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(54) Title: COMPOSITIONS FOR POLISHING ALUMINUM/COPPER AND TITANIUM IN DAMASCENE STRUCTURES

(57) Abstract: The invention provides a chemical-mechanical polishing composition for polishing a substrate. The polishing composition comprises an oxidizing agent, calcium ion, an organic carboxylic acid, and water, wherein the polishing composition has a pH of 1.5 to 7. The invention further provides a method of chemically-mechanically polishing a substrate with the aforementioned polishing composition.

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COMPOSITIONS FOR POLISHING ALUMINUM/COPPER AND TITANIUM IN DAMASCENE STRUCTURES

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. 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 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, thereby forming the circuit device.

[0003] One way to fabricate planar metal circuit traces on a silicon dioxide substrate is referred to as the damascene process. In accordance with this process, the silicon dioxide dielectric surface having optionally a layer of silicon nitride deposited thereon is patterned by applying a photoresist, exposing the photoresist to irradiation through a pattern to define trenches and/or vias, and then using a conventional dry etch process to form holes and trenches for vertical and horizontal interconnects. The silicon nitride functions as a "hard mask" to protect the silicon dioxide surface that is not part of the trenches and/or vias from damage during etching. The patterned surface is coated with an adhesion-promoting layer such as titanium or tantalum and/or a diffusion barrier layer such as titanium nitride or tantalum nitride. The adhesion-promoting layer and/or the diffusion barrier layer are then over-coated with a metal layer. Chemical-mechanical polishing is employed to reduce the thickness of the metal 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 nitride surface is obtained. The vias and trenches remain filled with electrically conductive metal forming the circuit interconnects.

[0004] Tungsten and copper have been increasingly used as the electrically conductive metal. However, aluminum, which has been used in earlier generation processes to fabricate circuit interconnects via subtractive processes such as etching techniques, is now under consideration for use in damascene processes. The combination of aluminum and titanium offers potentially lower resistivity than other metal / barrier layer combinations, with corresponding potential improvement in circuit performance. However, compositions useful in the chemical-mechanical polishing of aluminum typically exhibit considerably lower removal rates in the polishing of underlying titanium. Thus, use of such polishing compositions in aluminum damascene fabrication processes to polish aluminum as well as titanium require overpolishing of aluminum remaining in circuit lines, resulting in considerable dishing of the lines. Thus, there remains in the art a need for improved compositions and methods for the chemical-mechanical polishing of substrates comprising aluminum as a conducting material and titanium as a barrier material.

BRIEF SUMMARY OF THE INVENTION

[0005] The invention provides a chemical-mechanical polishing composition comprising (a) an abrasive, (b) an oxidizing agent selected from the group consisting of peroxides, persulfates, ferric salts, and combinations thereof, (c) 25 to 400 ppm of calcium ion, (d) an organic carboxylic acid, and (e) water, wherein the polishing composition has a pH of 1.5 to 7.

[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 comprising (a) an abrasive, (b) an oxidizing agent selected from the group consisting of peroxides, persulfates, ferric salts, and combinations thereof, (c) 25 to 400 ppm of calcium ion, (d) an organic carboxylic acid, and (e) water, wherein the polishing composition has a pH of 1.5 to 7, (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. The polishing composition comprises (a) an abrasive, (b) an oxidizing agent selected from the group consisting of peroxides, persulfates, ferric salts, and combinations thereof, (c) 25 to 400 ppm of calcium ion, (d) an organic carboxylic acid, and (e) water, wherein the polishing composition has a pH of 1.5 to 7.

[0008] Any suitable amount of abrasive can be present in the polishing composition. In an embodiment, the polishing composition can have no abrasive or substantially no abrasive. Typically, 0.0001 wt.% or more abrasive can be present in the polishing composition (e.g., 0.0005 wt.% or more, or 0.001 wt.% or more, or 0.01 wt.% or more). The amount of abrasive in the polishing composition preferably will not exceed 10 wt.%, and more preferably will not exceed 8 wt.%. Even more preferably the abrasive will comprise 0.0001 wt.% to 10 wt.% (e.g., 0.0005 wt.% to 5 wt.%, or 0.001 wt.% to 2 wt.%) of the polishing composition.

[0009] 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. More preferably, the abrasive is alumina or silica.

[0010] When the abrasive is alumina, the alumina can be any suitable form of alumina. Preferably, the alumina is fumed alumina or α-alumina. When the abrasive is α-alumina, at least a portion of the surface of the α-alumina can be coated with a negatively-charged polymer or copolymer. For example, 5 wt.% or more (e.g., 10 wt.% or more, or 50 wt.% or more, or substantially all, or all) of the surface of the α-alumina can be coated with a negatively-charged polymer or copolymer. The negatively-charged polymer or copolymer can be any suitable polymer or copolymer. Preferably, the negatively-charged polymer or copolymer comprises repeating units selected from the group consisting of carboxylic acid, sulfonic acid, and phosphonic acid functional groups. More preferably, the anionic polymer comprises repeating units selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, maleic anhydride, vinyl sulfonic acid, 2-(methacryloyloxy)ethanesulfonic acid, styrene sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, vinylphosphonic acid, 2-(methacroyloxy)ethylphosphate, and combinations thereof. Most preferably, the negatively-charged polymer or copolymer is selected from the group consisting of poly(2-acrylamido-2-methylpropane sulfonic acid) and polystyrenesulfonic acid. Since particles of α-alumina typically have a positively-charged surface, the association of the polymer or copolymer with particles of α-alumina results in deprotonation of at least part of the acidic functional groups on the polymer or copolymer, thus rendering the polymer or copolymer negatively-charged in association with the particles.

[0011] The polishing composition can comprise any suitable amount of alumina. Typically, the polishing composition comprises 0.0001 wt.% or more (e.g., 0.0005 wt.% or more, or 0.001 wt.% or more, or 0.01 wt.% or more) of alumina. Preferably, the polishing composition comprises 10 wt.% or less (e.g., 5 wt.% or less, or 2 wt.% or less) of alumina. Even more preferably, the polishing composition comprises 0.0001 wt.% to 10 wt.% (e.g., 0.0005 wt.% to 5 wt.%, or 0.001 wt.% to 2 wt.%) of alumina.

[0012] When the abrasive is silica, the silica can be any suitable form of silica, such as fumed silica or precipitated silica. Preferably, the silica is a condensation-polymerized silica. Condensation-polymerized silica includes silica prepared by sol-gel processes and by hydrothermal processes. Non-limiting examples of suitable silica include commercially available products from Eka Chemicals (Bindzil silicas), Nissan Chemical (Snowtex silicas), Nyacol Nano Technologies (NexSil silicas), and Cabot Corporation (Cab-o-Sperse fumed silicas).

[0013] The polishing composition can comprise any suitable amount of silica. Generally, the polishing composition comprises 0.001 wt.% or more (e.g., 0.01 wt.% or more, or 0.1 wt.% or more) of silica. Typically, the polishing composition comprises 20 wt.% or less (e.g., 10 wt.% or less) of silica. Preferably, the polishing composition comprises 0.1 wt.% to 10 wt.% (e.g., 0.25 wt.% to 7.5 w.t%, or 0.5 wt.% to 5 wt.%) of silica.

[0014] The abrasive comprises particles that typically have an average particle size (e.g., average particle diameter) of 20 nm to 500 nm. In the context of the invention, average particle size refers to the average size of the smallest sphere that encloses the particle. Preferably, the abrasive particles have an average particle size of 30 nm to 400 nm (e.g., 40 nm to 300 nm, or 50 nm to 200 nm).

[0015] The abrasive desirably is suspended in the polishing composition, more specifically in the water component 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 liquid carrier. 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.

[0016] The polishing composition comprises an oxidizing agent selected from the group consisting of peroxides, persulfates, ferric salts, and combinations thereof. The function of the oxidizing agent is to oxidize at least a part of a substrate, such as a layer or layers comprising aluminum, an alloy of aluminum such as aluminum-copper, or titanium. Non-limiting examples of peroxides include hydrogen peroxide and its adducts such as urea hydrogen peroxide, percarbonates, and perborates. Non-limiting examples of suitable persulfates include ammonium persulfate, sodium persulfate, and potassium persulfate. Non-limiting ferric salts include ferric nitrate, ferric chloride, and ferric sulfate. Preferably, the oxidizing agent is selected from the group consisting of hydrogen peroxide, ammonium persulfate, ferric nitrate, and combinations thereof.

[0017] The polishing composition can comprise any suitable amount of oxidizing agent. Generally, the polishing composition comprises 0.01 wt.% or more (e.g., 0.1 wt.% or more) of oxidizing agent. Typically, the polishing composition comprises 10 wt.% or less (e.g., 5 wt.% or less) of oxidizing agent.

[0018] The polishing composition typically comprises 25 ppm or more (e.g., 30 ppm or more, or 40 ppm or more, or 50 ppm or more) of calcium ion. Preferably, the polishing composition comprises 400 ppm or less (e.g., 350 ppm or less, or 300 ppm or less, or 250 ppm or less, or even 200 ppm or less) of calcium ion. More preferably, the polishing composition comprises 25 ppm to 400 ppm (e.g., 30 ppm to 350 ppm, or 40 ppm to 300 ppm, or even 50 ppm to 200 ppm) of calcium ion. Advantageously, the presence of calcium ion provides for enhancement of the removal rate of titanium layers exhibited by the inventive polishing composition. The calcium ion contained in the polishing composition can be provided by any suitable source of calcium ion. Preferably, the calcium ion contained in the polishing composition is provided by at least one water-soluble calcium salt. Non-limiting examples of suitable calcium salts include calcium acetate and calcium chloride, hydrates thereof, and combinations thereof.

[0019] The polishing composition comprises an organic carboxylic acid. Organic carboxylic acids useful in the polishing composition include dicarboxylic and tricarboxylic acids and their salts. The organic carboxylic acid can further comprise functional groups selected from the group consisting of hydroxyl, carbonyl, and halogen. Preferably, the organic carboxylic acid is selected from the group consisting of citric acid, malonic acid, succinic acid, tartaric acid, salts thereof, and combinations thereof. More preferably, the organic carboxylic acid is succinic acid.

[0020] It will be appreciated that the aforementioned carboxylic 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, succinates include succinic acid, as well as mono- and di-salts thereof.

[0021] The polishing composition can comprise any suitable amount of the organic carboxylic acid. Generally, the polishing composition comprises 0.1 wt.% or more (e.g., 0.5 wt.% or more) of the organic carboxylic acid. Typically, the polishing composition comprises 10 wt.% or less (e.g., 5 wt.% or less) of the organic carboxylic acid. Preferably, the polishing composition comprises 0.5 wt.% to 5 wt.% and more preferably 1 wt.% to 4 wt.% of the organic carboxylic acid.

[0022] The polishing composition has a pH of 7 or less (e.g., 6 or less). Preferably, the polishing composition has a pH of 1 or more (e.g., 1.5 or more, or 2 or more). Even more preferably, the polishing composition has a pH of 2 to 6 (e.g., 3 to 5). The polishing composition optionally comprises pH adjusting agents, for example, potassium hydroxide, ammonium hydroxide, alkylammonium hydroxides, and/or nitric acid. The polishing composition can optionally comprise pH buffering systems, for example, ammonium acetate or monosodium citrate. Many such pH buffering systems are well known in the art.

[0023] The polishing composition optionally further comprises one or more other additives. Such additives include any suitable surfactant and/or rheological control agent, including viscosity enhancing agents and coagulants (e.g., polymeric rheological control agents, such as, for example, urethane polymers), acrylates comprising one or more acrylic subunits (e.g., vinyl acrylates and styrene acrylates), and polymers, copolymers, and oligomers thereof, and salts thereof. Suitable surfactants include, for example, cationic surfactants, anionic surfactants, anionic polyelectrolytes, nonionic surfactants, amphoteric surfactants, fluorinated surfactants, mixtures thereof, and the like.

[0024] The polishing composition 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 composition typically is 1 ppm to 500 ppm, and preferably is 10 ppm to 200 ppm.

[0025] The polishing composition 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, oxidizing agent, etc.) as well as any combination of ingredients (e.g., abrasive, oxidizing agent, calcium ion, organic carboxylic acid, etc.).

[0026] For example, the oxidizing agent, calcium ion, and organic carboxylic acid can be dissolved in water by addition of the oxidizing agent, calcium ion, and organic carboxylic acid to water in any order, or even simultaneously. The abrasive can then be added and dispersed by any method that is capable of dispersing the abrasive in the polishing composition. The polishing composition can be prepared prior to use, with one or more components, such as the oxidizing agent, added to the polishing composition shortly before use (e.g., within 1 minute before use, or within 1 hour before use, or within 7 days before use). The pH can be adjusted at any suitable time, and is preferably adjusted prior to the addition of the abrasive to the polishing composition. The polishing composition also can be prepared by mixing the components at the surface of the substrate during the polishing operation.

[0027] The polishing composition also can be provided as a concentrate which is intended to be diluted with an appropriate amount of water and typically the oxidizing agent prior to use. If the oxidizing agent is a liquid, an appropriate volume of the oxidizing agent can be added to the water prior to dilution of the concentrate with the water, or an appropriate volume of the oxidizing agent can be added to the concentrate before, during, or after addition of the water to the concentrate. If the oxidizing agent is a solid, the oxidizing agent can be dissolved in the water or a portion thereof before dilution of the concentrate with the water and/or an aqueous solution of the oxidizing agent. A solid oxidizing agent also can be added as a solid to the concentrate before, during, or after dilution of the concentrate with the water to provide the polishing composition. The oxidizing agent can be incorporated into the polishing composition by any suitable method capable of incorporating the oxidizing agent into the polishing composition, such as by mixing.

[0028] The polishing composition concentrate can comprise an abrasive, calcium ion, a carboxylic acid, and water in amounts such that, upon dilution of the concentrate with an appropriate amount of water and oxidizing agent, 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, calcium ion, and carboxylic acid 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) and an appropriate amount of oxidizing agent, each component will be present in the polishing composition in an amount within the ranges set forth above for each component. Preferably, the water-soluble components present in the concentrate, such as the calcium ion and the carboxylic acid, will be present in amounts such that the components are fully dissolved in the water of the concentrate, and in amounts such that the concentration of the water-soluble components in the concentrate, more specifically in the water of the concentrate, is less than the maximum solubility of the water-soluble components in the water of the concentrate at ambient conditions (e.g., at a temperature of 20°C). Furthermore, the concentrate can contain an appropriate fraction of the water, along with optionally some or all of the oxidizing agent, present in the final polishing composition in order to ensure that the abrasive, oxidizing agent (if present), calcium ion, carboxylic acid, and other suitable additives are at least partially or fully dissolved in the concentrate, preferably fully dissolved in the concentrate.

[0029] 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.

[0030] Although the polishing composition of the invention is useful for polishing any substrate, the polishing composition is particularly useful in the polishing of a substrate comprising at least one metal layer comprising aluminum or an aluminum-containing alloy such as aluminum-copper, at least one metal layer comprising titanium, and at least one dielectric layer. The titanium can be in the form of titanium metal, alloys thereof, nitrides thereof, and combinations thereof. The dielectric 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, and preferably is a silicon-based metal oxide, more preferably a silicon oxide layer derived from tetraethylorthosilicate (TEOS).

[0031] The substrate can be any suitable substrate (e.g., an integrated circuit, metals, ILD layers, semiconductors, and thin films). Typically the substrate comprises a patterned dielectric layer having a barrier layer comprising titanium deposited thereon and an overcoating layer comprising aluminum. The polishing process will first remove the bulk of the overlying aluminum layer and then will begin removing the underlying titanium layer with aluminum still available to the polishing system. Towards the end of the polishing process, the dielectric layer will be exposed to the polishing composition. Advantageously, the inventive method allows for control of the selectivity for the polishing of the aluminum, titanium, and dielectric layers. Selectivity is defined herein as the ratio of the polishing rate of one layer compared to the polishing rate of a second, different layer.

[0032] The polishing composition of the invention is capable of polishing (e.g., planarizing) substrates comprising at least one aluminum layer, at least one titanium layer, and at least one dielectric layer with desirable removal rates, low erosion, and low dishing. In the context of the invention the term "layer" refers both to a continuous, bulk layer of material having a substantially homogeneous surface and to a surface comprising the material contained within a surface feature (e.g., a circuit line or a via). The relative selectivities for the polishing of aluminum, titanium, and dielectric layers can be controlled by selection of the abrasive (i.e., either alumina or silica) and by varying the amounts of the components present in the polishing composition.

[0033] When the inventive polishing composition comprises alumina, the removal rates observed for polishing of dielectric layers are low relative to aluminum and titanium, and thus the alumina-containing inventive polishing composition is "self-stopping" on the dielectric layer. The aluminum removal rate and the titanium removal rate for the inventive alumina-containing polishing composition can be controlled by selecting the amount of oxidizing agent and by controlling the pH of the polishing composition. In particular, the inventive alumina-containing polishing composition having a lower content of the oxidizing agent and a lower pH exhibits a higher selectivity for the polishing of aluminum as compared to titanium than the inventive alumina-containing polishing composition having a higher content of the oxidizing agent and a higher pH. In this regard, selectivity for the polishing of aluminum as compared to titanium refers to the ratio of the removal rate for aluminum to the removal rate for titanium exhibited by the polishing composition. Typically, the aluminum layer will overcoat the titanium layer so that the polishing process will first remove the bulk of the overlying aluminum layer and then will begin removing the underlying titanium layer with aluminum residing within the substrate feature(s) still available to the polishing system. When both aluminum and titanium are available to the polishing system, if the rate of aluminum polishing is significantly greater than the rate of titanium polishing, the aluminum layer can be overpolished, which leads to dishing and/or erosion of the aluminum layer. Thus, by increasing the pH and the content of oxidizing agent in the alumina-containing polishing composition, the rate of aluminum removal can be decreased relative to the rate of titanium removal, thereby reducing the extent of overpolishing of the aluminum layer residing in the circuit lines.

[0034] When the inventive polishing composition comprises silica, the polishing composition exhibits higher removal rates for titanium as compared to aluminum. The silica-containing embodiments are thus useful in removal of titanium-containing barrier layers while exhibiting reduced dishing and/or erosion of aluminum-containing circuit lines. Additionally, increasing the amount of silica in the polishing composition enhances the removal rate exhibited with respect to dielectric layers, thereby allowing for efficient planarization of the dielectric layers after barrier layer removal.

[0035] The polishing method of the invention is particularly suited for use in conjunction with a chemical-mechanical polishing 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 the substrate 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.

[0036] A substrate can be polished with the chemical-mechanical 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.

[0037] Desirably, the chemical-mechanical polishing 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 being polished 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 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.

[0038] The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

[0039] In each of these examples, the polishing experiments generally involved the use of a commercially available polishing apparatus equipped with a concentric groove pad over a subpad. The polishing parameters generally were 20.7 kPa (3 psi) downforce pressure of the substrate against the polishing pad, 50 rpm platen speed, 53 rpm carrier speed, and 180 mL/min polishing composition flow rate, except for Example 1. In Example 1, the platen speed was 90 rpm and the carrier speed was 93 rpm.

EXAMPLE 1

[0040] This example demonstrates the effect of calcium ion on the removal rates exhibited by the inventive polishing composition in the polishing of separate substrates comprising aluminum-copper and titanium.

[0041] Eight similar sets of two substrates, each of which substrates separately comprised aluminum-copper and titanium, were polished with eight different polishing compositions (Polishing Compositions 1A-1H). Each of the compositions comprised 0.56 wt.% of α-alumina treated with a negatively-charged polymer, 1.12 wt.% of succinic acid, and 3 wt.% of hydrogen peroxide, at a pH of 3.5 in water. The polishing compositions further comprised calcium ion, provided by calcium acetate hydrate, in an amount as recited in Table 1.

[0042] Following polishing, the removal rates (RR) for aluminum-copper and titanium were determined for each of the polishing compositions, and the results are summarized in Table 1.

Table 1

Polishing Composition	Calcium Ion (ppm)	Al-Cu RR (Å/min)	Ti RR (Å/min)
1A (comparative)	0	1071	246
1B (invention)	30	1103	243
1C (invention)	50	910	378
1D (invention)	80	963	356
1E (invention)	100	1000	356
1F (invention)	150	953	419
1G (invention)	200	547	336

[0043] As is apparent from the results set forth in Table 1, increasing the amount of calcium ion from none (Polishing Composition 1A) to 150 ppm (Polishing Composition 1F) resulted in an increase in the removal rate for titanium of 70%. Further increasing the amount of calcium ion to 200 ppm (Polishing Composition 1G) resulted in a removal rate for titanium less than the removal rate observed at 150 ppm but greater than the removal rate with no calcium ion, and also resulted in reduction of the removal rate for aluminum-copper as compared with the removal rate observed for polishing compositions with lesser amounts, or no, calcium ion. Thus, the results of this example demonstrate the dependence of aluminum-copper and titanium removal rates on the amount of calcium ion in the polishing composition of the invention.

EXAMPLE 2

[0044] This example demonstrates the effect of the amount of organic carboxylic acid on the removal rates for the polishing of separate substrates comprising aluminum-copper, titanium, and a silicon oxide dielectric material generated from tetraethylorthosilicate exhibited by the polishing composition of the invention. The silicon oxide dielectric material is referred to as “TEOS” herein.

[0045] Two similar sets of two substrates, each of which substrates separately comprised aluminum-copper, titanium, and TEOS, were polished with two different polishing compositions (Polishing Compositions 2A and 2B). Each of the compositions comprised 0.56 wt.% of silica (Bindzil CJ2-2, Eka Chemicals) and 3% of hydrogen peroxide. Polishing Composition 2A further comprised 1.38 wt.% of succinic acid, while Polishing Composition 2B further comprised 3.38 wt.% of succinic acid.

[0046] Following polishing, the removal rates (RR) for aluminum-copper, titanium, and TEOS were determined for each of the polishing compositions, and the results are summarized in Table 2.

Table 2

Polishing Composition	Al-Cu RR (Å/min)	Ti RR (Å/min)	TEOS RR (Å/min)	Selectivity (Ti RR / Al-Cu RR)
2A	1293	1504	161	1.16
2B	1482	1932	244	1.30

[0047] As is apparent from the results set forth in Table 2, increasing the amount of succinic acid from 1.38 wt.% (Polishing Composition 2A) to 3.38 wt.% (Polishing Composition 2B) resulted in an increase in the removal rate for aluminum-copper of 15% but resulted in a greater increase in the titanium removal rate of 28%. The removal rate for TEOS increased 51% but remained 16% and 13% of the removal rates of aluminum-copper and titanium, respectively. In addition, the selectivity, as defined by the ratio of the titanium removal rate to the aluminum-copper removal rate, increased from 1.16 to 1.30 upon increase in the amount of succinic acid present in the inventive polishing composition.

EXAMPLE 3

[0048] This example demonstrates the effect of the amount of silica on the removal rates for polishing of separate substrates comprising aluminum-copper, titanium, and a silicon oxide dielectric material generated from tetraethylorthosilicate exhibited by the polishing composition of the invention.

[0049] Two similar sets of two substrates, each of which substrates separately comprised aluminum-copper, titanium, and TEOS, were polished with two different polishing compositions (Polishing Compositions 3A and 3B). Each of the compositions comprised 3.38 wt.% of succinic acid and 3% of hydrogen peroxide. Polishing Composition 3A further comprised 0.56 wt.% of silica (Bindzil CJ2-2, Eka Chemicals), while Polishing Composition 3B further comprised 5.56 wt.% of the same silica.

[0050] Following polishing, the removal rates (RR) for aluminum-copper, titanium, and TEOS were determined for each of the polishing compositions, and the results are summarized in Table 2.

Table 3

Polishing Composition	Al-Cu RR (Å/min)	Ti RR (Å/min)	TEOS RR (Å/min)	Selectivity Al-Cu/TEOS	Selectivity Ti/TEOS
3A	1482	1932	244	6.07	7.92
3B	2788	3344	1750	1.59	1.91

[0051] As is apparent from the results set forth in Table 3, increasing the amount of silica present in the polishing composition from 0.56 wt.% to 5.56 wt.% resulted in increases in the removal rates observed for aluminum-copper, titanium, and TEOS of 88%, 73%, and 617%, respectively. The selectivity for the polishing of aluminum-copper as compared with TEOS, as defined by the ratio of the aluminum-copper removal rate to the TEOS removal rate, decreased from 6.07 to 1.59 with the increase in silica content of the polishing composition. Similarly, the selectivity for the polishing of titanium as compared with TEOS, as defined by the ratio of the titanium removal rate to the TEOS removal rate, decreased from 7.92 to 1.91 with the increase in silica content of the polishing composition.

[0052] 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.

CLAIMS

1. A chemical-mechanical polishing composition comprising:
   - (a) an abrasive,
   - (b) an oxidizing agent selected from the group consisting of peroxides, persulfates, ferric salts, and combinations thereof,
   - (c) 25 to 400 ppm of calcium ion,
   - (d) an organic carboxylic acid, and
   - (e) water,

wherein the polishing composition has a pH of 1.5 to 7.

2. The polishing composition of claim 1, wherein the abrasive is selected from the group consisting of silica and polymer-treated alumina.

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

4. The polishing composition of claim 2, wherein the abrasive is polymer-treated alumina comprising alumina treated with a negatively-charged polymer.

5. The polishing composition of claim 4, wherein the negatively-charged polymer is poly(2-acrylamido-2-methylpropane sulfonic acid) or polystyrenesulfonic acid.

6. The polishing composition of claim 1, wherein the polishing composition comprises 0.001 wt.% to 2 wt.% of abrasive.

7. The polishing composition of claim 1, wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, ammonium persulfate, ferric nitrate, and combinations thereof.

8. The polishing composition of claim 7, wherein the polishing composition comprises 0.1 wt.% to 5 wt.% of oxidizing agent.

9. The polishing composition of claim 1, wherein the organic carboxylic acid is selected from the group consisting of citric acid, malonic acid, and tartaric acid.

10. The polishing composition of claim 1, wherein the organic acid is succinic acid.

11. The polishing composition of claim 1, wherein the polishing composition comprises 50 to 200 ppm of calcium ion.

12. The polishing composition of claim 1, wherein the polishing composition has a pH of 2 to 6.

13. 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 comprising:

(a) an abrasive,

(b) an oxidizing agent selected from the group consisting of peroxides, persulfates, ferric salts, and combinations thereof,

(c) 25 to 400 ppm of calcium ion,

(d) an organic carboxylic acid, and

(e) water,

wherein the polishing composition has a pH of 1.5 to 7,

(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.

14. The method of claim 13, wherein the abrasive is selected from the group consisting of silica and polymer-treated alumina.

15. The method of claim 14, wherein the abrasive is condensation-polymerized silica.

16. The method of claim 14, wherein the abrasive is polymer-treated alumina comprising alumina treated with a negatively-charged polymer.

17. The method of claim 16, wherein the negatively-charged polymer is poly(2-acrylamido-2-methylpropane sulfonic acid) or polystyrenesulfonic acid.

18. The method of claim 13, wherein the polishing composition comprises 0.001 wt.% to 2 wt.% of abrasive.

19. The method of claim 13, wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, ammonium persulfate, ferric nitrate, and combinations thereof.

20. The method of claim 19, wherein the polishing composition comprises 0.1 wt.% to 5 wt.% of oxidizing agent.

21. The method of claim 13, wherein the organic acid is selected from the group consisting of citric acid, malonic acid, and tartaric acid.

22. The method of claim 13, wherein the organic acid is succinic acid.

23. The method of claim 13, wherein the polishing composition comprises 50 to 200 ppm of calcium ion.

24. The method of claim 13, wherein the polishing composition has a pH of 2 to 6.

25. The method of claim 13, wherein the substrate comprises at least one layer of aluminum, and at least a portion of the aluminum is removed to polish the substrate.

26. The method of claim 25, wherein the substrate further comprises at least one layer of titanium, and at least a portion of the titanium is removed to polish the substrate.

27. The method of claim 25, wherein the substrate further comprises at least one layer of a dielectric material, and at least a portion of the dielectric material is removed to polish the substrate.

28. The method of claim 13, wherein the substrate comprises at least one layer of an alloy of aluminum and copper, and at least a portion of the alloy of aluminum and copper is removed to polish the substrate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/024902

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 3/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

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

eKIPASS (KIPO internal) "CMP" "abrasive" "oxidizing agent" "calcium ion" "organic carboxylic acid"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6083840 A, (Arch Specialty Chemicals, Inc.), 04 Jul. 2000 (04.07.2000) see claims 1 and 12	1-28
A	US 6468913 B1, (Arch Speciality Chemicals, Inc.), 22 Oct. 2002 (22.10.2002) see claims 1, 25 and 30	1-28
A	US 6540935 B2, (Samsung Electronics Co. Ltd.), 01 Apr. 2003 (01.04.2003) see claims 1, 15 and 18	1-28

☐ 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 28 APRIL 2008 (28.04.2008)	Date of mailing of the international search report **28 APRIL 2008 (28.04.2008)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LEE, Young Jae Telephone No. 82-42-481-8305

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2007/024902

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