



US 20070117497A1

(19) **United States**

(12) **Patent Application Publication**

Moeggenborg et al.

(10) **Pub. No.: US 2007/0117497 A1**

(43) **Pub. Date: May 24, 2007**

(54) **FRICION REDUCING AID FOR CMP**

(22) Filed: **Nov. 22, 2005**

(75) Inventors: **Kevin J. Moeggenborg**, Naperville, IL (US); **Phillip W. Carter**, Naperville, IL (US)

Publication Classification

(51) **Int. Cl.**
B24B 1/00 (2006.01)
B24B 29/00 (2006.01)
(52) **U.S. Cl.** **451/41; 451/285**

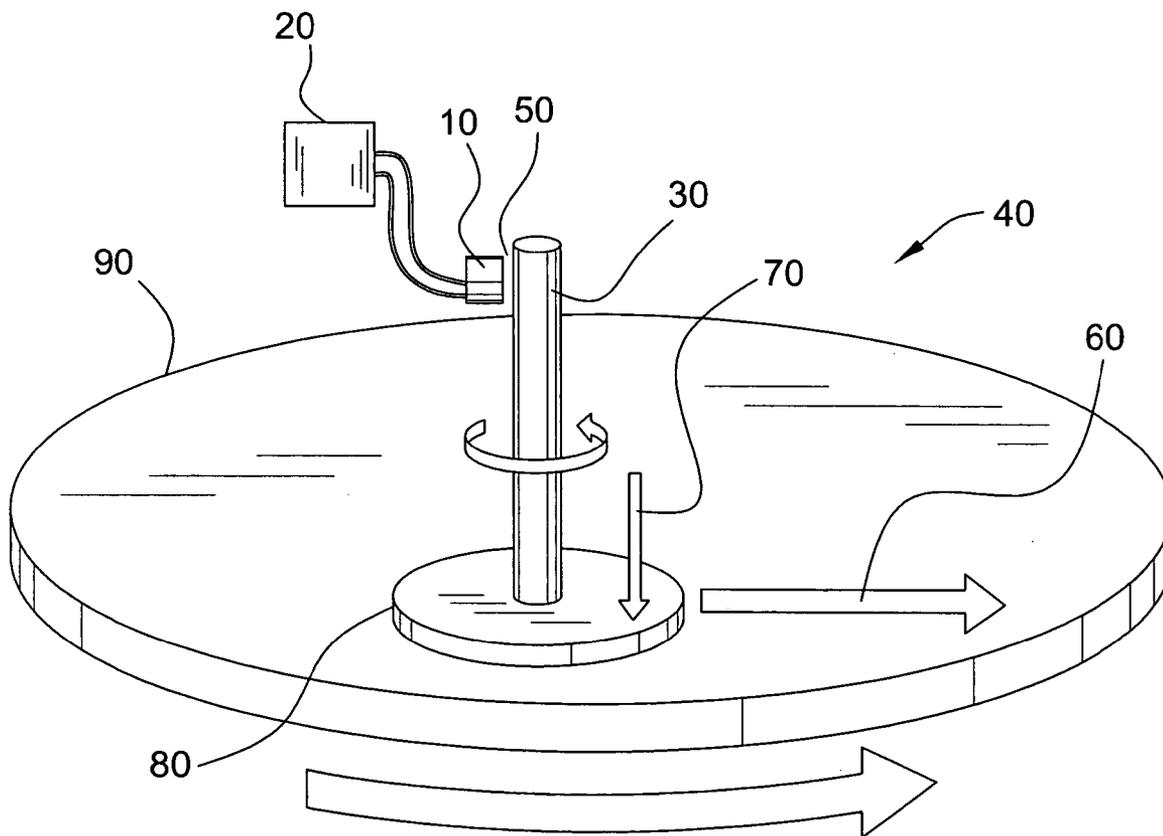
Correspondence Address:
STEVEN WESEMAN
ASSOCIATE GENERAL COUNSEL, I.P.
CABOT MICROELECTRONICS CORPORATION
870 NORTH COMMONS DRIVE
AURORA, IL 60504 (US)

(57) **ABSTRACT**

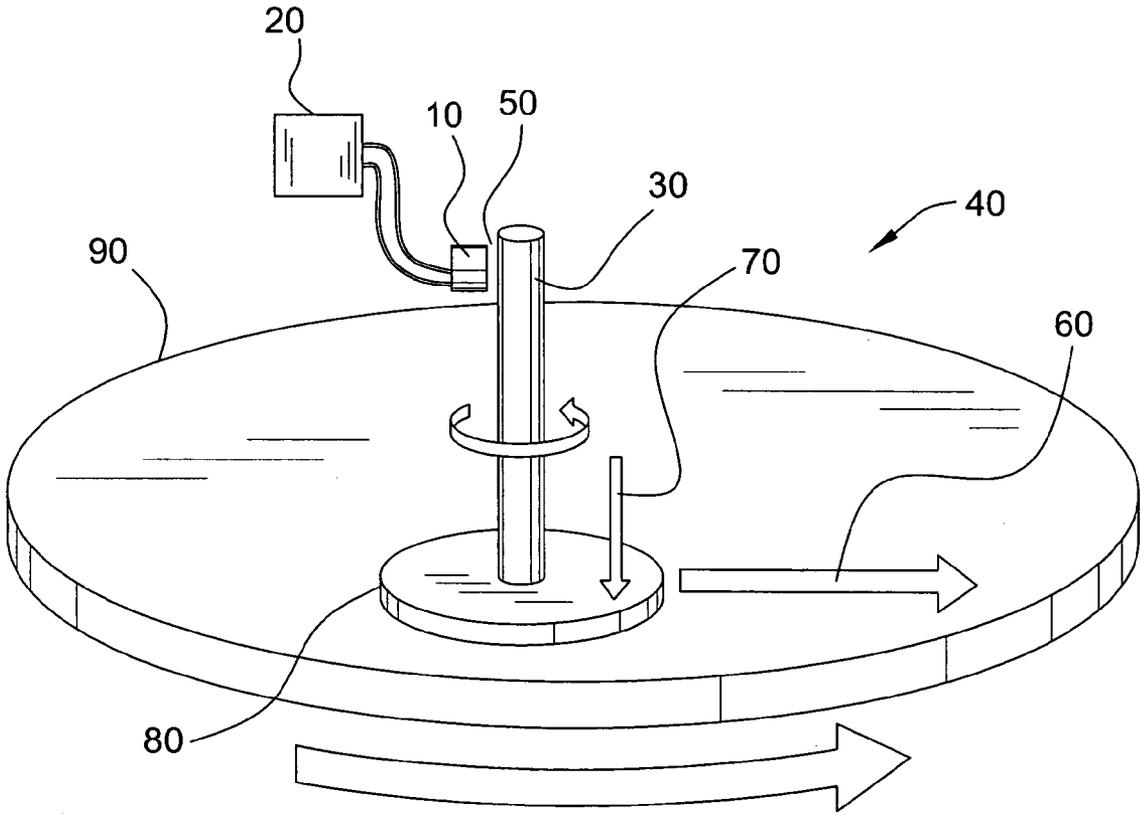
The invention provides a chemical-mechanical polishing system for polishing a substrate comprising a polishing agent, a water-soluble silicate compound, an oxidizing agent, and water, wherein the pH of the polishing system is about 8 to about 12. The invention further provides a method of chemically-mechanically polishing a substrate with the aforementioned polishing system. The polishing system provides for reduced friction during polishing of substrates.

(73) Assignee: **Cabot Microelectronics Corporation**, Aurora, IL (US)

(21) Appl. No.: **11/287,039**



Figure



FRICION REDUCING AID FOR CMP

BACKGROUND OF THE INVENTION

[0001] 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. In one manufacturing process, a dielectric substrate is patterned by a conventional dry etch process to form holes and trenches for vertical and horizontal interconnects. The patterned surface is then optionally coated with a diffusion barrier layer and/or an adhesion-promoting layer, followed by deposition of a metal layer to fill the trenches and holes. Chemical-mechanical polishing (CMP) is then employed to reduce the thickness of the metal layer, as well as the thickness of the diffusion barrier layer and/or adhesion-promoting layer, until the underlying dielectric layer is exposed, thus forming the circuit device.

[0002] In chemical-mechanical polishing, the surface of the substrate is contacted with a polishing composition and a polishing component, such as a polishing pad. Polishing compositions (also known as polishing slurries) typically contain an abrasive material in an aqueous solution and are applied to a surface by contacting the surface with a polishing pad saturated with the polishing composition. Chemical components of the polishing compositions are thought to react with surface materials of the substrate being polished, either by converting the surface materials to softer, more easily abradable derivatives of the materials, which derivatives are then removed by mechanical action of the abrasive material and/or the polishing pad, or by solubilizing the surface materials that are removed by mechanical action alone. In certain applications, the abrasive can be affixed to the surface of the polishing pad.

[0003] The frictional forces resulting from the relative motion of the substrate surface and the surface of the polishing pad with a polishing composition therebetween during the polishing process can lead to defectivity of the device being formed on the substrate via damage of the lines by scratching of the substrate by abrasive particles and/or the polishing pad and via delamination of the surface layers from the substrate. In addition, frictional heating of the polishing pad at the pad/slurry interface can lead to premature pad failure. Strategies to reduce frictional forces, such as incorporation of surfactants into polishing compositions, use of polishing pads composed of softer materials, or reduction of force applied to the substrate/polishing pad interface often result in the reduction of removal rates of the materials being polished, which can result in increased processing times, thus reducing throughput and increasing overall unit costs.

[0004] Further, in efforts to reduce the capacitance between conductive layers on microelectronic devices and thus to increase the frequency or speed at which the devices can operate, materials having lower dielectric constants than the commonly used silicon dioxide-based dielectrics are being employed to provide electrical isolation between circuit lines. Examples of low dielectric constant materials typically include organic polymer materials, inorganic and organic porous dielectric materials, and blended or composite organic and inorganic materials, which can be porous or

non-porous. Such materials are mechanically softer than silicon dioxide-based dielectrics and are more easily damaged during device manufacture. It would be highly desirable to incorporate low dielectric constant materials into semiconductor structures while still being able to utilize the conventional chemical-mechanical polishing (CMP) systems for polishing the surface of the resulting devices during semiconductor wafer processing.

[0005] Thus, a need remains for chemical-mechanical polishing compositions and systems exhibiting reduced friction between substrates and polishing components. These and other advantages of the invention, as well as additional inventive features, will be apparent from the description of the invention provided herein.

BRIEF SUMMARY OF THE INVENTION

[0006] The invention provides a chemical-mechanical polishing system for polishing a substrate comprising (a) a polishing component selected from the group consisting of a polishing pad, an abrasive, and a combination thereof, (b) a water-soluble silicate compound in an amount sufficient to provide about 0.1 wt. % or more of SiO₂, (c) an oxidizing agent that oxidizes at least part of a substrate, and (d) water, wherein the pH of the polishing system is about 8 to about 12. The invention further provides a method of chemically-mechanically polishing a substrate, which method comprises (i) contacting a substrate with a chemical-mechanical polishing system comprising (a) a polishing component selected from the group consisting of a polishing pad, an abrasive, and a combination thereof, (b) a water-soluble silicate compound in an amount sufficient to provide about 0.1 wt. % or more of SiO₂, (c) an oxidizing agent that oxidizes at least part of a substrate, and (d) water, and (ii) abrading at least a portion of the substrate to polish the substrate, wherein the pH of the polishing system is about 8 to about 12.

BRIEF DESCRIPTION OF THE DRAWING

[0007] The Figure illustrates a method for determination of the coefficient of friction for a chemical-mechanical polishing process.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The invention provides a chemical-mechanical polishing (CMP) system comprising a polishing component, a water-soluble silicate compound in an amount sufficient to provide about 0.1 wt. % or more of SiO₂, an oxidizing agent that oxidizes at least part of a substrate, and water, wherein the pH of the polishing system is about 8 to about 12. The water and any components dissolved or suspended therein form the polishing composition of the chemical-mechanical polishing system. The amounts of the components recited herein are based on the total weight of the polishing composition unless otherwise noted (i.e., the weight of the water and any components dissolved or suspended therein).

[0009] The polishing component is selected from the group consisting of a polishing pad, an abrasive, and the combination of a polishing pad and an abrasive. If an abrasive is present, the abrasive can be in any suitable form (e.g., abrasive particles). The abrasive can be fixed on the polishing pad and/or can be in particulate form and sus-

pended in the water. The polishing pad can be any suitable polishing pad, many of which are known in the art.

[0010] The abrasive can be any suitable abrasive, for example, the abrasive can be natural or synthetic, and can comprise metal oxide, carbide, nitride, carborundum, and the like. The abrasive also can be a polymer particle or a coated particle. The abrasive desirably comprises a metal oxide. Preferably, the metal oxide is selected from the group consisting of alumina, ceria, silica, zirconia, co-formed products thereof, and combinations thereof. The abrasive particles typically have an average particle size (e.g., average particle diameter) of about 20 nm to about 500 nm. Preferably, the abrasive particles have an average particle size of about 30 nm to about 400 nm (e.g., about 40 nm to about 300

[0011] nm, or about 50 nm to about 250 nm, or about 75 nm to about 200 nm).

[0012] When the abrasive is suspended in the water (i.e., when the abrasive is a component of the polishing composition), any suitable amount of abrasive can be present in the polishing composition. Typically, about 0.01 wt. % or more (e.g., about 0.05 wt. % or more) abrasive will be present in the polishing composition. More typically, about 0.1 wt. % or more abrasive will be present in the polishing composition. The amount of abrasive in the polishing composition typically will not exceed about 20 wt. %, more typically will not exceed about 10 wt. % (e.g., will not exceed about 5 wt. %). Preferably, the amount of abrasive in the polishing composition is about 0.05 wt. % to about 2 wt. %, and more preferably about 0.1 wt. % to about 1 wt. %.

[0013] The polishing system can comprise 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.

[0014] The polishing system comprises a water-soluble silicate compound. The water-soluble silicate compound can be any suitable water-soluble silicate compound. Desirably, the water-soluble silicate compound is an alkali metal silicate. Preferably, the water-soluble silicate compound is selected from the group consisting of potassium silicate, sodium silicate, potassium metasilicate, and sodium metasilicate. More preferably, the water-soluble silicate compound is potassium silicate.

[0015] Water-soluble silicate compounds suitable for use in the invention can be silicate glasses. Silicate glasses are typically prepared by high-temperature fusion of silica sand with a suitable alkali metal compound (e.g., sodium carbonate or potassium carbonate).

[0016] Water-soluble silicates have the general formula $M_2O \cdot mSiO_2 \cdot nH_2O$, where M is an alkali metal selected from the group consisting of sodium, potassium and lithium, and m, referred to as the modulus, and n are the number of moles of SiO_2 and H_2O , respectively, per mole of M_2O . The

modulus m is the molar ratio of SiO_2 to M_2O . The weight ratio of SiO_2 to M_2O is also commonly used to describe the composition of water-soluble alkali metal silicates. The modulus m can be any suitable positive nonzero number (e.g., about 1 or more), typically about 1 to about 4, and more typically about 2 to about 4 (e.g., about 2.8 to about 3.9, or about 3 to about 3.6).

[0017] In a preferred embodiment, the water-soluble silicate compound is potassium silicate having a general formula $K_2O \cdot mSiO_2$ wherein the modulus m (e.g., the molar ratio of SiO_2 to K_2O) is a positive nonzero number. The potassium silicate can have any suitable modulus. Desirably, the modulus is about 1 or more. Preferably, the modulus is about 2.8 to about 3.9. More preferably, the modulus is about 3 to about 3.6.

[0018] The water-soluble silicate compound is present in aqueous solution in the polishing composition. A method of providing the water-soluble silicate compound is to dissolve a solid form of the water-soluble silicate compound in water to provide a solution. Alternatively, a concentrated solution of the water-soluble silicate compound can be diluted to obtain the desired concentration of the water-soluble silicate compound in solution. Various grades of potassium silicate and sodium silicate solutions in water are available commercially, wherein the solutions are characterized by the particular modulus of the silicates used in their preparation, as well as wt. % SiO_2 and wt. % K_2O or Na_2O of the solutions. Zaclon, Inc. (Cleveland, Ohio) and PQ Corporation (Valley Forge, Pa.) are two major suppliers of both solid forms and solutions of potassium silicate and sodium silicate.

[0019] Aqueous solutions of potassium silicate also can be obtained by hydrothermal processes, wherein a silicon dioxide (e.g., SiO_2) source is reacted with aqueous solutions of potassium hydroxide under conditions of elevated temperature and/or pressure. Examples of suitable hydrothermal processes for production of aqueous solutions of potassium silicate are disclosed in U.S. Pat. Nos. 5,084,262 and 5,238,668.

[0020] The polishing composition of the polishing system can comprise any suitable amount of the water-soluble silicate compound. Generally, the content of the water-soluble silicate compound present in the polishing composition is expressed as the weight percent of SiO_2 provided by the water-soluble silicate compound, based on the total weight of water and any components dissolved therein. It will be understood that the formula " SiO_2 " is a formal representation to allow for the calculation of the amount of water-soluble silicate compound useful in the polishing composition regardless of the source thereof (e.g., aqueous solutions or solid forms of water-soluble silicate compounds of various compositions as described herein). Typically, the polishing composition comprises sufficient water-soluble silicate compound to provide about 0.1 wt. % or more (e.g., about 0.25 wt. % or more, about 0.5 wt. % or more, about 1 wt. % or more, about 1.5 wt. % or more, or about 2 wt. % or more) of SiO_2 . The polishing composition preferably comprises sufficient water-soluble silicate compound to provide about 8 wt. % or less (e.g., about 6 wt. % or less, or about 4 wt. % or less, or even about 3 wt. % or less) of SiO_2 . The polishing composition most preferably comprises about 0.25 wt. % to about 5 wt. % (e.g., about 0.5 wt. % to about 4 wt. %, or about 1 wt. % to about 3 wt. %) of SiO_2 .

[0021] The polishing composition of the polishing system comprises an oxidizing agent that oxidizes at least a part of a substrate. Any suitable oxidizing agent can be used in conjunction with the invention. Suitable oxidizing agents include inorganic and organic per-compounds, bromates, nitrates, chlorates, chromates, iodates, iron and copper salts (e.g., nitrates, sulfates, EDTA salts, and citrates), rare earth and transition metal oxides (e.g., osmium tetroxide), potassium ferricyanide, potassium dichromate, iodic acid, quinones, and the like. A per-compound (as defined by Hawley's Condensed Chemical Dictionary) is a compound containing at least one peroxy group ($-\text{O}-\text{O}-$) or a compound containing an element in its highest oxidation state. Examples of compounds containing at least one peroxy group include but are not limited to hydrogen peroxide and its adducts such as urea hydrogen peroxide and percarbonates, organic peroxides such as benzoyl peroxide, peracetic acid, and di-tert-butyl peroxide, monopersulfates (SO_5^{2-}), dipersulfates ($\text{S}_2\text{O}_8^{2-}$), and sodium peroxide. Examples of compounds containing an element in its highest oxidation state include but are not limited to periodic acid, periodate salts, perbromic acid, perbromate salts, perchloric acid, perchlorate salts, perboric acid, perborate salts, and permanganates. Preferably, the oxidizing agent is selected from the group consisting of hydrogen peroxide, iodates, permanganates, persulfates, hydrogen peroxymonosulfate sulfates, molybdates, ferric nitrate, nitrates, quinones, and combinations thereof. More preferably, the oxidizing agent is potassium iodate or hydrogen peroxide.

[0022] When the oxidizing agent is a salt, the oxidizing agent can have any suitable cation. Non-limiting examples of suitable cations include potassium, ammonium, and the like.

[0023] When the oxidizing agent is a quinone, the oxidizing agent can be any suitable quinone. Non-limiting examples of suitable quinones include benzoquinones, naphthoquinones, and anthraquinones. The quinone can be substituted at any available position with any suitable substituent(s) or combinations of substituents. Preferred substituents include groups that confer solubility or emulsifiability of the quinone in the water of the polishing composition. Suitable substituents include, without limitation, hydroxyl, amino, monoalkylamino, dialkylamino, sulfonic acid, carboxyl, phosphonic acid, salts thereof, and combinations thereof. In an embodiment, the quinone is substituted with at least one hydroxyl group. In other embodiments, the quinone is substituted with at least one acidic substituent or a salt thereof. Preferably, the at least one acidic substituent is selected from the group consisting of sulfonic acid, carboxyl, and phosphonic acid. More preferably, the at least one acidic substituent is sulfonic acid ($-\text{SO}_3\text{H}$). It will be appreciated that the acidic substituents are capable of forming salts, and in this regard the quinone having acidic substituents can exist as an acid, salt, or when di- or polysubstituted can exist as a partial salt (e.g., a monosalt of a disulfonic acid). Quinones having acidic substituents can be supplied for use in the inventive polishing composition in either acid form or salt form. Preferred anthraquinones are selected from the group consisting of anthraquinone-2,6-disulfonic acid, anthraquinone-2-sulfonic acid, anthraquinone-1,8-disulfonic acid, anthraquinone-1,5-disulfonic acid, acid blue 45, salts thereof, and combinations thereof. Preferred benzoquinones include 1,4-benzoquinone

and 2,5-dihydroxy-1,4-benzoquinone. Preferred naphthoquinones include 1,2-naphthoquinone-4-sulfonic acid and salts thereof.

[0024] The concentration of oxidizing agent in the polishing composition of the polishing system desirably is about 1 mM or more (e.g., about 2 mM or more, or about 3 mM or more, or about 5 mM or more). The concentration of oxidizing agent in the polishing composition preferably is about 1 M or less (e.g., about 0.5 M or less, or about 0.25 M or less, or about 0.1 M or less). The desired concentration of oxidizing agent can be achieved by any suitable means, such as by using about 0.05 wt. % to about 20 wt. % of the oxidizing agent based on the weight of the water and any components dissolved or suspended therein in the preparation of the polishing composition.

[0025] The polishing system has a pH of about 8 to about 12. Preferably, the polishing system has a pH of about 8 to about 11, more preferably about 9 to about 11. The pH of the polishing system can be achieved and/or maintained by any suitable means. More specifically, the polishing system can further comprise a pH adjustor, a pH buffering agent, or a combination thereof. Aqueous solutions of water-soluble silicate compounds obtained by dissolution of silicate glasses (e.g., alkali metal silicates) or prepared by hydrothermal processes have a strongly basic pH of about 11 or more, being composed of a salt of a strong base and a weak acid. The pH of the polishing system can be adjusted if desired by acidifying a strongly basic solution of water-soluble silicate compound by the addition of a sufficient amount of an acid to neutralize sufficient M_2O that is present to obtain the desired pH. The pH adjustor can be any suitable pH-adjusting compound. For example, the pH adjustor can be any suitable acid strong enough to produce the desired final pH. Examples of suitable acids include nitric acid, acetic acid, phosphoric acid, and the like. The pH can be increased if desired by the addition of a strong base. Examples of strong bases include potassium hydroxide, ammonium hydroxide, and tetraalkylammonium hydroxide (e.g., tetramethylammonium hydroxide).

[0026] The pH buffering agent can be any suitable buffering agent, for example, phosphates, acetates, borates, ammonium salts, and the like. When a buffering agent is used to adjust the pH of the polishing system, it will be understood that sufficient buffering agent will be added to the polishing system to neutralize sufficient M_2O to provide the desired pH. The polishing system can comprise any suitable amount of a pH adjustor and/or a pH buffering agent, provided such amount is sufficient to achieve and/or maintain the pH of the polishing system within the ranges set forth herein.

[0027] The pH of the polishing system can be adjusted at any suitable time. For example, the pH can be adjusted after addition of the water-soluble silicate compound to the polishing composition of the polishing system as described herein. A desired amount of a water-soluble silicate compound also can be added to the polishing composition, wherein the polishing composition comprises a sufficient amount of a pH adjustor and/or a pH buffering agent such that the desired pH is obtained after complete mixing of the water-soluble silicate compound with the polishing composition. In still other embodiments, the pH of the polishing system is adjusted at the point-of-use (e.g., at the surface of the substrate).

[0028] The polishing system optionally comprises a corrosion inhibitor (i.e., a film-forming agent). The corrosion inhibitor can be any suitable corrosion inhibitor for any component(s) of the substrate. Preferably, the corrosion inhibitor is a copper-corrosion inhibitor. For the purposes of this invention, a corrosion inhibitor is any compound, or mixture of compounds, that facilitates the formation of a passivation layer (i.e., a dissolution-inhibiting layer) on at least a portion of the surface being polished. Useful corrosion inhibitors include, for example, nitrogen-containing heterocyclic compounds. The corrosion inhibitor desirably comprises one or more 5- or 6-membered, heterocyclic, nitrogen-containing rings. Preferred corrosion inhibitors include 1,2,3-triazole, 1,2,4-triazole, benzotriazole, benzimidazole, benzothiazole, and derivatives thereof, such as, for example, hydroxy-, amino-, imino-, carboxy-, mercapto-, nitro-, urea-, thiourea-, or alkyl-substituted derivatives thereof. Most preferably, the corrosion inhibitor is selected from the group consisting of benzotriazole, 1,2,3-triazole, 1,2,4-triazole, and mixtures thereof. The polishing system of the invention can comprise any suitable amount of the corrosion inhibitor. Generally, the polishing composition of the polishing system comprises about 0.005 wt. % to about 1 wt. % (e.g., about 0.01 to about 0.5 wt. %, or about 0.02 to about 0.2 wt. %) of the corrosion inhibitor.

[0029] The polishing system optionally further comprises one or more other additives. Such additives include any suitable surfactant and/or Theological control agent. Suitable surfactants include, for example, cationic surfactants, anionic surfactants, anionic polyelectrolytes, nonionic surfactants, amphoteric surfactants, fluorinated surfactants, mixtures thereof, and the like.

[0030] The polishing system optionally further comprises an antifoaming agent. The anti-foaming agent can be any suitable anti-foaming agent. Suitable antifoaming agents include, but are not limited to, silicon-based and acetylenic diol-based antifoaming agents. The amount of anti-foaming agent present in the polishing composition of the polishing system typically is about 40 ppm to about 140 ppm.

[0031] The polishing system optionally further comprises a biocide. The biocide can be any suitable biocide, for example an isothiazolinone biocide. The amount of biocide used in the polishing system typically is about 1 ppm to about 500 ppm, and preferably is about 10 ppm to about 200 ppm.

[0032] The polishing composition of the polishing system can be prepared by any suitable technique, many of which are known to those skilled in the art. The polishing composition can be prepared in a batch or continuous process. Generally, the polishing composition can be prepared by combining the components thereof in any order. The term "component" as used herein includes individual ingredients (e.g., abrasive, water-soluble silicate compound, etc.) as well as any combination of ingredients (e.g., abrasive, water-soluble silicate compound, oxidizing agent, etc.).

[0033] The polishing composition of the polishing system 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 comprise an abrasive, a water-soluble silicate compound, an oxidizing agent, 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 abrasive, a water-soluble silicate compound, and oxidizing agent can each be present in the concentrate in an amount that is about 2 times (e.g., about 3 times, about 4 times, or about 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 water-soluble silicate compound, oxidizing agent, and other suitable additives are at least partially or fully dissolved in the concentrate.

[0034] Any of the components used in conjunction with the invention can be provided in the form of a mixture or solution in water. Two or more components then desirably are individually stored and subsequently mixed to form the polishing composition of the polishing system. In this regard, it is suitable for the polishing composition to be prepared (e.g., for all the components to be mixed together) and then delivered to the surface of the substrate. It is also suitable for the polishing composition to be prepared on the surface of the substrate, through delivery of the components of the polishing composition from two or more distinct sources, whereby the components of the polishing composition meet at the surface of the substrate (e.g., at the point-of-use). In either case, 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, such as the polishing rate, of the polishing system is altered.

[0035] The polishing composition can be supplied as a one package system comprising a water-soluble silicate compound, an oxidizing agent, and water. Alternatively, the water-soluble silicate compound and water can be supplied in a first container, and an oxidizing agent can be supplied in a second container, either in dry form, or as a solution or dispersion in water. Optional components, such as an abrasive, a surfactant, and/or a corrosion inhibitor, can be placed in the first and/or second containers or a 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 or solution. Moreover, it is suitable for the components in the first or second containers to have different pH values, or alternatively to have substantially similar, or even equal, pH values. If an optional component such as an abrasive is a solid, it may be supplied either in dry form or as a mixture in water. The oxidizing agent desirably is supplied separately from the other components of the polishing composition and is combined, e.g., by the end-user, with the other components of the polishing composition shortly before use (e.g., 1 week or less prior to use, 1 day or less prior to use, 1 hour or less prior to use, 10 minutes or less prior to use, or 1 minute or less prior to use). 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.

[0036] While the components of the polishing composition 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.

[0037] 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).

[0038] 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).

[0039] When two or more of the components of the polishing composition of the polishing system 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.

[0040] The invention further provides a method of polishing a substrate using the polishing system described herein. The method of polishing a substrate comprises (i) contacting a substrate with the aforementioned polishing system, and (ii) abrading or removing at least a portion of the substrate to polish the substrate.

[0041] In particular, the method of the invention comprises the steps of (i) contacting a substrate with a chemical-mechanical polishing system comprising a polishing component, a water-soluble silicate compound in an amount sufficient to provide about 0.1 wt. % or more of SiO₂, an oxidizing agent that oxidizes at least part of a substrate, and water, wherein the pH of the polishing system is about 8 to about 12, and (ii) abrading at least a portion of the substrate to polish the substrate.

[0042] In accordance with the invention, the substrate can be polished with the polishing system described herein by any suitable technique. The method of the invention is particularly well-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 system of the invention, and by the polishing pad moving relative to the substrate, with the other components of the polishing system therebetween, so as to abrade and remove a portion of the substrate so as to polish at least a portion of the substrate.

[0043] The substrate can be any suitable substrate that is capable of being polished by the inventive method. The substrate can comprise metals (e.g., copper, tantalum, aluminum, titanium, molybdenum, and the like), metal alloys (e.g., stainless steel, cobalt-chrome, and the like), semiconductors (e.g., gallium nitride, gallium arsenide, and the like), ceramics (e.g., silicon carbide), polymers (e.g., polycarbonate), optical materials (e.g., sapphire, zinc sulfide, zinc selenide, and the like), diamond, and insulating materials.

[0044] The substrate can comprise any suitable microelectronic substrate (e.g., an integrated circuit, metals, ILD layers, semiconductors, thin films, MEMS, magnetic heads) and can further comprise any suitable insulating, metal, or metal alloy layer (e.g., metal conductive layer). Preferably, the metal layer comprises tantalum. More preferably, the substrate further comprises a metal layer comprising copper. The insulating layer can be a metal oxide, porous metal oxide, glass, organic polymer, fluorinated organic polymer, or any other suitable high or low-k insulating layer. The

insulating layer preferably comprises a dielectric material which has a dielectric constant of about 3.5 or lower.

[0045] Examples of low dielectric constant (i.e., low-k dielectric) materials include but are not limited to fluorine doped silicon dioxide, an organically modified silicon glass such as carbon doped silicon dioxide (CDO), fluorinated carbon, and organic materials such as fluorinated and unfluorinated parylene and polyimide. The low-k dielectrics can be porous or nonporous. Examples of porous low dielectric materials are porous hydrosilsesquioxane or porous methyl silsesquioxane, porous silica structures such as aerogel, low temperature deposited silicon carbon films, low temperature deposited Si—O—C films, and methyl doped porous silica. Preferably, the insulating layer is an organically modified silicon glass or a carbon-doped silicon dioxide.

[0046] Advantageously, the polishing system of the invention allows for reduction of the coefficient of friction associated with chemical-mechanical polishing of a substrate, while maintaining acceptable polishing rates.

[0047] 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 substrate are known in the art. Desirably, the inspection or monitoring of the progress of the polishing process with respect to a substrate 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 substrate.

[0048] The following example further illustrates the invention but, of course, should not be construed as in any way limiting its scope

EXAMPLE

[0049] This example demonstrates the reduction in the coefficient of friction observed in the polishing of a substrate comprising tantalum using the inventive method.

[0050] Similar substrates comprising a 250 nm layer of tantalum were polished with different polishing compositions (Polishing Compositions A and B). Each of Polishing Compositions A and B contained 0.5 wt. % of ceria and 0.20 wt. % of potassium iodate in water at a pH of 11. Polishing Composition B further contained 3 wt. % of potassium silicate.

[0051] The substrates were polished for 60 seconds using a polyurethane polishing pad on a Logitech Model CDP polisher using the following polishing parameters: 13.8 kPa (2 psi) downforce pressure of the substrate against the polishing pad, 66 rpm platen speed, 70 rpm carrier speed, 160 mL/min polishing composition flow rate, and use of a polyurethane polishing pad. Following polishing, the removal rate was determined using resistivity measurements.

[0052] The coefficient of friction was determined by the relationship of the displacement of the carrier shaft during the polishing operation to the force generated by friction between the polishing pad and the substrates. Referring to the Figure, a non-contact capacitive displacement sensor (10) electrically connected to a recording device (20) was positioned adjacent to the carrier shaft (30) of the polisher (40) with a gap (50) therebetween. Displacement of the carrier shaft caused by force F (60) resulting from frictional force generated during the polishing of the substrates

resulted in a change in the output voltage of the sensor. A calibration curve was obtained by measurement of sensor output voltage as a function of known force applied to the carrier shaft in a direction normal to the central axis of the carrier shaft. The average force F_a applied to the carrier shaft during the polishing experiments was determined from the calibration curve using the average output voltage over the 60 second polishing time. The coefficient of friction μ was calculated from force F_a and downforce pressure (70) of the substrate (80) against the polishing pad P (90) from the equation: $\mu = F_a/P$. The results are set forth in the Table.

TABLE

Effect of Potassium Silicate on Coefficient of Friction and Tantalum Removal Rate		
Polishing Composition	Removal Rate ($\text{\AA}/\text{min}$)	Coefficient of Friction (μ)
A (comparative)	339	0.45
B (invention)	300	0.35

[0053] As is apparent from the results set forth in the Table, the presence of 3 wt. % of potassium silicate in the inventive polishing composition resulted in an approximately 20% reduction in the coefficient of friction observed in the polishing of a substrate comprising a layer of tantalum, while the tantalum removal rate was decreased by only approximately 12%. Thus, the results of this example demonstrate the friction reduction achievable by the polishing composition and method of the invention.

[0054] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0055] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0056] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the

invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

1. A chemical-mechanical polishing system for polishing a substrate comprising:

- (a) a polishing component selected from the group consisting of a polishing pad, an abrasive, and a combination thereof,
- (b) a water-soluble silicate compound in an amount sufficient to provide about 0.1 wt. % or more of SiO_2 ,
- (c) an oxidizing agent that oxidizes at least part of a substrate, and
- (d) water,

wherein the pH of the polishing system is about 8 to about 12, and wherein the water-soluble silicate compound is present in aqueous solution in the polishing system.

2. The polishing system of claim 1, wherein the water-soluble silicate compound is selected from the group consisting of potassium silicate, sodium silicate, potassium metasilicate, and sodium metasilicate.

3. The polishing system of claim 2, wherein the water-soluble silicate compound is potassium silicate.

4. The polishing system of claim 3, wherein the potassium silicate is present in an amount sufficient to provide about 0.25 wt. % or more of SiO_2 .

5. The polishing system of claim 3, wherein the potassium silicate has a $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of about 2.8 to about 3.9.

6. The polishing system of claim 5, wherein the potassium silicate has a $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of about 3 to about 3.6.

7. The polishing system of claim 1, wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, iodates, permanganates, persulfates, hydrogen peroxymonosulfate sulfates, molybdates, ferric nitrate, nitrates, quinones, and combinations thereof.

8. The polishing system of claim 1, wherein the polishing system further comprises an abrasive wherein the abrasive is suspended in the water.

9. The polishing system of claim 8, wherein the abrasive is selected from the group consisting of alumina, ceria, silica, zirconia, and combinations thereof.

10. The polishing system of claim 1, wherein the polishing system comprises a polishing pad and an abrasive wherein the abrasive is fixed to the polishing pad.

11. The polishing system of claim 1, wherein the water-soluble silicate compound is present in an amount of about 0.5 wt. % or more.

12. The polishing system of claim 1, wherein the pH is about 9 to about 11.

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

- (i) contacting a substrate with a chemical-mechanical polishing system comprising:
 - (a) a polishing component selected from the group consisting of a polishing pad, an abrasive, and a combination thereof,

- (b) a water-soluble silicate compound in an amount sufficient to provide about 0.1 wt. % or more of SiO_2 ,

- (c) an oxidizing agent that oxidizes at least part of a substrate, and

- (d) water, wherein the pH of the polishing system is about 8 to about 12, and wherein the water-soluble silicate compound is present in aqueous solution in the polishing system, and

- (ii) abrading at least a portion of the substrate to polish the substrate.

14. The method of claim 13, wherein the water-soluble silicate compound is selected from the group consisting of potassium silicate, sodium silicate, potassium metasilicate, and sodium metasilicate.

15. The method of claim 14, wherein the water-soluble silicate compound is potassium silicate.

16. The method of claim 15, wherein the potassium silicate is present in an amount sufficient to provide about 0.25 wt. % or more of SiO_2 .

17. The method of claim 15, wherein the potassium silicate has a $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of about 2.8 to about 3.9.

18. The method of claim 17, wherein the potassium silicate has a $\text{SiO}_2:\text{K}_2\text{O}$ molar ratio of about 3 to about 3.6.

19. The method of claim 13, wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, iodates, permanganates, persulfates, hydrogen peroxymonosulfate sulfates, molybdates, ferric nitrate, nitrates, quinones, and combinations thereof.

20. The method of claim 13, wherein the polishing system further comprises an abrasive wherein the abrasive is suspended in the water.

21. The method of claim 20, wherein the abrasive is selected from the group consisting of alumina, ceria, silica, zirconia, and combinations thereof.

22. The method of claim 13, wherein the polishing system comprises a polishing pad and an abrasive wherein the abrasive is fixed to the polishing pad.

23. The method of claim 13, wherein the water-soluble silicate compound is present in an amount of about 0.5 wt. % or more.

24. The method of claim 13, wherein the pH is about 9 to about 11.

25. The method of claim 13, wherein the substrate comprises a metal layer.

26. The method of claim 25, wherein the metal layer comprises tantalum.

27. The method of claim 26, wherein the metal layer further comprises copper.

28. The method of claim 13, wherein the substrate comprises a dielectric layer which has a dielectric constant of about 3.5 or lower.

29. The method of claim 28, wherein the dielectric layer is an organically modified silicon glass.

30. The method of claim 28, wherein the dielectric layer is carbon-doped silicon dioxide.

31. The method of claim 28, wherein the substrate further comprises a metal layer.

32. The method of claim 31, wherein the metal layer comprises tantalum.

33. The method of claim 32, wherein the metal layer further comprises copper.