(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 November 2007 (08.11.2007)

PCT

(10) International Publication Number
WO 2007/126672 A1

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

(21) International Application Number:
PCT/US2007/007123

(22) International Filing Date: 22 March 2007 (22.03.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/408,334 21 April 2006 (21.04.2006) US

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

(72) Inventors: **ZHANG, Jian**; c/o Legal Department, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US). **CARTER, Phillip**; c/o Legal Department, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US). **LI, Shoutian**; c/o Legal Department, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US).

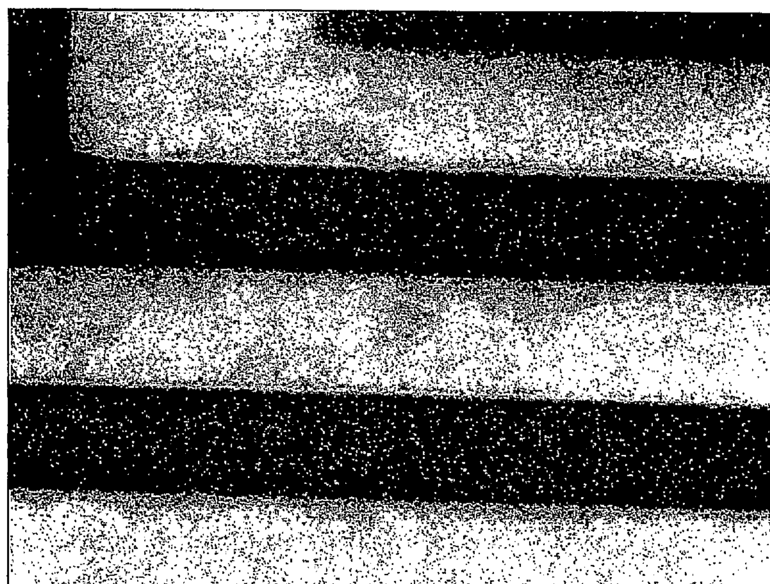
(74) Agents: **WESEMAN, Steven** et al.; Associate General Counsel, Intellectual Property, Cabot Microelectronics Corporation, 870 North Commons Drive, Aurora, Illinois 60504 (US).

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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL,

[Continued on next page]

(54) Title: CMP METHOD FOR COPPER-CONTAINING SUBSTRATES



(57) Abstract: The invention provides a chemical-mechanical polishing composition comprising an abrasive, a benzotriazole derivative, an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and water, wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate having a molecular weight of less than 500 Daltons. The invention further provides a method of chemically-mechanically polishing a substrate with the aforementioned polishing composition.

WO 2007/126672 A1

PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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

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

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

CMP METHOD FOR COPPER-CONTAINING SUBSTRATES

FIELD OF THE INVENTION

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

BACKGROUND OF THE INVENTION

[0002] Development of the next generation of semiconductor devices has emphasized the use of metals with lower resistivity values, such as copper, than previous generation metals such as aluminum in order to reduce capacitance between conductive layers on the devices and to increase the frequency at which a circuit can operate. The use of copper in semiconductor device manufacturing presents special challenges in that prior art processes such as deposition and etch processes have proven unsatisfactory due to difficulties in etching copper. Thus, new methods for manufacturing interconnects using copper have been developed.

[0003] One such method is referred to as the damascene process. In accordance with this process, the surface of the dielectric material, which typically comprises doped silicon dioxide, undoped silicon dioxide, or a low-κ dielectric, is patterned by a conventional dry etch process to form holes and trenches for vertical and horizontal interconnects. The patterned surface is coated with a diffusion barrier layer such as tantalum, tantalum nitride, titanium, or titanium nitride. The diffusion barrier layer is then over-coated with a copper layer. Chemical-mechanical polishing is employed to reduce the thickness of the copper over-layer, as well as the thickness of any adhesion-promoting layer and/or diffusion barrier layer, until a planar surface that exposes elevated portions of the silicon dioxide surface is obtained. The vias and trenches remain filled with electrically conductive copper forming the circuit interconnects.

[0004] The necessity of providing a diffusion barrier layer between the copper and dielectric materials is due to the tendency of copper to diffuse into the surrounding dielectric material. Tantalum and tantalum nitride have found wide acceptance in the industry as barrier layer materials and are typically applied to a substrate by physical vapor deposition (PVD) prior to deposition of copper. Planarization of the substrate thus requires removal of copper and then the diffusion barrier to expose the underlying dielectric and complete production of the circuit.

[0005] The properties of tantalum and tantalum nitride differ from those of copper, being considerably more chemically inert, such that polishing compositions suitable for the polishing of copper are often unsuitable for the removal of underlying tantalum and tantalum nitride. Thus, a two-step approach is generally used for the polishing of copper-tantalum substrates, with the first step employing a first polishing composition to remove most of the copper, and the second step employing a second polishing composition to remove the remaining copper and the barrier film (e.g., tantalum).

[0006] Typically, tantalum polishing compositions have been formulated with a highly basic pH of 9 or more. The basic polishing compositions tend to also exhibit high removal rates for underlying dielectric layers, which can lead to erosion of the substrate and result in nonplanarity of the substrate. Recently, acidic tantalum polishing compositions have been developed having pH values of less than 4. Although such acidic polishing compositions are selective for tantalum over dielectric layers, the copper features tend to suffer from pitting defects at such low pH values.

[0007] In addition, tantalum polishing compositions typically contain an oxidizing agent in order to remove residual copper remaining from the copper removal step. The oxidizing agent, however, increases the copper removal rate exhibited by the tantalum polishing compositions so that during the tantalum removal process, copper remaining within the trenches is simultaneously removed. This within-trench copper removal is particularly problematic in wider lines and is referred to as "dishing." Dishing leads to nonplanarity of the polishing surface, as well as to potential damage to the copper lines.

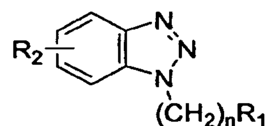
[0008] To this end, polishing compositions intended for use with copper-containing substrates have been devised which include inhibitors of copper overpolishing that act by reducing etching of copper within trenches by the oxidizing agent and other components of polishing compositions. Typically, such inhibitors comprise nitrogen-containing compounds, for example, amines and small molecular weight nitrogen-containing heterocyclic compounds such as benzotriazole, 1,2,3-triazole, and 1,2,4-triazole. For example, U.S. Patent 6,585,568 describes a CMP polishing slurry for polishing a copper-based metal film formed on an insulating film, comprising a polishing material, an oxidizing agent, and water, as well as a benzotriazole compound and a triazole compound, wherein the ratio of the triazole compound to the benzotriazole compound is 5 to 70. U.S. Patent 6,375,693 discloses a slurry for polishing a tantalum-based barrier layer for copper-based metallurgy, consisting of hydrogen

peroxide for oxidizing copper, a copper oxidation inhibitor, a sulfated fatty acid surfactant that regulates complexing between copper and the oxidation inhibitor, and colloidal silica, wherein the oxidation inhibitor is selected from the group consisting of 1-H benzotriazole, 1-hydroxybenzotriazole, 1-methylbenzotriazole, 5-methylbenzotriazole, benzimidazole, 2-methylbenzimidazole, and 5-chlorobenzotriazole.

[0009] However, despite the improvements achieved in the reduction of dishing and erosion in the chemical-mechanical polishing of copper/tantalum substrates with the use of heterocyclic copper inhibitors, problems with pitting and dishing remain, particularly at low pH values. Further, polishing compositions suitable for copper remain substantially different from polishing compositions suitable for tantalum, thereby requiring a two-step process for the planarization of such substrates. Thus, there remains a need in the art for improved polishing systems and methods for the chemical-mechanical planarization of substrates comprising copper and tantalum layers.

BRIEF SUMMARY OF THE INVENTION

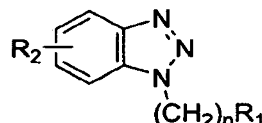
[0010] The invention provides a chemical-mechanical polishing composition comprising, consisting essentially of, or consisting of (a) an abrasive, (b) 0.5 mM to 100 mM of a benzotriazole compound having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6, and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H, (c) an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and (d) water, wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate having a molecular weight of less than 500 Daltons.

[0011] The invention also provides a method of chemically-mechanically polishing a substrate, which method comprises (i) providing a substrate, (ii) contacting the substrate with a polishing pad and a chemical-mechanical polishing composition comprising, consisting

essentially of, or consisting of (a) an abrasive, (b) 0.5 mM to 100 mM of a benzotriazole compound having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6, and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H, (c) an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and (d) water, wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate having a molecular weight of less than 500 Daltons, (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.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[0012] FIG. 1 is a SEM image of a copper blanket wafer surface after polishing with a chemical-mechanical polishing composition comprising benzotriazole.

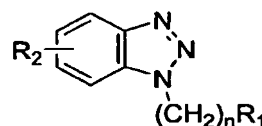
[0013] FIG. 2 is a SEM image of a copper blanket wafer surface after polishing with a chemical-mechanical polishing composition comprising 5-methylbenzotriazole.

[0014] FIG. 3 is a SEM image of a copper pattern wafer after polishing with a chemical-mechanical polishing composition comprising benzotriazole.

[0015] FIG. 4 is a SEM image of a copper pattern wafer after polishing with a chemical-mechanical polishing composition comprising 5-methylbenzotriazole.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The invention provides a chemical-mechanical polishing composition comprising, consisting essentially of, or consisting of (a) an abrasive, (b) 0.5 mM to 100 mM of a benzotriazole compound having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6, and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H, (c) an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and (d) water, wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate having a molecular weight of less than 500 Daltons.

[0017] 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 metal oxide is silica.

[0018] The silica can be any suitable form of silica. Useful forms of silica include but are not limited to fumed silica, precipitated silica, and condensation-polymerized silica. More preferably, the silica is a condensation-polymerized silica. Condensation-polymerized silica particles typically are prepared by condensing $Si(OH)_4$ to form colloidal particles. The precursor $Si(OH)_4$ can be obtained, for example, by hydrolysis of high purity alkoxysilanes, or by acidification of aqueous silicate solutions. Such abrasive particles can be prepared in accordance with U. S. Patent 5,230,833 or can be obtained as any of various commercially available products, such as the Fuso PL-1, PL-2, and PL-3 products (Fuso Chemical Company, Ltd., Japan) and the Nalco 1050, 2327, and 2329 products (Nalco Chemical Company, Naperville, IL), as well as other similar products available from DuPont, Bayer, Applied Research, Nissan Chemical, and Clariant.

[0019] The abrasive also can be an alumina-doped silica. An example of a suitable alumina-doped silica is the Nalco 1034 A product (Nalco Chemical Company).

[0020] As is well known in the art, many abrasive particles, such as metal oxide particles, comprise, at the lowest level of structure, primary particles. Primary particles are formed by covalent bonds between atoms comprising the particles and are stable to all but the harshest conditions. At the next level of structure, primary particles are associated into secondary particles, generally referred to as aggregates. Aggregate particles comprise primary particles

and are bonded together by covalent bonds and typically are resistant to degradation by, for example, mechanical energy inputs such as high-shear mixing. At the next level of structure, aggregates are more loosely associated into agglomerates. Typically, agglomerates can be disassociated into the constituent aggregates via mechanical energy inputs. Depending on the particular composition and method of preparation, primary particles and secondary particles (e.g., aggregates) can have shapes ranging from spherical to elliptical, and some aggregates can have extended, chain-like, structures. For example, pyrogenic, or fumed, silica typically exists in the form of aggregates having a chain-like structure. Precipitated silicas, for example, silicas prepared by neutralization of sodium silicate, have an aggregate structure in which approximately spherical primary particles are associated into aggregates that resemble a "bunch of grapes." Both primary abrasive particles and aggregated primary particles (e.g., secondary particles) can be characterized as having an average particle size. In this regard, particle size refers to the diameter of the smallest sphere that encloses the particle.

[0021] The abrasive typically has an average primary particle size of 5 nm or more (e.g., 10 nm or more, or 15 nm or more, or 20 nm or more). Preferably, the abrasive has an average primary particle size of 150 nm or less (e.g., 100 nm or less, or 75 nm or less, or 50 nm or less, or even 30 nm or less). More preferably, the abrasive has an average primary particle size of 5 nm to 50 nm, or 10 nm to 40 nm, or 15 nm to 35 nm, or 20 nm to 30 nm.

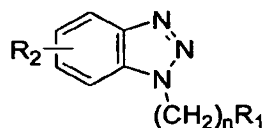
[0022] When the abrasive comprises aggregates of primary particles, the abrasive typically has an aggregate particle size of 20 nm or more (e.g., 30 nm or more, or 40 nm or more, or 50 nm or more). Preferably, the abrasive has an aggregate particle size of 250 nm or less (e.g., 200 nm or less, or 150 nm or less, or 100 nm or less, or even 75 nm or less). More preferably, the abrasive has an aggregate particle size of 20 nm to 125 nm, or 30 nm to 100 nm.

[0023] The abrasive desirably is suspended in the polishing composition, more specifically in the water of the polishing composition. The polishing composition preferably is colloidally stable. The term colloid refers to the suspension of abrasive particles in the water. Colloidal stability refers to the maintenance of that suspension over time. In the context of this invention, an abrasive composition is considered colloidally stable if, when the abrasive composition 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.

[0024] Any suitable amount of abrasive can be present in the polishing composition. Typically, 0.01 wt.% or more abrasive can be present in the polishing composition (e.g., 0.05 wt.% or more, or 0.1 wt.% or more). The amount of abrasive in the polishing composition preferably will not exceed 10 wt.%, and more preferably will not exceed 5 wt.% (e.g., will not exceed 2.5 wt.%, or will not exceed 1 wt.%). Even more preferably the abrasive will comprise 0.05 wt.% to 2.5 wt.% (e.g., 0.1 wt.% to 1 wt.%) of the polishing composition.

[0025] The polishing composition comprises a benzotriazole compound having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6 (i.e., 0, 1, 2, 3, 4, 5, or 6), and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H. Preferably, n is an integer of 0 to 3 (i.e., 0, 1, or 2), and R_2 is selected from the group consisting of H, C_1-C_3 alkyl (i.e., $-CH_2-$, $-CH_2CH_2-$ or $-CH_2CH_2CH_2-$), F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H. More preferably, the benzotriazole is selected from the group consisting of 4-methylbenzotriazole, 5-methylbenzotriazole, 1H-benzotriazole-1-carboxaldehyde, 1-(isocyanomethyl)-1H-benzotriazole, 1H-benzotriazole-1-acetonitrile, 1H-benzotriazole-1-methanol, and combinations thereof.

[0026] The polishing composition can comprise any suitable concentration of the benzotriazole compound. Typically, the concentration of the benzotriazole compound in the polishing composition is 0.5 mM or more (e.g., 1 mM or more, or 2 mM or more, or 5 mM or more). Preferably, the concentration of the benzotriazole compound in the polishing composition is 100 mM or less (e.g., 75 mM or less, or 50 mM or less). More preferably, the concentration of the benzotriazole compound in the polishing composition is 0.5 mM to 75 mM (e.g., 1 mM to 50 mM, or 2 mM to 20 mM, or even 5 mM to 20 mM). The desired concentration of the benzotriazole compound can be achieved by any suitable means, such as by using 0.006 wt.% to 1.2 wt.% of the benzotriazole compound based on the weight of the

water and any components dissolved or suspended therein in the preparation of the polishing composition.

[0027] The polishing composition comprises an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof. The iodate compound can be any suitable compound comprising the iodate anion, IO_3^-. Examples of suitable iodate compounds include but are not limited to potassium iodate, ammonium iodate, and tetraalkylammonium iodates.

[0028] When the polishing composition comprises an iodate compound, typically the concentration of the iodate compound in the polishing composition is 0.1 mM or more (e.g., 0.2 mM or more, or 0.5 mM or more, or 1 mM or more). Preferably, the concentration of the iodate compound in the polishing composition is 1M or less (e.g., 0.75 M or less, or 0.5 M or less, or 0.25 M or less). More preferably, the concentration of the iodate compound in the polishing composition is 0.5 mM to 100 mM (e.g., 1 mM to 75 mM, or 5 mM to 50 mM).

[0029] The organic oxidizing agent can be any suitable organic oxidizing agent wherein the organic oxidizing agent has an oxidized form and a reduced form. The oxidized form of the organic oxidizing agent has a standard reduction potential of greater than -0.7 volts. The oxidized form of the organic oxidizing agent also comprises at least one aromatic ring in conjugation with at least one additional unsaturated moiety.

[0030] The oxidized and reduced form of organic oxidizing agent are related in that the carbon skeletal framework of the organic oxidizing agent, that is, the carbon-carbon bond connectivities that define the structure of the organic oxidizing agent, are the same in both forms. Although the oxidized and the reduced forms of the organic oxidizing agent typically comprise different functional groups that are related in that the functional groups are interconvertible with one another via processes of oxidation and reduction, the overall general structure of the organic oxidizing agent is the same for both forms. Typically, the oxidized form and reduced form of the organic oxidizing agent differ by two electrons, although it is suitable for the oxidized form and reduced form to differ by one (unpaired) electron and thus for one form to exist as a free radical.

[0031] Desirably, the organic oxidizing agent will be water-soluble or water-emulsifiable. As utilized herein, the term "water-soluble" refers to an organic oxidizing agent that has a solubility of at least 0.1 mg/ml (e.g., at least 1 mg/ml) in water at 25°C. As utilized herein,

the term "water-emulsifiable" refers to an organic oxidizing agent that forms a stable, oil-in-water emulsion at 25°C.

[0032] The oxidized form of the organic oxidizing agent preferably has a standard reduction potential of greater than -0.7 volts (e.g., greater than -0.6 volts, or greater than -0.5 volts, or even greater than -0.4 volts), when measured against a standard hydrogen electrode at standard conditions of concentration and temperature. Standard conditions of concentration and temperature are measured at 1 molal concentration for all dissolved materials, 1 atmosphere pressure (101.33 kPa) for all gases, and a system temperature of 25°C.

[0033] The organic oxidizing agent 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 organic oxidizing agent in the liquid carrier of the polishing composition. Suitable substituents include, without limitation, hydroxyl, amino, monoalkylamino, dialkylamino, sulfonic acid, phosphonic acid, salts therof, and combinations thereof. Preferably, the organic oxidizing agent is substituted with one or more sulfonic acid groups ($-SO_3H$).

[0034] It will be appreciated that the acidic substituents are capable of forming salts, and in this regard the organic oxidizing agent having acidic substituents can exist as an acid, salt, or when di- or polysubstituted as a partial salt (e.g., a monosalt of a disulfonic acid). Organic oxidizing agents having acidic substituents can be supplied for use in the inventive polishing composition in either acid form or salt form.

[0035] When the organic oxidizing agent comprises an acidic substituent in the form of a salt, the counterion can be any suitable countercation. For example, the countercation can be ammonium, alkylammonium, di-, tri-, and tetra-alkylammonium, cesium, potassium, sodium, and the like. The choice of countercation will depend on the type of substrate being polished and on the solubility or emulsifiability of the particular salt in the liquid carrier.

[0036] In a preferred embodiment, the organic oxidizing agent is at least one anthraquinone compound. The anthraquinone compound can be any derivative of the basic structure embodied by the term. Preferred anthraquinone compounds 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.

[0037] When the polishing composition comprises an organic oxidizing agent, typically the concentration of the organic oxidizing agent in the polishing composition is 0.1 mM or more (e.g., 0.2 mM or more, or 0.5 mM or more, or 1 mM or more). Preferably, the concentration of the organic oxidizing agent in the polishing composition is 10 mM or less (e.g., 8 mM or less, or 6 mM or less). More preferably, the concentration of the organic oxidizing agent in the polishing composition is 0.2 mM to 10 mM (e.g., 0.5 mM to 8 mM). The desired concentration of organic oxidizing agent can be achieved by any suitable means, such as by using 0.003 wt.% to 0.3 wt.% of organic oxidizing agent based on the weight of the water and any components dissolved or suspended therein in the preparation of the polishing composition.

[0038] The polishing composition comprises water. Desirably, the water is the liquid carrier for the other components of the polishing composition, i.e., the other components of the polishing composition are dissolved or suspended din the water. The water preferably is deionized water as added to form the polishing composition.

[0039] The polishing composition can have any suitable pH. Typically, the polishing composition has a pH of 1 or more (e.g., 2 or more). Preferably, the polishing composition has a pH of 13 or less (e.g., 12 or less). In one preferred embodiment, the polishing composition has a pH of 1 to 7 (e.g., 2 to 5, or 2 to 4, or even 2 to 3).

[0040] The pH of the polishing composition can be achieved and/or maintained by any suitable means. More specifically, the polishing composition can further comprise a pH adjustor, a pH buffering agent, or a combination thereof. The pH adjustor can be any suitable pH-adjusting compound. For example, the pH adjustor can be nitric acid, ammonium hydroxide, potassium hydroxide, potassium carbonate, or a combination thereof. The pH buffering agent can be any suitable buffering agent, for example, phosphates, sulfates, borates, ammonium salts, and the like. The polishing composition can comprise any suitable amount of a pH adjustor and/or a pH buffering agent, provided that a suitable amount is used to achieve and/or maintain the pH of the polishing composition within the ranges set forth.

[0041] It is well known in the art that when a copper surface is contacted with an oxidizing agent, a layer of copper oxide is formed on the surface of the copper. In order to facilitate the solubilization of the copper oxide to soluble forms of copper (II) ion and thus to enhance the rate at which copper can be removed from a substrate being polished, various additives have been included in chemical-mechanical polishing compositions for use in the

polishing of copper. In particular, organic carboxylic acids, dihydroxybenzene compounds, and trihydroxybenzene compounds have been utilized in copper polishing compositions to enhance the polishing rate for copper layers.

[0042] In some embodiments, the inventive polishing composition is selective for the polishing of copper versus tantalum. In other embodiments, the inventive polishing composition is selective for the polishing of tantalum versus copper. Advantageously, embodiments of the inventive polishing composition exhibiting selectivity for copper versus tantalum provide for satisfactory copper removal rates without the necessity for incorporation of copper rate enhancing compounds. Moreover, in tantalum-selective embodiments of the inventive polishing composition, copper rate-enhancing compounds disadvantageously reduce the selectivity for tantalum versus copper otherwise exhibited by the inventive polishing compositions. Accordingly, the polishing composition desirably comprises substantially no component that solubilizes, i.e., that acts to solubilize, copper oxide, apart from any inorganic acid and/or buffer used to adjust the pH of the polishing composition. In particular, the polishing composition desirably comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and preferably comprises no organic carboxylic acid, having a molecular weight of less than 500 Daltons. An organic carboxylic acid is a compound having one or more carboxylic acid functional group(s) represented by -COOH. The polishing composition also desirably comprises no dihydroxybenzene or trihydroxybenzene compound having a molecular weight of less than 500 Daltons, such as catechol or pyrogallol. Polymeric compounds having molecular weights of 500 Daltons or more and having multiple carboxylic acid structural groups, such as polyacrylates, vinyl acrylates, and styrene acrylates, are not precluded from being present in the polishing composition. In some embodiments, the polishing composition does not comprise any compound having any number of carboxylic acid functional groups.

[0043] 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, nonionic surfactants, amphoteric surfactants, fluorinated surfactants, mixtures

thereof, and the like. The polishing composition also optionally comprises a biocide, such as an isothiazolidinone biocide.

[0044] The polishing composition desirably comprises no component that competes with the benzotriazole compound for reaction sites on the surface of copper being polished. In particular, the polishing composition desirably comprises no alkyl having a molecular weight of less than 500 Daltons. Preferably, the polishing composition comprises no alkyl sulfate having a molecular weight of less than 1000 Daltons (e.g., less than 10,000 Daltons). Alkyl sulfates are represented by the formula $ROSO_3M$ wherein R represents an alkyl or an alkylaryl, and M is hydrogen, ammonium, tetraalkylammonium, or a metal cation (e.g., sodium).

[0045] 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, benzotriazole compound, oxidizing agent, pH adjustor, etc.) as well as any combination of ingredients (e.g., abrasive, benzotriazole compound, oxidizing agent, pH adjustor, etc.).

[0046] For example, the abrasive can be dispersed in water. The benzotriazole compound then can be added, and mixed with the abrasive and water by any method that is capable of incorporating the components into the polishing composition. The oxidizing agent can be added at any time during the preparation of 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 just before use (e.g., within 1 minute before use, or within 1 hour before use, or within 7 days before use). The polishing composition also can be prepared by mixing the components at the surface of the substrate during the polishing operation.

[0047] The polishing composition can be supplied as a one-package system comprising an abrasive, a benzotriazole compound, an oxidizing agent, and water. Alternatively, the abrasive can be supplied as a dispersion in water in a first container, and the oxidizing agent can be supplied in a second container, either in dry form, or as a solution or dispersion in water, with the benzotriazole compound supplied in the first or second container, or in a third container. Optional components, such as a pH adjustor, can be placed in the first and/or

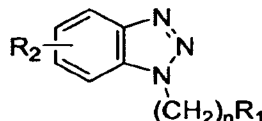
second containers or a third container. Furthermore, the components in the first or second container can be in dry form while the components in the remaining container(s) can be in the form of an aqueous dispersion. Moreover, it is suitable for the components in the first, second, or third containers to have different pH values, or alternatively to have substantially similar, or even equal, pH values. If an optional component such as a pH adjustor or buffer is a solid, it may be supplied either in dry form or as a mixture in water. The oxidizing agent can be supplied separately from the other components of the polishing composition and can be combined, for example, 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.

[0048] The polishing composition of the invention 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 the abrasive, benzotriazole compound, 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, benzotriazole compound, and oxidizing agent can each be present in the concentration 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 of 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 water present in the final polishing composition in order to ensure that the abrasive, benzotriazole compound, oxidizing agent, and other suitable additives are at least partially or fully dissolved in the concentrate. It is also suitable to provide the polishing composition in the form of two or more concentrates, each concentrate individually containing less than all of the components of the polishing composition, wherein upon combination of the concentrates and dilution of the combination 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.

[0049] The invention also provides a method of polishing a substrate with the polishing composition described herein. The method of polishing a substrate comprises (i) contacting a substrate with the aforementioned polishing composition, and (ii) abrading or removing at least a portion of the substrate to polish the substrate.

[0050] In particular, the invention provides a method of chemically-mechanically polishing a substrate comprising (i) providing a substrate, (ii) contacting the substrate with a polishing pad and a chemical-mechanical polishing composition comprising, consisting essentially of, or consisting of (a) an abrasive, (b) 0.5 mM to 100 mM of a benzotriazole having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6, and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H, (c) an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and (d) water, wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate, (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.

[0051] 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 copper. The substrate can be any suitable substrate (e.g., an integrated circuit, metals, ILD layers, semiconductors, and thin films) and preferably further comprises at least one metal layer comprising tantalum (e.g., a barrier layer). The tantalum can be in the form of tantalum metal, alloys thereof, oxides thereof, nitrides thereof, and combinations thereof. The substrate typically further comprises a suitable insulating layer. 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 is a silicon-based metal oxide, carbon-doped silicon dioxide, or organically modified silicon glass.

[0052] The polishing composition of the invention is capable of planarizing or polishing a copper-containing metal layer of a substrate with desirable planarization efficiency, uniformity, removal rate, and low defectivity. The copper removal rate can be controlled by selecting the amount of benzotriazole compound to be incorporated into the polishing composition. With low levels of the benzotriazole compound, the copper removal rate exhibited by the inventive polishing composition can be relatively high, thus allowing use of the polishing composition to polish copper layers rapidly and with minimal pitting of the copper layers. With higher levels of the benzotriazole compound, the copper removal rate exhibited by the inventive polishing composition can be close to zero, thus allowing for the use of the inventive polishing composition in the removal of a barrier layer (e.g., a tantalum layer) on a patterned substrate, with attendant reduction of dishing of copper lines on the substrate.

[0053] In some instances, it is desirable to transform the inventive polishing composition from a copper-selective polishing composition to a tantalum-selective polishing composition in situ, e.g., during the polishing process. This can be accomplished by adjusting the concentration of the benzotriazole compound during the polishing process. For example, a substrate comprising a layer of copper over a layer of tantalum can be polished with a polishing composition comprising a concentration of a benzotriazole compound, wherein the polishing composition exhibits a faster removal rate for copper than for tantalum. At a suitable time point during the polishing process, e.g., when substantially or nearly all of the desired copper to be removed has been removed by the polishing composition, the concentration of the benzotriazole compound in the polishing composition can be increased so that the polishing composition exhibits a slower removal rate for copper than for tantalum.

[0054] A substrate can be planarized or polished with the 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.

[0055] Desirably, the CMP apparatus further comprises an in situ polishing endpoint detection system, many of which are known in the art. Techniques for inspecting and monitoring the polishing process by analyzing light or other radiation reflected from a surface of the workpiece are known in the art. Such methods are described, for example, in U.S. Patent 5,196,353, U.S. Patent 5,433,651, U.S. Patent 5,609,511, U.S. Patent 5,643,046, U.S. Patent 5,658,183, U.S. Patent 5,730,642, U.S. Patent 5,838,447, U.S. Patent 5,872,633, U.S. Patent 5,893,796, U.S. Patent 5,949,927, and U.S. Patent 5,964,643. Desirably, the inspection or monitoring of the progress of the polishing process with respect to a workpiece being polished enables the determination of the polishing end-point, i.e., the determination of when to terminate the polishing process with respect to a particular workpiece.

[0056] The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

EXAMPLE 1

[0057] This example demonstrates the effect on copper corrosion of a blanket layer of copper exhibited by the polishing composition of the invention.

[0058] Similar substrates comprising a blanket layer of copper were polished under identical polishing conditions with polishing compositions comprising 1 wt.% of aluminum-doped silica having a 25 nm primary particle size (Nalco 1034A) and 0.2 wt.% (9 mM) potassium iodate in water at a pH of 2.2. Composition 1A (comparative) further comprised 10 mM benzotriazole. Composition 1B (invention) further comprised 10 mM 5-methylbenzotriazole. After polishing, the substrate surfaces were imaged using scanning electron microscopy (SEM). The SEM image of the surface polished with Composition 1A is depicted in FIG. 1, and the SEM image of the surface polished with Composition 1B is depicted in FIG. 2.

[0059] As is apparent by visual inspection of the copper surfaces depicted in FIGS. 1 and 2, the inventive polishing composition allows for formation of a copper surface having considerably less pitting than that observed for the control polishing composition.

EXAMPLE 2

[0060] This example demonstrates the effect on copper corrosion of a copper pattern wafer exhibited by the polishing composition of the invention.

[0061] Similar substrates comprising a copper pattern wafer were polished under identical polishing conditions with polishing compositions comprising 1 wt.% of aluminum-doped silica having a 25 nm primary particle size (Nalco 1034 A) and 0.2 wt.% (9 mM) potassium iodate in water at a pH of 2.2. Composition 2A (comparative) further comprised 10 mM benzotriazole. Composition 2B (invention) further comprised 10 mM 5-methylbenzotriazole. After polishing, the substrate surfaces were imaged using scanning electron microscopy (SEM). The SEM image of the surface polished with Composition 2A is depicted in FIG. 3, and the SEM image of the surface polished with Composition 2B is depicted in FIG. 4. The magnification of the SEM image depicted in FIG. 4 is 10x that of FIG. 3.

[0062] Regions of corrosion (10) are observed on the copper pattern lines depicted in FIG. 3 after polishing with the comparative polishing composition. By way of contrast, the copper pattern lines depicted in FIG. 4 at a magnification 10x greater than that of FIG. 3 show no evidence for corrosion after polishing with the inventive polishing composition.

EXAMPLE 3

[0063] This example shows the effect of concentration of benzotriazole compounds on removal rates for copper and tantalum layers observed with the polishing compositions of the invention.

[0064] Nine different polishing compositions were used to separately chemically-mechanically polish similar copper layers and tantalum layers. Each of the compositions comprised 0.5 wt.% of condensation-polymerized silica having a 25 nm primary particle size and 0.2 wt.% (9 mM) potassium iodate in water at a pH of 2.2. Composition 3A (control) contained no further ingredients (i.e., no benzotriazole or benzotriazole compound). Composition 3B (comparative) additionally contained benzotriazole at 1 mM concentration. Composition 3C (comparative) additionally contained benzotriazole at 50 mM concentration. Composition 3D (invention) additionally contained 5-methylbenzotriazole at 1 mM concentration. Composition 3E (invention) additionally contained 5-methylbenzotriazole at 50 mM concentration. Composition 3F (invention) additionally contained 1H-benzotriazol-1-ylmethyl isocyanide at 1 mM concentration. Composition 3G (invention) additionally contained 1H-benzotriazol-1-ylmethyl isocyanide at 50 mM concentration. Composition 3H (invention) additionally contained 1H-benzotriazole-1-carboxaldehyde at 1 mM

concentration. Composition 3I (invention) additionally contained 1H-benzotriazole-1-carboxaldehyde at 50 mM concentration.

[0065] The polishing parameters were as follows: 10 kPa (1.5 psi) downforce pressure of the substrate against the polishing pad, 110 rpm platen speed, 102 rpm carrier speed, 150 mL/min polishing composition flow rate, and use of a Politex CMP pad.

[0066] Following use of the polishing compositions, the copper and tantalum removal rates ("Cu RR" and "Ta RR," respectively) were determined, and the selectivities, defined by the ratio of the copper to tantalum removal rates, were calculated. The results are set forth in Table 1.

Table 1: Effect of benzotriazole compounds on copper and tantalum removal rates

Polishing Composition	Benzotriazole Compound	Conc. (mM)	Cu RR (Å/min)	Ta RR (Å/min)	Selectivity (Cu RR/Ta RR)
3A (control)	None (control)	0	3200	600	5.33
3B (comparative)	benzotriazole	1	3130	620	5.05
3C (comparative)	benzotriazole	50	990	480	2.06
3D (invention)	5-methylbenzotriazole	1	3390	595	5.70
3E (invention)	5-methylbenzotriazole	50	15	780	0.02
3F (invention)	1-(isocyanomethyl)-1H-benzotriazole	1	3650	240	15.21
3G (invention)	1-(isocyanomethyl)-1H-benzotriazole	50	10	90	0.11
3H (invention)	1H-benzotriazole-1-carboxaldehyde	1	3300	500	6.60
3I (invention)	1H-benzotriazole-1-carboxaldehyde	50	5	510	0.01

[0067] As is apparent from the results set forth in Table 1, all of the inventive polishing compositions containing the benzotriazole compounds at a concentration of 1 mM (i.e., Compositions 3D, 3F, and 3H) exhibited copper removal rates ranging from 1.03 to 1.14 times higher than the copper removal rates exhibited for the control Composition 3A and from 1.05 to 1.17 times higher than observed for comparative Composition 3B, which contained unsubstituted benzotriazole at a concentration of 1 mM. The selectivities exhibited by Compositions 3D, 3F, and 3H, containing 1 mM of benzotriazole compounds, were 1.07 to 2.85 times greater than for the control composition, and were 1.13 to 3.01 times greater than for Composition 3B, containing 1 mM of benzotriazole. Compositions 3E, 3G, and 3I

containing 50 mM of benzotriazole compounds exhibited near zero copper removal rates, while comparative Composition 3C, containing 50 mM benzotriazole, exhibited a copper removal rate of 990 Å/min. Compositions 3E and 3I further exhibited increased tantalum removal rates, while Composition 3F exhibited a reduced but appreciable tantalum removal rate, as compared to comparative Composition 3C.

EXAMPLE 4

[0068] This example demonstrates removal rates for copper and tantalum exhibited by the inventive polishing composition as compared with a polishing composition containing benzotriazole.

[0069] Two different polishing compositions were used to separately chemically-mechanically polish similar copper layers and tantalum layers. Each of the compositions comprised 0.5 wt.% of condensation-polymerized silica having a 25 nm primary particle size and 0.2 wt.% (9 mM) potassium iodate in water at a pH of 2.2. Composition 4A (comparative) further contained benzotriazole at a concentration of 10 mM. Composition 4B (invention) further contained 5-methylbenzotriazole at a concentration of 10 mM.

[0070] The polishing parameters were as follows: 10 kPa (1.5 psi) downforce pressure of the substrate against the polishing pad, 103 rpm platen speed, 97 rpm carrier speed, 200 mL/min polishing composition flow rate, and use of a Politex CMP pad.

[0071] Following use of the polishing compositions, the layers were rinsed with deionized water, and the copper and tantalum removal rates ("Cu RR" and "Ta RR," respectively) were determined. The results are set forth in Table 2.

Table 2: Effect of benzotriazole compounds on copper and tantalum removal rates

Polishing Composition	Cu RR (Å/min)	Ta RR (Å/min)
4A (comparative)	3100	850
4B (invention)	98	956

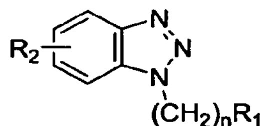
[0072] As is apparent from the results set forth in Table 2, Composition 4B, containing 5-methylbenzotriazole at a concentration of 10 mM, exhibited a copper removal rate that was 0.032 times the copper removal rate observed with Composition 4A, which contained benzotriazole at a concentration of 10 mM. Further, the tantalum removal rate exhibited by Composition 4B was 1.12 times greater than that observed with comparative Composition 4A.

CLAIMS

1. A chemical-mechanical polishing composition comprising:

(a) an abrasive,

(b) 0.5 mM to 100 mM of a benzotriazole compound having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6, and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H,

(c) an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and

(d) water,

wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate having a molecular weight of less than 500 Daltons.

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

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

4. The polishing composition of claim 1, wherein the benzotriazole compound is selected from the group consisting of 4-methylbenzotriazole, 5-methylbenzotriazole, 1H-benzotriazole-1-carboxaldehyde, 1-(isocyanomethyl)-1H-benzotriazole, 1H-benzotriazole-1-acetonitrile, 1H-benzotriazole-1-methanol, and combinations thereof.

5. The polishing composition of claim 1, wherein the oxidizing agent is an iodate compound.

6. The polishing composition of claim 5, wherein the iodate compound is present at a concentration of 0.1 mM to 1 M.

7. The polishing composition of claim 1, wherein the oxidizing agent is an organic oxidizing agent.

8. The polishing composition of claim 7, wherein the organic oxidizing agent is selected from the group consisting of anthraquinones, indigos, and combinations thereof.

9. The polishing composition of claim 8, wherein the organic oxidizing agent is 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.

10. The polishing composition of claim 7, wherein the organic oxidizing agent is present at a concentration of 0.1 mM to 10 mM.

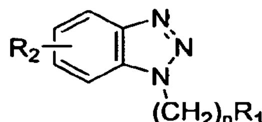
11. A method of chemically-mechanically polishing a substrate, which method comprises:

(i) providing a substrate,

(ii) contacting the substrate with a polishing pad and a chemical-mechanical polishing composition comprising:

(a) an abrasive,

(b) 0.5 mM to 100 mM of a benzotriazole compound having the general structure



wherein R_1 is selected from the group consisting of H, -OH, -CHO, -CN, and -NC, n is an integer of 0 to 6, and R_2 is selected from the group consisting of H, C_1-C_6 alkyl, F, Cl, and Br, with the proviso that when R_1 is H and n = 0, then R_2 cannot be H,

(c) an oxidizing agent selected from the group consisting of iodate compounds, organic oxidizing agents, and mixtures thereof, and

(d) water,

wherein the polishing composition comprises substantially no organic carboxylic acid having a molecular weight of less than 500 Daltons, and wherein the polishing composition comprises no alkyl sulfate having a molecular weight of less than 500 Daltons,

(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.

12. The method of claim 11, wherein the abrasive is condensation-polymerized silica.

13. The method of claim 12, wherein the condensation-polymerized silica is present in an amount of 0.1 wt.% to 10 wt.%.

14. The method of claim 11, wherein the benzotriazole compound is selected from the group consisting of 4-methylbenzotriazole, 5-methylbenzotriazole, 1H-benzotriazole-1-carboxaldehyde, 1-(isocyanomethyl)-1H-benzotriazole, 1H-benzotriazole-1-acetonitrile, 1H-benzotriazole-1-methanol, and combinations thereof.

15. The method of claim 11, wherein the oxidizing agent is an iodate compound.

16. The method of claim 15, wherein the iodate compound is present at a concentration of 0.1 mM to 1 M.

17. The method of claim 11, wherein the oxidizing agent is an organic oxidizing agent.

18. The method of claim 17, wherein the organic oxidizing agent is selected from the group consisting of anthraquinones, indigos, and combinations thereof.

19. The method of claim 18, wherein the organic oxidizing agent is 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.

20. The method of claim 17, wherein the organic oxidizing agent is present at a concentration of 0.1 mM to 10 mM.

21. The method of claim 11, wherein the substrate comprises copper.

22. The method of claim 21, wherein the substrate further comprises a barrier layer comprising tantalum.

23. The method of claim 22, wherein the substrate further comprises a dielectric layer.

24. The method of claim 23, wherein the dielectric layer is selected from the group consisting of silicon dioxide, carbon-doped silicon dioxide, and organically modified silicon glass.

FIG. 1
(Prior Art)

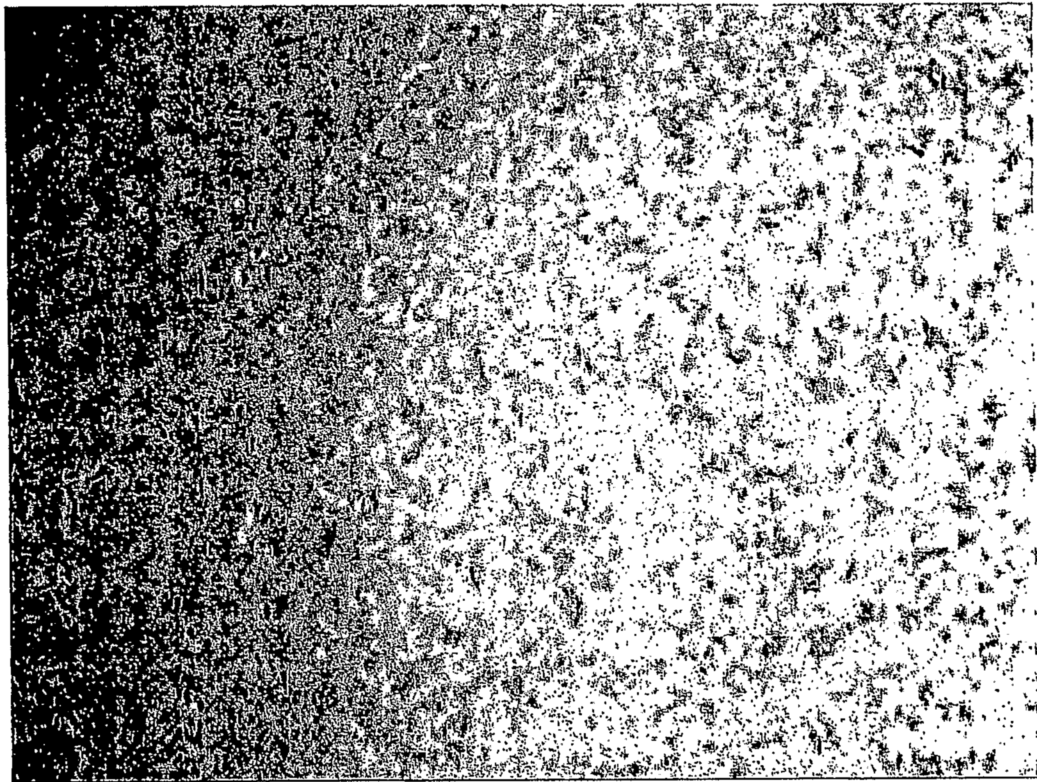


FIG. 2

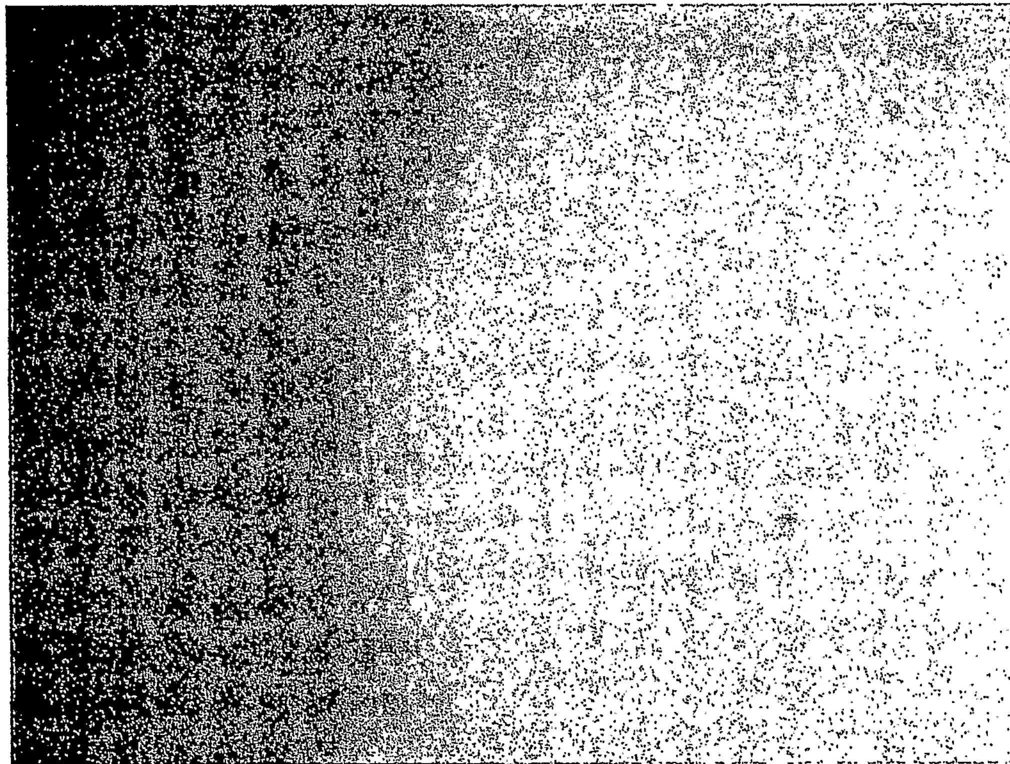


FIG. 3
(Prior Art)

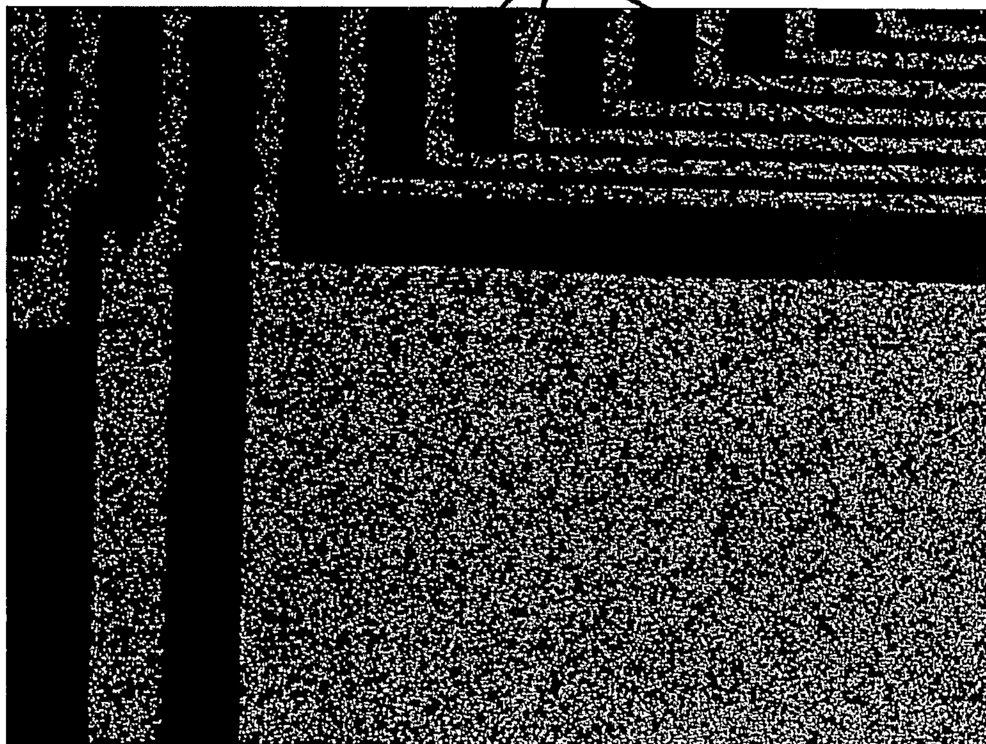
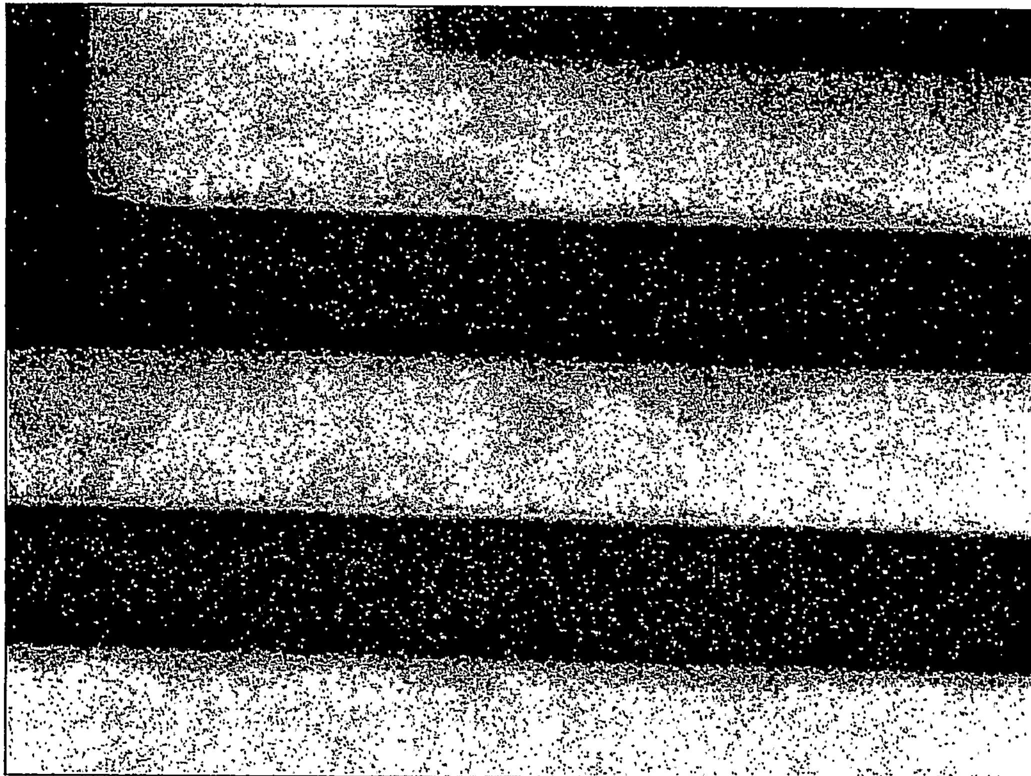


FIG. 4



INTERNATIONAL SEARCH REPORT	International application No. **PCT/US2007/007123**

A. CLASSIFICATION OF SUBJECT MATTER

C09K 3/14(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 : C09K, H01L

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

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

eKIPASS (KIPO internal), USPAT, PAJ, CAPLUS(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6936541 B2 (Bian et al.) 30 Aug. 2005 See the abstract and Example.	1-24
A	US 6632377 B1 (Brusic et al.) 14 Oct. 2003 See the abstract and Examples 1, 2.	1-24
A	US 6375693 B1 (Cote et al.) 23 Apr. 2002 See the abstract and column 5.	1-24

☐ 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	Date of mailing of the international search report
30 AUGUST 2007 (30.08.2007)	**30 AUGUST 2007 (30.08.2007)**

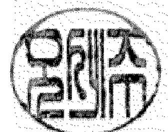
Name and mailing address of the ISA/KR

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

Facsimile No. 82-42-472-7140

Authorized officer

OH, Se Zu



Telephone No. 82-42-481-8156

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2007/007123

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6936541 B2	30.08.2005	US2004023492A1	05.02.2004
US 6632377 B1	14.10.2003	EP1096556A1	02.05.2001
		KR2000029148A	25.05.2000
		SG99289A1	27.10.2003
		TW505689B	11.10.2002
US 6375693 B1	23.04.2002	JP2001015464A2	19.01.2001
		JP3686307B2	24.08.2005
		US2002066234A1	06.06.2002
		US6743268B	01.06.2004