13.9	Clean
150ppm LEUTENSOL® NP-40 (Invention)	PETEOS	13.8	Clean
400ppm IGEPAL® CO-890 (Invention)	PETEOS	13.9	Clean
400ppm LEUTENSOL® NP-40 (Invention)	PETEOS	15.2	Clean
None (comparative)	Poly	9.0	Spots
None (comparative)	Poly	11.8	Spots
150ppm IGEPAL® CO-890 (Invention)	Poly	5.6	Clean
150ppm LEUTENSOL® NP-40 (Invention)	Poly	5.7	Clean
400ppm IGEPAL® CO-890 (Invention)	Poly	6.6	Clean
400ppm LEUTENSOL® NP-40 (Invention)	Poly	3.3	Clean
400ppm LEUTENSOL® NP-40 (Invention)	Poly	5.4	Clean

[0055] The results in Table 1 demonstrate that surfactants comprising a lipophilic alkoxy-substituted aryl group and a hydrophilic polyoxyethylene group having an average mol. wt. greater than 500 g/mol are effective to reduce localized regions of high polysilicon and PETEOS removal.

[0056] FIG. **3** shows the loss (pre polish – post polish thickness) profiles of wafers polished with slurries containing 0, 150 and 400 ppm of IGEPAL® CO-890. The results indicate that addition of the surfactant smoothed out the profile across the diameter of the wafer. The degree of smoothness can be quantified by fitting the thickness (y) to the linear position (x) at the 49 measurement points to a second order polynomial expression. The following equations and least squares fits (i.e., the square of the correlation coefficient expressed as a percentage) were obtained from the combined data from all wafers at the surfactant levels shown:

a. No surfactant: $y = 0.0238x^2 + 2.5426x + 8732.1$; $R^2 = 9\%$

b. 150 ppm surfactant: $y = 0.353x^2 - 16.081x + 8588.8$; $R^2 = 71\%$

c. 400 ppm surfactant: $y = 0.4392x^2 - 20.344x + 8751.2$; $R^2 = 95\%$.

[0057] Clearly the methods and compositions of this invention create a profile that fits a polynomial equation more closely than the fit obtained with a conventional CMP composition containing no surfactant, as evidenced by the higher R^2 value when the method of the invention is applied. This result indicates that the post-polishing surface of the wafers is significantly improved by the methods and compositions of the invention.

[0058] Another way to describe local areas of high removal is by a dishing number obtained by use of an atomic force microscope (AFM) 5 mm profile scan. Table 2 shows the results of such an AFM measurement on wafers polished with 0 and 400 ppm of IGEPAL® CO-890. In Table 2 the measurement position "center" refers to a profile near the center of the wafer, "edge" refers to a profile near the edge of the wafer, and "middle" refers to a profile between the center and edge measurements.

Table 2: AFM Dishing Data.

Surfactant	**Measurement Position**	**Average Dishing (Å)**
None	Center	832
None	Middle	804
None	Edge	864
400ppm LEUTENSOL®	Center	195
400ppm LEUTENSOL®	Middle	200
400ppm LEUTENSOL®	Edge	177

[0059] Clearly the presence of the surfactant in the compositions of the invention lowered the events of local high removal rates as seen by the reduction in the average pit depth.

EXAMPLE 2

[0060] This example demonstrates the effectiveness of using a composition with a non-ionic surfactant wherein the hydrophilic portion has a number average molecular weight at least 500 g/mol for polishing silicon wafers at a low polishing rate. PETEOS and polysilicon square wafers (4 cm^2) were polished with several CMP compositions of the invention using a conventional CMP apparatus. The CMP slurries used were similar to the slurries used for Example 1 with respect to pH, ceria concentration, and polishing additive. Each slurry also contained a surfactant in the amount shown in Table 3. The polishing parameters used to polish the wafers were the same as in Example 1 except that the flow rate was 100 mL/min and the polish time for polysilicon wafers was 30 seconds. The thickness of each wafer was measured at

9 equally spaced points across the area of the wafer, pre- and post-polishing. Table 3 shows the polishing rate for TEOS and polysilicon wafers with compositions containing various surfactants. The average molecular weight of the hydrophile is also shown in Table 3.

Table 3: Polishing Rates.

Slurry description	Surfactant	Conc. (ppm)	Hydrophile mol. wt. (g/mol)	TEOS Rate (Å /min)	Polysilicon Rate (Å /min)
1 (comparative)	IGEPAL® CO-630	50	396	2679	360
2 (invention)	IGEPAL® CO-730	150	528	2569	280
3 (invention)	IGEPAL® DM-710	400	660	2714	200
4 (invention)	ICANOL® NP-40	50	1760	2450	140
5 (invention)	ICANOL® NP-40	150	1760	2538	80
6 (invention)	ICANOL® NP-40	400	1760	2488	20
7 (invention)	IGEPAL® CO-890	50	1760	2909	100
8 (invention)	IGEPAL® CO-890	150	1760	2465	40
9 (invention)	IGEPAL® CO-890	400	1760	2312	20
10 (invention)	IGEPAL® CO-897	400	1760	2530	120
11 (invention)	IGEPAL® CO-990	50	4400	2664	120
12 (invention)	IGEPAL® CO-990	150	4400	2529	40
13 (invention)	IGEPAL® CO-990	400	4400	2293	40
14 (comparative)	PLURONIC® 31R1	50	325	2133	400
15 (comparative)	PLURONIC® 31R1	150	325	2340	300
16 (comparative)	PLURONIC® 31R1	400	325	2464	300
17 (comparative)	PLURONIC® L101	400	380	1965	180
18 (comparative)	PLURONIC® L101	150	380	2154	340
19 (comparative)	PLURONIC® 17R2	50	430	2669	400
20 (comparative)	PLURONIC® 17R2	150	430	2597	360
21 (comparative)	PLURONIC® 17R2	400	430	2537	320
22 (invention)	PLURONIC® P84	150	1672	2358	80
23 (invention)	PLURONIC® P84	400	1672	2231	40
24 (invention)	PLURONIC® F38	400	3760	2487	140
25 (invention)	PLURONIC® F108	50	11660	2204	60
26 (invention)	PLURONIC® F108	150	11660	2278	60
27 (invention)	PLURONIC® F108	400	11660	2130	20
28 (comparative)	SILWET® 7280	150	240	2690	512
29 (comparative)	SILWET® 7280	400	240	2688	522
30 (invention)	SILWET® L7607	150	750	2554	490
31 (invention)	SILWET® L7607	400	750	2607	472
32 (invention)	SILWET® L8600	150	1575	2643	382
33 (invention)	SILWET® L8600	400	1575	2701	302
34 (invention)	SILWET® L-7600	150	3000	2616	320
35 (invention)	SILWET® L-7600	400	3000	2715	284
36 (invention)	SILWET® 7001	150	9000	2362	100
37 (invention)	SILWET® 7001	400	9000	2159	80
38 (comparative)	none	0	0	2136	450
39 (comparative)	none	0	0	2559	400
40 (comparative)	none	0	0	2842	350
41 (comparative)	none	0	0	1785	420
42 (comparative)	none	0	0	1781	422

[0061] The data from Table 3 are plotted in FIG. **4**, **5** and **6**. FIG. **4** is a plot of polishing rates on polysilicon wafers using a slurry comprising polyoxyethylene alkylphenyl ether surfactants with different sized polyoxyethylene portions and illustrates the drop in removal rate when the hydrophilic polyoxyethylene mol. wt. is greater that 500 g/mol. FIG. **5** is a plot of polishing rates on polysilicon wafers using a slurry comprising polyoxyethylene-polyoxypropylene copolymer surfactants with different polyoxyethylene chain lengths, and illustrates the drop in removal rate where the polyoxyethylene mol. wt. is greater that 500 g/mol. Finally, FIG. **6** is a plot of the polishing rates on polysilicon wafers using a slurry comprising ethoxylated polydimethicone copolymer surfactants with different polyoxyethylene chain lengths, and illustrates the drop in removal rate where the polyoxyethylene mol. wt. is greater that 500 g/mol.

CLAIMS

What is claimed is:

1. A CMP composition having a pH of about 5.5 or less and comprising an aqueous carrier containing a ceria abrasive in a concentration of about 0.005 wt. % to about 0.5 wt. %, wherein the ceria has an average primary particle size of between about 40 nm to about 120 nm, a polishing additive bearing a functional group having a pKa of about 4 to about 9, and a non ionic surfactant comprising a hydrophilic portion and a lipophilic portion wherein the hydrophilic portion has a number average molecular weight of 500 g/mol or higher.

2. The CMP composition of claim 1 wherein the surfactant comprises a polyoxyethylene alkylphenyl ether.

3. The CMP composition of claim 1 wherein the surfactant comprises a polydimethicone copolymer.

4. The CMP composition of claim 1 wherein the surfactant comprises a polyoxyethylene-polyoxypropylene copolymer.

METHODS AND COMPOSITIONS FOR POLISHING SILICON-CONTAINING SUBSTRATES

ABSTRACT

The invention provides chemical-mechanical polishing (CMP) compositions and methods for polishing a silicon-containing substrate. A method of the invention comprises the steps of contacting a silicon-containing substrate with a polishing pad and an aqueous CMP composition, and causing relative motion between the polishing pad and the substrate while maintaining a portion of the CMP composition in contact with the surface of the substrate to abrade at least a portion of the substrate. The CMP composition comprises a ceria abrasive, a polishing additive bearing a functional group with a pK_a of about 4 to about 9, a nonionic surfactant with an hydrophilic portion and a lipophilic portion wherein the hydrophilic portion has a number average molecular weight of about 500 g/mol or higher, and an aqueous carrier, wherein the pH of the composition is 7 or less. The method reduces defects on the wafers, particularly local areas of high removal. The method is also useful for polishing dielectric silicon-containing substrates at a high rate relative to semiconductor silicon-containing substrates.

(FIG. 4)