

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 January 2008 (31.01.2008)

PCT

(10) International Publication Number
WO 2008/013678 A1

(51) International Patent Classification:
C09K 3/14 (2006.01)

(21) International Application Number:
PCT/US2007/015872

(22) International Filing Date: 12 July 2007 (12.07.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/491,612 24 July 2006 (24.07.2006) US

(71) Applicant: **CABOT MICROELECTRONICS CORPORATION** [US/US]; Legal Department, 870 North Commons Drive, Aurora, Illinois 60504 (US).

(72) Inventors: **VACASSY, Robert**; c/o Legal Department, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US). **BAYER, Benjamin**; c/o Legal Department, Cabot Microelectronics Corporation, 870 N. Commons Drive, Aurora, Illinois 60504 (US). **CHEN, Zhan**; c/o Legal Department, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US). **CHAMBERLAIN, Jeffrey**; c/o Legal Department, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US).

(74) Agents: **WESEMAN, Steven** et al.; Associate General Counsel, Intellectual Property, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, IL 60504 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: RATE-ENHANCED CMP COMPOSITIONS FOR DIELECTRIC FILMS

(57) Abstract: The invention provides a chemical-mechanical polishing composition consisting essentially of silica, an oxidizing agent, a quaternary ammonium compound, and water. The invention further provides a method of chemically-mechanically polishing a substrate with the aforementioned polishing composition. The polishing composition provides for enhanced polishing rates when used to polish dielectric films.



WO 2008/013678 A1

RATE-ENHANCED CMP COMPOSITIONS FOR DIELECTRIC FILMS

FIELD OF THE INVENTION

[0001] The invention pertains to chemical-mechanical polishing compositions and methods.

BACKGROUND OF THE INVENTION

[0002] Integrated circuits are made up of millions of active devices formed in or on a substrate, such as a silicon wafer. The active devices are chemically and physically connected into a substrate and are interconnected through the use of multilevel interconnects to form functional circuits. Typical multilevel interconnects comprise a first metal layer, an interlevel dielectric layer, and a second and sometimes subsequent metal layer(s). Interlevel dielectrics, such as doped and undoped silicon dioxide (SiO_2) and/or low- κ dielectrics, are used to electrically isolate the different metal layers. As each layer is formed, typically the layer is planarized to enable subsequent layers to be formed on top of the newly formed layer.

[0003] Tungsten is increasingly being used as a conductive material to form the interconnections in integrated circuit devices. One way to fabricate planar tungsten circuit traces on a silicon dioxide substrate is referred to as the damascene process. In accordance with an embodiment of this process, the tungsten damascene process starts with a fully planarized dielectric surface that is patterned with vertical contact holes, or vias, to provide for electrical connection between layers and/or trenches to define circuit lines. An adhesion-promoting layer, typically titanium or titanium nitride, is applied to the substrate surface to adhere the metal to the dielectric surface and to prevent the metal and the dielectric material from reacting. Tungsten is then deposited using a chemical vapor deposition process to fill the holes and/or trenches. Chemical-mechanical polishing (CMP) is employed to reduce the thickness of the tungsten over-layer, as well as the thickness of any adhesion-promoting layer and/or diffusion barrier layer, until a planar surface that exposes elevated portions of the silicon dioxide surface is obtained. The vias and trenches remain filled with electrically conductive tungsten forming the circuit interconnects.

[0004] Polishing compositions useful for the CMP of tungsten and other metals often have an acidic pH. Such polishing compositions typically planarize dielectric layers at considerably lower rates than the metals. As the overlying layer of metal is removed, thereby exposing the underlying dielectric surface, metal remaining in the holes and/or trenches

continues to be removed while the dielectric surface is more slowly planarized, which results in erosion of metal within the holes and/or trenches and subsequent nonplanarity of the substrate surface. Thus, a need remains in the art for polishing compositions and methods that are effective for polishing both metals and dielectric materials at similar rates in one single polishing step.

BRIEF SUMMARY OF THE INVENTION

[0005] The invention provides a chemical-mechanical polishing composition consisting essentially of (a) silica having an average primary particle size of 10 nm to 40 nm, (b) an oxidizing agent selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, percarbonate salts, benzoyl peroxide, peracetic acid, sodium peroxide, di-*tert*-butyl peroxide, monopersulfate salts, dipersulfate salts, iron (III) compounds, and combinations thereof, (c) a quaternary ammonium compound comprising a cation with the structure $R_1R_2R_3R_4N^+$ wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of C_2 - C_6 alkyls and C_7 - C_{12} arylalkyls, and (d) water, wherein the polishing composition has a pH of 1 to 5.

[0006] The invention also provides a method of chemically-mechanically polishing a substrate, which method comprises (i) contacting a substrate with a polishing pad and a chemical-mechanical polishing composition consisting essentially of (a) silica having an average primary particle size of 10 nm to 40 nm, (b) an oxidizing agent selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, percarbonate salts, benzoyl peroxide, peracetic acid, sodium peroxide, di-*tert*-butyl peroxide, monopersulfate salts, dipersulfate salts, iron (III) compounds, and combinations thereof, (c) a quaternary ammonium compound comprising a cation with the structure $R_1R_2R_3R_4N^+$ wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of C_2 - C_6 alkyls and C_7 - C_{12} arylalkyls, and (d) water, wherein the polishing composition has a pH of 1 to 5, (ii) moving the polishing pad relative to the substrate with the chemical-mechanical polishing composition therebetween, and (iii) abrading at least a portion of the substrate to polish the substrate.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The invention provides a chemical-mechanical polishing composition consisting essentially of (a) silica having an average primary particle size of 10 nm to 40 nm, (b) an

oxidizing agent selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, percarbonate salts, benzoyl peroxide, peracetic acid, sodium peroxide, di-*tert*-butyl peroxide, monopersulfate salts, dipersulfate salts, iron (III) compounds, and combinations thereof, (c) a quaternary ammonium compound comprising a cation with the structure $R_1R_2R_3R_4N^+$ wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of C_2 - C_6 alkyls and C_7 - C_{12} arylalkyls, and (d) water, wherein the polishing composition has a pH of 1 to 5.

[0008] The polishing composition contains silica as an abrasive. The silica can be any suitable form of silica. Useful forms of silica include but are not limited to fumed silica, precipitated silica, and condensation-polymerized silica. Preferably, the silica is a condensation-polymerized silica. Condensation-polymerized silica particles typically are prepared by condensing $Si(OH)_4$ to form colloidal particles. The precursor $Si(OH)_4$ can be obtained, for example, by hydrolysis of high purity alkoxysilanes, or by acidification of aqueous silicate solutions. Such abrasive particles can be prepared in accordance with U. S. Patent 5,230,833 or can be obtained as any of various commercially available products, such as the Fuso PL-1, PL-2, and PL-3 products, and the Nalco 1050, 2327, and 2329 products, as well as other similar products available from DuPont, Bayer, Applied Research, Nissan Chemical, and Clariant.

[0009] As is well known in the art, abrasive particles comprise, at the lowest level of structure, primary particles. Primary particles are formed by covalent bonds between atoms comprising the particles and are stable to all but the harshest conditions. At the next level of structure, primary particles are associated into secondary particles, generally referred to as aggregates. Aggregate particles comprise primary particles and are bonded together by covalent bonds and electrostatic interactions, and typically are resistant to degradation by, e.g., mechanical energy inputs such as high-shear mixing. At the next level of structure, aggregates are more loosely associated into agglomerates. Typically, agglomerates can be disassociated into the constituent aggregates via mechanical energy inputs. Depending on the particular composition and method of preparation, primary particles and secondary particles (e.g., aggregates) can have shapes ranging from spherical to elliptical, and some aggregates can have extended, chain-like structures. For example, pyrogenic, or fumed, silica typically exists in the form of aggregates having a chain-like structure. Precipitated silicas, for example, silicas prepared by neutralization of sodium silicate, have an aggregate structure in

which approximately spherical primary particles are associated into aggregates that resemble a "bunch of grapes." Both primary abrasive particles and aggregated primary particles (e.g., secondary particles) can be characterized as having an average particle size. In this regard, particle size refers to the diameter of the smallest sphere that encloses the particle. It is to be noted that monodispersed silica particles can be prepared under certain conditions, wherein the monodispersed particles are substantially nonaggregated.

[0010] The abrasive typically has an average primary particle size of 10 nm or more (e.g., 15 nm or more, or 20 nm or more). Preferably, the abrasive has an average primary particle size of 40 nm or less (e.g., 35 nm or less, or 30 nm or less). More preferably, the abrasive has an average primary particle size of 10 nm to 40 nm, or 15 nm to 35 nm.

[0011] When the abrasive comprises aggregates of primary particles, the abrasive typically has an average aggregate particle size of 20 nm or more (e.g., 30 nm or more, or 40 nm or more, or 50 nm or more). Preferably, the abrasive has an average aggregate particle size of 150 nm or less (e.g., 100 nm or less, or 90 nm or less, or 80 nm or less). More preferably, the abrasive has an average aggregate particle size of 20 nm to 150 nm, or 30 nm to 100 nm, or 40 nm to 90 nm, or 50 nm to 80 nm.

[0012] The abrasive desirably is suspended in the polishing composition, more specifically in the water of the polishing composition. When the abrasive is suspended in the polishing composition, the abrasive preferably is colloidally stable. The term colloid refers to the suspension of abrasive particles in the water. Colloidal stability refers to the maintenance of that suspension over time. In the context of this invention, an abrasive is considered colloidally stable if, when the abrasive is placed into a 100 ml graduated cylinder and allowed to stand unagitated for a time of 2 hours, the difference between the concentration of particles in the bottom 50 ml of the graduated cylinder ($[B]$ in terms of g/ml) and the concentration of particles in the top 50 ml of the graduated cylinder ($[T]$ in terms of g/ml) divided by the initial concentration of particles in the abrasive composition ($[C]$ in terms of g/ml) is less than or equal to 0.5 (i.e., $\{[B] - [T]\}/[C] \leq 0.5$). The value of $[B]-[T]/[C]$ desirably is less than or equal to 0.3, and preferably is less than or equal to 0.1.

[0013] Any suitable amount of silica can be present in the polishing composition. Typically, 0.1 wt.% or more silica can be present in the polishing composition (e.g., 0.5 wt.% or more, or 1 wt.% or more, or 2 wt.% or more). The amount of silica in the polishing composition preferably will not exceed 10 wt.%, and more preferably will not exceed 8 wt.%.

Even more preferably the silica will comprise 0.5 wt.% to 10 wt.% (e.g., 1 wt.% to 8 wt.%) of the polishing composition.

[0014] The polishing composition contains an oxidizing agent that acts on, i.e., oxidizes copper. The oxidizing agent is selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, percarbonate salts, benzoyl peroxide, peracetic acid, sodium peroxide, di-*tert*-butyl peroxide, monopersulfate salts, dipersulfate salts, nitrate salts, iron (III) compounds, and combinations thereof. The recited oxidizing agents, with the exception of iron (III) compounds, are referred to herein as per-type oxidizing agents. When the polishing composition contains nitrate salts, generally the polishing composition also will contain at least one other oxidizing agent selected from the specified group. Preferably, the oxidizing agent is selected from the group consisting of hydrogen peroxide, iron (III) compounds, and combinations thereof. More preferably, the oxidizing agent is a combination of hydrogen peroxide and an iron (III) compound, most preferably a combination of hydrogen peroxide and ferric nitrate.

[0015] The polishing composition can contain any suitable amount of the oxidizing agent. The polishing composition typically contains 0.1 wt.% or more (e.g., 0.5 wt.% or more, or 1 wt.% or more, or 1.5 wt.% or more) of the oxidizing agent. Preferably, the polishing composition contains 10 wt.% or less (e.g., 9 wt.% or less, or 8 wt.% or less, or 7 wt.% or less) of the oxidizing agent.

[0016] When the polishing composition contains a combination of a per-type oxidizing agent and an iron (III) compound, typically the polishing composition will contain 1 ppm or more (e.g., 5 ppm or more, or 10 ppm or more, or 20 ppm or more) of the iron (III) compound. Preferably, 100 ppm or less (e.g., 90 ppm or less, or 80 ppm or less) of the iron (III) compound is present in the polishing composition. In such a situation, the polishing composition desirably contains an amount of the per-type oxidizing agent as generally recited for the oxidizing agent. Without wishing to be bound by any particular theory, when the polishing composition is used to polish a substrate comprising a metal, it is believed that the iron (III) compound serves to oxidize the metal by accepting an electron from the metal, thereby becoming reduced to an iron (II) compound. The per-type compound serves to reoxidize the iron (II) compound to an iron (III) compound, although it is possible for the per-type oxidizing agent to oxidize the metal directly in addition to its role as re-oxidizer for the iron (III) compound.

[0017] The polishing composition contains a quaternary ammonium compound comprising a cation with the structure $R_1R_2R_3R_4N^+$, wherein the R_1 , R_2 , R_3 , and R_4 groups of the tetraalkylammonium cation are independently selected from the group consisting of straight-chain, branched, or cyclic C_2 - C_6 alkyl or C_7 - C_{12} arylalkyl residues. The quaternary ammonium compound comprises any suitable anion. Examples of suitable anions include hydroxide, chloride, bromide, iodide, nitrate, sulfate, hydrogensulfate, phosphate, hydrogenphosphate, dihydrogenphosphate, and sulfonate (e.g., p-toluenesulfonate). In some embodiments, the polishing composition can comprise two or more quaternary ammonium compounds, which quaternary ammonium compounds are as recited herein.

[0018] Examples of suitable tetraalkylammonium cations include tetraethylammonium, tetrapropylammonium, tetrabutylammonium, tetrapentylammonium, tetrahexylammonium, benzyltrimethylammonium, and the like. Preferably, the tetraalkylammonium cation is tetraethylammonium, tetrapropylammonium, or tetrabutylammonium. Specific examples of suitable tetraalkylammonium compounds include but are not limited to tetraethylammonium hydroxide, tetraethylammonium nitrate, tetrapropylammonium hydroxide, tetrapropylammonium nitrate, tetrabutylammonium hydroxide, and tetrabutylammonium nitrate.

[0019] It will be appreciated that the specific nature of the tetraalkylammonium compound in the polishing composition will depend on the particular anion associated with the tetraalkylammonium compound that is used to prepare the polishing composition and on the pH of the polishing composition. For example, if a tetraalkylammonium hydroxide is used to formulate the polishing composition and the pH of the polishing composition at the point-of-use (e.g., on the surface of a substrate being polished with the polishing composition) is acidic (i.e., wherein the pH of the polishing composition is less than 7), the equilibrium concentration of hydroxide will be decreased relative to the initial concentration of hydroxide supplied by the tetraalkylammonium hydroxide, due to rapid acid-base reaction of the hydroxide with the particular acid or acids used to adjust the pH of the polishing composition. Thus, at an acidic pH, the actual tetraalkylammonium compound present in the polishing composition will comprise the conjugate base of the acid used to adjust the pH of the polishing composition. For example, a polishing composition comprising tetraalkylammonium hydroxide in water adjusted with nitric acid to a pH of 3 will comprise tetraalkylammonium nitrate at that particular pH.

[0020] The polishing composition can contain any suitable amount of the quaternary compound. Typically, 10 ppm or more (e.g., 100 ppm or more) of the quaternary compound will be present in the polishing composition. More typically, 250 ppm or more (e.g., 500 ppm or more) of the quaternary compound will be present in the polishing composition. The amount of the quaternary compound typically will not exceed 5000 ppm (e.g., will not exceed 2500 ppm). Preferably, the amount of the quaternary compound is 250 ppm to 2500 ppm (e.g., 500 ppm to 2250 ppm, or 750 ppm to 2000 ppm).

[0021] The polishing composition desirably has a pH that is 9 or less (e.g., 8 or less, or 6 or less, or 4 or less). Preferably, the polishing composition has a pH of 1 or more (e.g., 2 or more). Even more preferably, the polishing composition has a pH of 2 to 5 (e.g., 2 to 4). The polishing composition optionally contains pH adjusting agents, for example, nitric acid or potassium hydroxide. The polishing composition optionally contains a pH buffering system, for example, potassium hydrogen phthalate. Many such pH buffering systems are well known in the art.

[0022] When the polishing composition contains a combination of an iron (III) compound and a per-type oxidizing agent, the polishing composition optionally comprises a stabilizer. It is well known that hydrogen peroxide and other per-type oxidizing agents are not stable in the presence of many metal ions, including iron (III) compounds, without the use of stabilizers. Without the stabilizer, the metal ion or ions and per-type oxidizing agent may react in a manner that degrades the per-type oxidizing agent over time.

[0023] A suitable stabilizer improves the stability of the per-type oxidizing agent but does not materially affect the chemistry of the chemical-mechanical polishing composition in that the presence of the stabilizer does not substantially affect the removal rate exhibited by the polishing composition when used to chemically-mechanically polish a given substrate. Useful stabilizers include but are not limited to phosphoric acid, organic acids (e.g., malonic acid, citric acid, adipic acid, oxalic acid, phthalic acid, and ethylenediaminetetraacetic acid), nitriles, and other ligands that are capable of binding to metal ions and reducing their reactivity towards per compounds. It will be appreciated that the aforementioned acids can exist in the form of a salt (e.g., a metal salt, an ammonium salt, or the like), an acid, or as a partial salt thereof. For example, malonates include malonic acid, as well as mono- and di-salts thereof. Preferred stabilizers are selected from the group consisting of malonic acid,

citric acid, adipic acid, oxalic acid, and mixtures thereof. An especially preferred stabilizer is malonic acid.

[0024] The stabilizer can be present in the polishing composition in any suitable amount. Desirably, the amount of stabilizer is based on the amount of the iron (III) compound that is present in the composition. Preferably, the amount of stabilizer will be 1 molar equivalent or more (e.g., 2 molar equivalents or more) as compared to the amount of the iron (III) compound. The amount of stabilizer will typically be less than 5 molar equivalents as compared to the amount of the iron (III) compound.

[0025] The polishing composition optionally contains a biocide to inhibit bacterial growth in the polishing composition during storage. Non-limiting examples of suitable biocides include the Kathon[®] biocides from Rohm and Haas, Philadelphia, PA.

[0026] Desirably, the polishing composition does not contain a corrosion inhibitor. In the context of the invention, a corrosion inhibitor is a component that functions to reduce the removal rate and/or the static etch rate of a metal being polished with the inventive polishing composition when added to the polishing composition. Examples of corrosion inhibitors include anionic surfactants, nonionic surfactants, amphoteric surfactants and polymers, and heterocyclic organic compounds. Anionic surfactants include surfactants having functional groups selected from the group consisting of sulfonate, sulfate, carboxylate, phosphate, and derivatives thereof. Nonionic surfactants include silicon-based compounds, fluorine-based compounds, esters, ethylene oxide derivatives, alcohol, ethoxylates, ethers, glycosides, and derivatives thereof. Amphoteric surfactants include polycarboxylates, polyacrylamides, cellulose, polyvinylalcohols, polyvinylpyrrolidones, and derivatives thereof. Examples of heterocyclic organic compounds that function as corrosion inhibitors include azoles such as imidazole and derivatives thereof, and triazoles, such as benzotriazole, tolyltriazole, and the like.

[0027] The chemical-mechanical polishing composition can be produced by any suitable technique, many of which are known to those skilled in the art. For example, the silica, oxidizing agent(s) and quaternary ammonium compound(s) may be combined in water before applying the polishing composition to a substrate, or they may be applied separately, e.g., in the form of aqueous dispersions or aqueous solutions, to a polishing pad or to a substrate before or during substrate polishing. Generally, the components of the polishing composition may be prepared by combining the ingredients in any order. The term "component" as used

herein includes individual ingredients (e.g., silica, oxidizing agent(s), quaternary ammonium compound(s), etc.) as well as any combination of ingredients.

[0028] For example, the oxidizing agent(s) and the quaternary ammonium compound(s) can be combined in water at predetermined concentrations and mixed until such components are completely dissolved. A concentrated dispersion of silica then can be added, and the mixture diluted to give the desired concentration of silica in the final polishing composition. Optionally, a stabilizer, a biocide, and/or a pH adjusting agent can be added to the polishing composition at any time during the preparation of the polishing composition, e.g., before or after addition of the oxidizing agent(s) and the quaternary ammonium compound(s), and before or after adding the silica, and mixed by any method that is capable of incorporating the ingredients into the polishing composition. The mixture can be filtered, if desired, to remove large particulate contaminants such as agglomerated silica or other contaminants before use.

[0029] The polishing composition can be prepared prior to use, with one or more components, such as the oxidizing agent(s), added to the polishing composition just before use (e.g., within 1 minute before use, or within 5 minutes before use, or within 1 hour before use, or within 24 hours before use, or within 7 days before use). For example, when the polishing composition contains a per-type oxidizing agent and an iron (III) compound, the per-type oxidizing agent may decompose in the presence of the iron (III) compound. In such a situation, the per-type oxidizing agent or the iron (III) compound may be added to the polishing composition immediately before use (e.g., within 1 minute before use, or within 5 minutes before use, or within 1 hour before use, or within 24 hours before use, or within 7 days before use).

[0030] The chemical-mechanical polishing composition can be supplied as a one package system containing silica, the oxidizing agent(s), the quaternary ammonium compound(s), and water. Optionally, one or more oxidizing agent(s) can be placed in a second or third container. Furthermore, the components in the first or second container can be in dry form while the components in the corresponding container can be in the form of an aqueous dispersion. If the oxidizing agent(s) is a solid, it may be supplied either in dry form or as an aqueous mixture, separately from the other components of the polishing composition. Other two-container, or three- or more container combinations of the components of the polishing composition are within the knowledge of one of ordinary skill in the art.

[0031] The polishing composition also can be provided as a concentrate which is intended to be diluted with an appropriate amount of water prior to use. In such an embodiment, the polishing composition concentrate can contain silica, an oxidizing agent(s), a quaternary ammonium compound(s), and water in amounts such that, upon dilution of the concentrate with an appropriate amount of water, each component of the polishing composition will be present in the polishing composition in an amount within the appropriate range recited above for each component. For example, the silica, an oxidizing agent(s), and quaternary ammonium compound(s) can each be present in the concentrate in an amount that is 2 times (e.g., 3 times, 4 times, or 5 times) greater than the concentration recited above for each component so that, when the concentrate is diluted with an equal volume of water (e.g., 2 equal volumes water, 3 equal volumes of water, or 4 equal volumes of water, respectively), each component will be present in the polishing composition in an amount within the ranges set forth above for each component. Furthermore, as will be understood by those of ordinary skill in the art, the concentrate can contain an appropriate fraction of the water present in the final polishing composition in order to ensure that the oxidizing agent(s), quaternary ammonium compound(s), and other optional components (e.g., a stabilizer and/or a biocide) are at least partially or fully dissolved in the concentrate. In another embodiment, the polishing composition concentrate can contain silica, quaternary ammonium compound(s), and water in amounts such that, upon dilution of the concentrate with an appropriate amount of a solution of an oxidizing agent(s) in water, each component of the polishing composition will be present in the polishing composition in an amount within the appropriate range recited above for each component.

[0032] While the components of the polishing system can be combined well before or even shortly before use, the components of the polishing composition can be combined at or near the point-of-use. As utilized herein, the term "point-of-use" refers to the point at which the polishing composition is contacted with the substrate surface. When the components of the polishing composition are to be combined using point-of-use mixing, the components of the polishing composition are separately stored in two or more storage devices.

[0033] In order to mix components of the polishing composition contained in storage devices at or near the point-of-use, the storage devices typically are provided with one or more flow lines leading from each storage device to the point-of-use of the polishing composition (e.g., the platen or the substrate surface). By the term "flow line" is meant a

path of flow from an individual storage container to the point-of-use of the component stored therein. The one or more flow lines can each lead directly to the point-of-use, or, in the case that more than one flow line is used, two or more of the flow lines can be combined at any point into a single flow line that leads to the point-of-use. Furthermore, any of the one or more flow lines (e.g., the individual flow lines or a combined flow line) can first lead to one or more of the other devices (e.g., pumping device, measuring device, mixing device, etc.) prior to reaching the point-of-use of the component(s). The flow rate at which the components of the polishing composition are delivered to the surface of the substrate (i.e., the delivered amount of the particular components of the polishing composition) can be altered prior to the polishing process and/or during the polishing process, such that the polishing characteristics, for example, the polishing rate, of the polishing composition are altered.

[0034] The components of the polishing composition can be delivered to the point-of-use independently (e.g., the components are delivered to the substrate surface whereupon the components are mixed during the polishing process), or the components can be combined immediately before delivery to the point-of-use. Components are combined "immediately before delivery to the point-of-use" if they are combined less than 10 seconds prior to reaching the point-of-use, preferably less than 5 seconds prior to reaching the point-of-use, more preferably less than 1 second prior to reaching the point of use, or even simultaneous to the delivery of the components at the point-of-use (e.g., the components are combined at a dispenser). Components also are combined "immediately before delivery to the point-of-use" if they are combined within 5 m of the point-of-use, such as within 1 m of the point-of-use or even within 10 cm of the point-of-use (e.g., within 1 cm of the point of use).

[0035] When two or more of the components of the polishing composition are combined prior to reaching the point-of-use, the components can be combined in the flow line and delivered to the point-of-use without the use of a mixing device. Alternatively, one or more of the flow lines can lead into a mixing device to facilitate the combination of two or more of the components. Any suitable mixing device can be used. For example, the mixing device can be a nozzle or jet (e.g., a high pressure nozzle or jet) through which two or more of the components flow. Alternatively, the mixing device can be a container-type mixing device comprising one or more inlets by which two or more components of the polishing composition are introduced to the mixer, and at least one outlet through which the mixed components exit the mixer to be delivered to the point-of-use, either directly or via other

elements of the apparatus (e.g., via one or more flow lines). Furthermore, the mixing device can comprise more than one chamber, each chamber having at least one inlet and at least one outlet, wherein two or more components are combined in each chamber. If a container-type mixing device is used, the mixing device preferably comprises a mixing mechanism to further facilitate the combination of the components. Mixing mechanisms are generally known in the art and include stirrers, blenders, agitators, paddled baffles, gas sparger systems, vibrators, etc.

[0036] The invention further provides a method of chemically-mechanically polishing a substrate comprising (i) contacting a substrate with a polishing pad and the polishing composition described herein, (ii) moving the polishing pad relative to the substrate with the polishing composition therebetween, and (iii) abrading at least a portion of the substrate to polish the substrate.

[0037] The method of the invention can be used to polish any suitable substrate, and is especially useful for polishing substrates comprising an insulating layer such as metal oxide, porous metal oxide, and glass (e.g., borophosphosilicate glass). Suitable metal oxides include silicon oxide. When the insulating layer comprises a silicon oxide, the silicon oxide can be derived from any suitable precursor. Preferably, the silicon oxide is derived from silane precursors, more preferably from oxidized silane precursors such as tetraethylorthosilicate (TEOS). The silicon oxide can be prepared using any suitable method, for example, by plasma-enhanced deposition of tetraethylorthosilicate (PETEOS).

[0038] The method of the invention can be used to polish any suitable substrate comprising a dielectric layer. In that regard, the inventive method is useful in conjunction with the polishing of an interlayer dielectric (ILD). The inventive method is especially useful for polishing substrates comprising an insulating layer and further comprising a metal selected from the group consisting of tungsten, copper, tantalum, tantalum nitride, aluminum, titanium, titanium nitride, and combinations thereof, and is especially useful for polishing substrates comprising silicon oxide and tungsten. Suitable substrates include wafers used in the semiconductor industry. The polishing composition is particularly well-suited for planarizing or polishing a substrate comprising tungsten and silicon oxide that has undergone so-called damascene processing. Damascene processing typically involves providing a silicon substrate upon which is deposited a layer of silicon oxide and then an adhesion layer (e.g., titanium or titanium nitride). A pattern of trenches and/or vias is defined on the top

layer of the substrate by photolithography, and then the patterned regions are etched to provide trenches and/or vias in the substrate surface. The substrate is overcoated with tungsten to fill the trenches and/or vias, and the excess tungsten is removed by chemical-mechanical polishing using a polishing composition so that the tungsten in the trenches and/or vias is substantially level with the silicon oxide resident on the substrate surface. Desirably, the polishing of the substrate to remove the tungsten and expose the silicon oxide is carried out with the polishing composition of the invention, preferably such that the tungsten is substantially removed and the silicon dioxide is adequately planarized without excessive erosion of tungsten on the substrate surface. Advantageously, when the polishing composition comprises a low level of the oxidizing agent, or even substantially no oxidizing agent, the polishing composition can be used to buff the substrate after removal of the excess tungsten, or the polishing composition can be used to chemically-mechanically polish dielectric layers (e.g., substrates comprising interlayer dielectrics).

[0039] The polishing method of the invention is particularly suited for use in conjunction with a chemical-mechanical polishing (CMP) apparatus. Typically, the apparatus comprises a platen, which, when in use, is in motion and has a velocity that results from orbital, linear, or circular motion, a polishing pad in contact with the platen and moving with the platen when in motion, and a carrier that holds a substrate to be polished by contacting and moving relative to the surface of the polishing pad. The polishing of the substrate takes place by the substrate being placed in contact with the polishing pad and the polishing composition of the invention and then the polishing pad moving relative to the substrate, so as to abrade at least a portion of the substrate to polish the substrate.

[0040] A substrate can be polished with the inventive polishing composition with any suitable polishing pad (e.g., polishing surface). Suitable polishing pads include, for example, woven and non-woven polishing pads. Moreover, suitable polishing pads can comprise any suitable polymer of varying density, hardness, thickness, compressibility, ability to rebound upon compression, and compression modulus. Suitable polymers include, for example, polyvinylchloride, polyvinylfluoride, nylon, fluorocarbon, polycarbonate, polyester, polyacrylate, polyether, polyethylene, polyamide, polyurethane, polystyrene, polypropylene, coformed products thereof, and mixtures thereof.

[0041] Desirably, the CMP apparatus further comprises an in situ polishing endpoint detection system, many of which are known in the art. Techniques for inspecting and

monitoring the polishing process by analyzing light or other radiation reflected from a surface of the workpiece are known in the art. Such methods are described, for example, in U.S. Patent 5,196,353, U.S. Patent 5,433,651, U.S. Patent 5,609,511, U.S. Patent 5,643,046, U.S. Patent 5,658,183, U.S. Patent 5,730,642, U.S. Patent 5,838,447, U.S. Patent 5,872,633, U.S. Patent 5,893,796, U.S. Patent 5,949,927, and U.S. Patent 5,964,643. Desirably, the inspection or monitoring of the progress of the polishing process with respect to a workpiece being polished enables the determination of the polishing end-point, i.e., the determination of when to terminate the polishing process with respect to a particular workpiece.

[0042] This example further illustrates the invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE

[0043] In this example, the polishing experiments generally involved use of a commercially available polishing tool with 17.5 kPa (2.5 psi) downforce pressure of the substrate against the polishing pad, 22.5 kPa (3.3 psi) subcarrier pressure, 17.5 kPa (2.5 psi) back side pressure, 22.5 kPa (3.3 psi) ring pressure, 100 rpm platen speed, 55 rpm carrier speed, 150 mL/min polishing composition flow rate, and ex-situ conditioning of a concentric grooved CMP pad.

[0044] This example shows the effect of the average primary particle size of condensation-polymerized silica on the removal rate of silicon dioxide observed with the polishing composition of the invention.

[0045] Similar silicon dioxide layers were separately polished with three different polishing compositions (Compositions A-C). Each of the polishing compositions comprised 8 wt.% of a condensation-polymerized silica, 1000 ppm tetrabutylammonium hydroxide, 65 ppm malonic acid, 0.0506 wt.% ferric nitrate, 26 ppm of Kathon[®] biocide, and 2 wt.% hydrogen peroxide, at a pH of 3.3. The condensation-polymerized silicas used were the PL-2, PL-5, and PL-7 products of Fuso Chemical Co., Osaka, Japan. Composition A (invention) further comprised 8 wt.% silica having a 25 nm average primary particle diameter (Fuso PL-2). Composition B (comparative) further comprised 8 wt.% silica having a 50 nm average primary particle diameter (Fuso PL-5). Composition C (comparative) further comprised 8 wt.% silica having a 70 nm average primary particle diameter (Fuso PL-7).

[0046] Following use of the polishing compositions, the silicon dioxide ("oxide") removal rates were determined. The results are set forth in the Table.

Table: Effect of silica primary particle size on silicon dioxide removal rate

Polishing Composition	Silica Average Primary Particle Size (nm)	Oxide Rate (Å/min)
A	25	2525
B	50	1129
C	70	774

[0047] The results shown in the Table demonstrate that the use of condensation-polymerized silica having an average primary particle size of 25 nm provides significantly enhanced removal rates in the polishing of silicon dioxide layers as compared with condensation-polymerized silica having an average primary particle size of 50 nm or 70 nm.

CLAIMS

1. A chemical-mechanical polishing composition consisting essentially of:
 - (a) silica having an average primary particle size of 10 nm to 40 nm,
 - (b) an oxidizing agent selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, percarbonate salts, benzoyl peroxide, peracetic acid, sodium peroxide, di-*tert*-butyl peroxide, monopersulfate salts, dipersulfate salts, nitrate salts, iron (III) compounds, and combinations thereof,
 - (c) a quaternary ammonium compound comprising a cation with the structure $R_1R_2R_3R_4N^+$ wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of C_2 - C_6 alkyls and C_7 - C_{12} arylalkyls, and
 - (d) water,

wherein the polishing composition has a pH of 1 to 5.

2. The polishing composition of claim 1, wherein the silica is condensation-polymerized silica.

3. The polishing composition of claim 2, wherein the silica is present in an amount of 0.1 wt.% to 10 wt.%.

4. The polishing composition of claim 3, wherein the silica is present in an amount of 0.5 wt.% to 8 wt.%.

5. The polishing composition of claim 1, wherein the oxidizing agent is a combination of hydrogen peroxide and an iron (III) compound.

6. The polishing composition of claim 5, wherein the iron (III) compound is ferric nitrate.

7. The polishing composition of claim 6, wherein the hydrogen peroxide is present in an amount of 1 wt.% to 10 wt.%, and the ferric nitrate is present in an amount of 0.1 ppm to 100 ppm.

8. The polishing composition of claim 1, wherein the quaternary ammonium compound is present in an amount of 100 ppm to 5000 ppm.

9. The polishing composition of claim 8, wherein the quaternary ammonium compound comprises a cation selected from the group consisting of tetraethylammonium, tetrapropylammonium, tetrabutylammonium, and tetrapentylammonium.

10. A method of chemically-mechanically polishing a substrate, which method comprises:

- (i) contacting a substrate with a polishing pad and a chemical-mechanical polishing composition consisting essentially of:
 - (a) silica having an average primary particle size of 10 nm to 40 nm,
 - (b) an oxidizing agent selected from the group consisting of hydrogen peroxide, urea hydrogen peroxide, percarbonate salts, benzoyl peroxide, peracetic acid, sodium peroxide, di-*tert*-butyl peroxide, monopersulfate salts, dipersulfate salts, nitrate salts, iron (III) compounds, and combinations thereof,
 - (c) a quaternary ammonium compound comprising a cation with the structure $R_1R_2R_3R_4N^+$ wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of C_2 - C_6 alkyls and C_7 - C_{12} arylalkyls, and
 - (d) water,wherein the polishing composition has a pH of 1 to 5,
 - (ii) moving the polishing pad relative to the substrate with the chemical-mechanical polishing composition therebetween, and
 - (iii) abrading at least a portion of the substrate to polish the substrate.
- 11. The method of claim 10, wherein the silica is condensation-polymerized silica.
 - 12. The method of claim 11, wherein the silica is present in an amount of 0.1 wt.% to 10 wt.%.
 - 13. The method of claim 12, wherein the silica is present in an amount of 0.5 wt.% to 8 wt.%.
 - 14. The method of claim 10, wherein the oxidizing agent is a combination of hydrogen peroxide and an iron (III) compound.
 - 15. The method of claim 14, wherein the iron (III) compound is ferric nitrate.
 - 16. The method of claim 15, wherein the hydrogen peroxide is present in an amount of 0.1 wt.% to 10 wt.%, and the ferric nitrate is present in an amount of 1 ppm to 100 ppm.
 - 17. The method of claim 10, wherein the quaternary ammonium compound is present in an amount of 100 ppm to 5000 ppm.

18. The method of claim 17, wherein the quaternary ammonium compound comprises a cation selected from the group consisting of tetraethylammonium, tetrapropylammonium, tetrabutylammonium, and tetrapentylammonium.

19. The method of claim 10, wherein the substrate comprises silicon oxide.

20. The method of claim 19, wherein the substrate further comprises a metal selected from the group consisting of tungsten, copper, tantalum, tantalum nitride, aluminum, titanium, titanium nitride, and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/015872**A. CLASSIFICATION OF SUBJECT MATTER****C09K 3/14(2006.01)i**

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)

IPC 8 : C09K, H01L

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)
eKIPASS (KIPO internal), USPAT, PAJ, CAPLUS (STN)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005-0076580 A1 (TAMBOLI et al.) 14 April 2005 See [0019]-[0029], [0040]-[0043].	1-20
Y	KR 10-2003-0043198 A (CHEIL INDUSTRIES INC.) 02 June 2003 See page 2.	1-20
A	US 6440857 B1 (LI et al.) 27 August 2002 See the abstract and examples.	1-20

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 DECEMBER 2007 (26.12.2007)

Date of mailing of the international search report

26 DECEMBER 2007 (26.12.2007)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701,
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

OH, Se Zu

Telephone No. 82-42-481-8156



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2007/015872

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005-0076580 A1	14.04.2005	EP 1522565A2 JP 2005117046A2	13.04.2005 28.04.2005
KR 10-2003-0043198 A	02.06.2003	KR 10-0449610B	21.09.2004
US 6440857 B1	27.08.2002	None	