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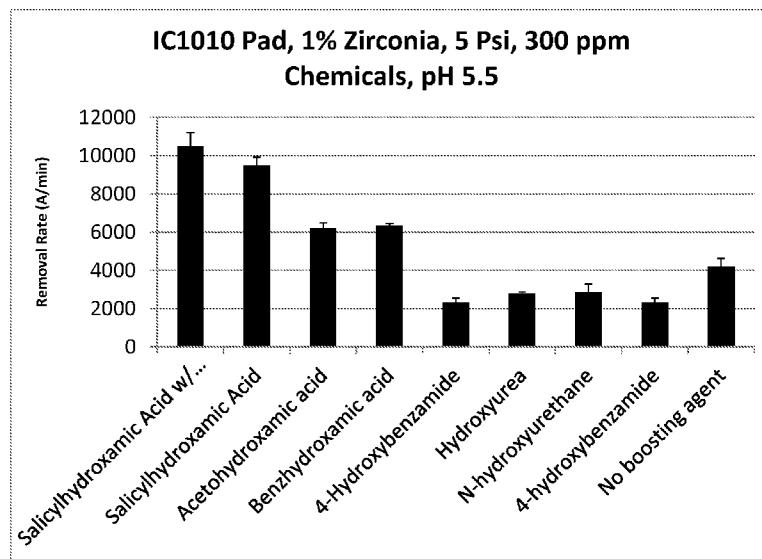
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[Continued on next page]

(54) Title: METHODS AND COMPOSITIONS FOR PROCESSING DIELECTRIC SUBSTRATE

Figure 2



(57) Abstract: Described are materials and methods for processing (polishing or planarizing) a substrate that contains pattern dielectric material using a polishing composition (aka "slurry") and an abrasive pad, e.g., CMP processing.

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METHODS AND COMPOSITIONS FOR PROCESSING DIELECTRIC SUBSTRATE

FIELD OF THE INVENTION

5 The invention relates to materials and methods for processing (polishing or planarizing) a substrate that contains dielectric material, using a polishing composition (aka “slurry”) and an abrasive pad, e.g., CMP processing.

BACKGROUND

10 In processes of fabricating microelectronic devices, multiple layers of conducting, semiconducting, and dielectric materials are deposited onto a surface of a substrate in a stepwise fashion. Portions of the layers may be removed, followed by further processing by selectively adding and removing materials, all with great precision. As layers are deposited onto and then removed from the substrate, the uppermost surface of the
15 substrate may become non-planar. Before adding more material, the non-planar surface is sometimes processed by “planarization” to produce a smooth surface for a subsequent layer and processing.

Planarizing or polishing a non-planar surface is a process where material of a non-planar surface is removed to leave a highly planar surface. Planarization is useful to
20 remove undesired surface topography such as a rough (un-even) surface, or defects such as agglomerated materials, crystal lattice damage, scratches, or contaminated layers or materials. In one particular use, planarization removes excess material that has been deposited over a substrate surface to fill features such as channels or holes of a lower layer or layers, if the deposited layer exhibits an un-even surface.

25 Chemical-mechanical planarization, or chemical-mechanical polishing (CMP), is an established commercial technique for planarizing substrates in microdevice fabrication. CMP uses a liquid chemical composition known as a CMP composition, alternately a polishing composition, a polishing slurry, or just slurry, in combination with a CMP pad, to mechanically and chemically remove material from a non-planar substrate
30 surface. A slurry can be typically applied to a substrate by contacting the surface of the substrate with a CMP polishing pad to which the slurry has been applied. Material is typically removed from the substrate surface by a combination of mechanical activity of

abrasive material contained in the slurry, and chemical activity of chemical materials of the slurry.

To continually advance toward reduced sizes of microelectronic devices, components that make up devices must be smaller and must be positioned ever more 5 closely together. Electrical isolation between circuits is important for ensuring peak semiconductor performance, but becomes increasingly difficult with smaller devices. To that end, various fabrication methods involve etching shallow trenches into a semiconductor substrate and then filling the trenches with insulating material, thereby isolating nearby active regions of an integrated circuit. One example of such a process is 10 referred to as shallow trench isolation (STI). This is a process in which a semiconductor layer is formed on a substrate, shallow trenches are formed in the semiconductor layer via etching or photolithography, and dielectric material is deposited over the etched surface to fill the trenches.

To ensure complete filling of trenches, an excess amount of the dielectric material 15 is deposited over the etched surface. The deposited dielectric material (e.g., a silicon oxide) conforms to the topography of the underlying semiconductor substrate, including at the trenches. Thus, after the dielectric material has been placed, the surface of the deposited dielectric material is characterized by an uneven combination of raised areas of the dielectric material separated by trenches in the dielectric material, the raised areas and 20 trenches corresponding to raised areas and trenches of the underlying surface. The region of the substrate surface that includes the raised dielectric material and trenches is referred to as a pattern field of the substrate, e.g., as “pattern material,” “pattern oxide,” “pattern dielectric,” etc. This region is characterized by a “step height,” which is the difference in height of the raised areas of the dielectric material relative to the trench height. Excess 25 dielectric material that makes up the raised areas is removed by a CMP process to produce a planar surface.

Chemical Mechanical polishing processes for removing pattern dielectric materials can be characterized by performance parameters that include various polishing rates (i.e., removal rates), trench loss, planarization efficiency, and a highly desired 30 property of “self-stopping” behavior.

Removal rates refer to rates of removal of material from a surface of a substrate, usually expressed in terms of units of length (thickness) per unit of time (e.g., Angstroms (Å) per minute). Different removal rates relating to different regions of a substrate or to different stages of a removal step can be important in assessing process performance. A 5 “pattern removal rate” (alternately “active” removal rate) is the rate of removal of material from a desired (“active” or “target”) area of a substrate, such as removal of dielectric material from raised areas of pattern dielectric at a stage of a process during which a substrate exhibits a substantial step height. “Blanket removal rate” refers to a rate of removal of dielectric material from a planarized (i.e., “blanket”) dielectric material 10 at an end of a polishing step, when step height has been significantly (e.g., essentially entirely) reduced.

In various dielectric polishing steps (e.g., during STI processing or when processing a NAND or 3D-NAND substrate) the rate of removal of pattern dielectric is a rate-limiting factor of the overall process. Therefore, high removal rates of pattern 15 dielectric are desired, to increase throughput. Chemical materials can be included in a slurry to increase removal rate of material of a substrate at an active or “target” region of the substrate. Such a compound, sometimes referred to as a removal rate “accelerator” or “booster,” is only useful if it does not also produce a different and overriding negative effect on the slurry or CMP process, such as instability of the slurry, higher defectivity, 20 undesired topography, etc. In the past, different types of chemical removal rate accelerators have been used in combination with other specific slurry ingredients, in certain specific substrate processing applications. United States Patent 6,863,592 describes phosphate and phosphite compounds as potential removal rate accelerators used in combination with metal oxide abrasive particles and anionic polymeric passivation 25 agent. See also United States Patent 6,914,001, listing phosphates, phosphites, phosphoric acids, etc., as potential “removal rate accelerators.” United States Patent 6,436,834 lists other types of chemicals as “abrasion accelerators.”

In addition to a high active removal rate, another performance factor that is important in processing a dielectric substrate is planarization efficiency (PE), which 30 relates to “trench loss.” During removal of raised area dielectric material, an amount of material of trenches will also be removed. This removal of material from trenches is

referred to as “trench loss.” In a useful CMP process, the rate of removal of material from trenches is well below the rate of removal from raised areas. Trench loss is the amount (thickness, e.g., in Angstroms (Å)) of material removed from trenches in achieving planarization of pattern material by eliminating an initial step height. Trench

5 loss is calculated as the initial trench thickness minus a final trench thickness.

Planarization efficiency relates to the amount of step height reduction achieved per amount of trench loss that occurs, while getting to a planar surface, i.e., step height reduction divided by trench loss.

In processing certain substrates, a high removal rate of silicon nitride can also be
10 desirable and advantageous. Silicon nitride is often used in 3D NAND fabrication as a liner to protect a (dielectric) trench area and improve planarization efficiency. When processing a substrate that includes a silicon nitride “liner” to protect dielectric trench areas, the silicon nitride liner on the pattern active area must be removed first (without unduly affecting the trench area) with a relatively fast removal rate. When processing
15 such substrates, a slurry can preferably exhibit a relatively fast silicon nitride removal rate, in combination with a desirably high removal rate for the pattern dielectric and a desirably high planarization efficiency.

SUMMARY

20 Described herein are CMP polishing compositions (aka “slurries”) and method for using a polishing composition to process (e.g., planarize, polish) a surface of a substrate that includes a region of dielectric material, i.e., a substrate with at least a portion of its surface having dielectric material, especially pattern dielectric that includes raised areas and trenches. The substrate can be any substrate that includes an area of dielectric
25 material, examples including substrates undergoing fabrication into a flat panel display, integrated circuit, memory or rigid disk, inter-layer dielectric (ILD) device, microelectromechanical system (MEMS), 3D NAND device, among others.

In one exemplary method, the polishing composition and methods are particularly well suited for planarizing or polishing a substrate that has undergone shallow trench
30 isolation (STI) or a similar process, whereby a continuous layer of dielectric material

such as silicon oxide is coated over a structured lower layer of semiconductor material such as silicon.

Another type of substrate for which slurries and processes of the present description are particularly useful is a 3D NAND flash memory device substrate.

5 Processing a 3D NAND flash memory device involves building memory components in three dimensions, whereas previous flash memory components have been built in only two dimensions. Like processes for preparing many other microelectronic devices, steps of fabricating 3D NAND devices can include coating dielectric material over a structured substrate, then removing an amount of resultant pattern dielectric to planarize the
10 dielectric material. The process includes factors of step height reduction, trench loss, and planarization efficiency that are familiar to processes for earlier types of devices that include pattern dielectric. But, new to processes of preparing a 3D NAND device, substrates exhibit step heights of increased size that have not generally been present in pattern dielectric materials of earlier substrates.

15 Step heights present at pattern dielectric regions of 3D NAND device substrates may exceed one or two microns (i.e., 10,000 or 20,000 angstroms), which is much higher than step heights of previous pattern dielectric materials. A greater step height necessarily requires that a significantly higher amount of dielectric material must be removed from an area of pattern dielectric to produce a planarized surface. Past steps of
20 removing pattern dielectric have involved removal of amounts of dielectric material in a range from as low as 5 angstroms, to as high as about 7,000 angstroms. With 3D NAND devices, a dielectric removal (planarization or polishing) step may be required to remove at least 10,000 angstroms of dielectric material from a raised area, e.g., up to or exceeding 20,000, 30,000, or 40,000 angstroms. As 3D NAND and other types of
25 devices and their fabrication processes continue to advance and improve, this amount of removed material could increase to even higher levels, e.g., up to 50,000 angstroms, 70,000 angstroms, or more.

For efficiency and throughput of commercial fabrication processes, the time required to remove this increased amount of dielectric material cannot be extended.

30 Steps required to remove this dielectric material in a commercial process should take not

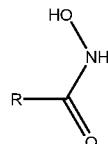
more than 3 minutes, e.g., should take less than 2 minutes or most preferably less than 1 minute.

The substrate can include the pattern dielectric region at a surface, and may optionally contain other regions or fields that are not pattern dielectric. In preferred methods the surface does not contain metal (e.g., tungsten, aluminum, silver, copper), or contains not more than a minor amount of metal, e.g., less than 50 percent metal based on total surface area, preferably less than 30, 20, 10, 5, or 1 percent metal based on total surface area.

The polishing compositions include a liquid carrier, abrasive particles dispersed in the liquid carrier, and removal rate accelerator effective to increase a pattern removal rate of dielectric material. A polishing composition may optionally also include other chemical materials, additives, or minor ingredients such as surfactant, catalyst, oxidant, inhibitor, pH-adjuster, among others. The slurry has a pH that is below about 7.

The removal rate accelerator has the formula (Formula 1):

15



wherein R is selected from the group consisting of: a straight or branched alkyl group, an aryl group, a substituted aryl group, and an alkoxy group that may be straight or branched (e.g., -OR² wherein R² is a straight or branched alkyl group), any of which may be

20 substituted. In certain preferred removal rate accelerator compounds, R can be selected from: a lower alkyl (e.g., C1 to C5), phenyl, hydroxyphenyl, a straight or branched lower alkoxy such as methoxy, ethoxy, or tert-butoxy, any of which may optionally be substituted or further substituted. In certain removal rate accelerator compounds, R can be selected from: a halogen-substituted lower alkyl (e.g., C1 to C5), a halogen-substituted phenyl, a halogen-substituted hydroxyphenyl, or a straight or branched halogen-substituted lower alkoxy such as halogen-substituted methoxy, halogen-substituted ethoxy, or halogen-substituted tert-butoxy.

25 The term “alkyl” as used herein refers to a branched or straight un-substituted, saturated hydrocarbon group. The term “alkoxy” refers to a saturated straight or

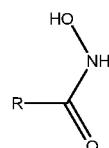
branched hydrocarbon group containing a carbon backbone interrupted by at least one divalent (-O-) oxygen atom, e.g., -O-C_nH_{2n+1} or -C_jH_{2j}-O-C_nH_{2n+1}. A “substituted” group refers to a hydrocarbon group in which a carbon-bonded hydrogen is replaced by a non-hydrogen atom such as a halogen or by a functional group such as an amine, hydroxide, 5 etc. A “halogen-substituted” group refers to a group in which a carbon-bonded hydrogen is replaced by a halogen atom such as a fluorine, chlorine, bromine, or iodine atom.

Examples of removal rate accelerator compounds of Formula 1 include acetohydroxamic acid, benzhydroxamic acid, salicylhydroxamic acid, N-hydroxyurethane, or N-boc hydroxylamine, respectively.

10 Preferred polishing compositions can be used to process a CMP substrate that contains a region of pattern dielectric. Preferred slurries and processes can result in a high removal rate of the pattern dielectric material, most preferably also in combination with high planarization efficiency.

15 In one aspect, the invention relates to a method of polishing a dielectric-containing surface of a substrate, the method. The method includes providing a substrate having a surface that includes dielectric material; providing a polishing pad; providing a chemical-mechanical polishing composition that includes: an aqueous medium, abrasive particles dispersed in the aqueous medium, and removal rate accelerator of the formula (Formula 1):

20



wherein R is selected from: a straight or branched alkyl group, an aryl group, a substituted aryl group, an alkoxy group that may be straight or branched, a halogen-substituted alkyl group, a halogen-substituted phenyl group (e.g., a halogen-substituted hydroxyphenyl group), and a straight or branched halogen-substituted alkoxy group. The slurry has a pH of below about 7. The method further includes contacting the substrate with the polishing pad and the chemical-mechanical polishing composition; and moving the polishing pad and the chemical-mechanical polishing composition relative to the

substrate to abrade at least a portion of the silicon oxide layer on a surface of the substrate to polish the substrate.

In another aspect, the invention relates to a chemical-mechanical polishing composition useful for polishing a dielectric-containing substrate. The composition includes: aqueous medium, abrasive particles dispersed in the aqueous medium, and removal rate accelerator of Formula 1 wherein R is selected from: straight or branched alkyl, aryl, substituted aryl, alkoxy, halogen-substituted alkyl, halogen-substituted phenyl (e.g., halogen-substituted hydroxyphenyl), straight or branched halogen-substituted alkoxy. The slurry has a pH of below about 7.

In yet another aspect, the invention relates to a chemical-mechanical polishing composition useful for polishing a dielectric-containing substrate. The composition includes: aqueous medium, ceria or ceria-containing particles dispersed in the aqueous medium, and a chemical compound of Formula 1 wherein R is selected from: straight or branched alkyl, aryl, substituted aryl, alkoxy, halogen-substituted alkyl, halogen-substituted phenyl (e.g., halogen-substituted hydroxyphenyl), and straight or branched halogen-substituted alkoxy. The slurry has a pH of below about 7.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an illustration of a cross-sectional view of an example substrate useful according to the present description.

Figures 2 and 3 show comparative removal rates of slurries, including slurries that contain removal rate accelerator of Formula 1.

Figure 4 shows comparative removal rates of slurries, including a slurry that contains removal rate accelerator of Formula 1.

25

DETAILED DESCRIPTION

Described as follows are CMP polishing compositions, aka “CMP compositions,” “polishing slurries,” “polishing compositions,” “slurries,” and the like, that are useful for removing dielectric material from a dielectric-containing surface of a substrate. The slurry is useful for polishing or planarizing a surface of a substrate that contains a region of pattern dielectric material. Preferred slurries can be useful to polish or planarize the

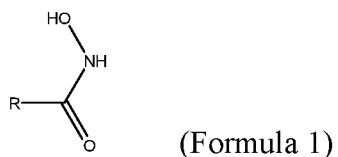
pattern dielectric material using a process that also performs at a high removal rate of the pattern dielectric material, and that provides low trench loss and high polishing efficiency.

A slurry as described includes liquid carrier, removal rate accelerator, and

5 abrasive particles dispersed in the liquid carrier. The slurry may optionally include other chemical materials, additives, or minor ingredients such as surfactant, catalyst, oxidant, inhibitor, pH-adjuster, among others.

The removal rate accelerator is a compound comprising a substituted hydroxamic acid or a hydroxamine derivative having the structure:

10



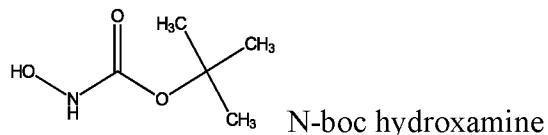
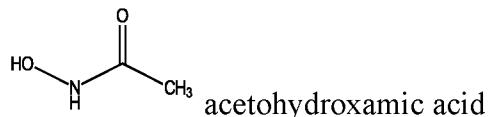
wherein R is selected from a straight or branched alkyl, an aryl, a substituted aryl, or an alkoxy group having a straight or branched alkoxy. The term “alkyl” allows for

15 branching and straight-chain groups and refers to saturated groups (e.g., $-C_nH_{2n+1}$). A “substituted” group refers to a group in which a carbon-bonded hydrogen is replaced by a non-hydrogen atom such as a halogen or by a functional group such as an amine, hydroxide, etc. The removal rate accelerator can be included in a polishing composition in any chemical form, such as a free acid form or as a salt. In preferred compounds of
20 Formula 1 include, the hydrogen of the amine-substituted hydroxy group has a pK_a of at least 7, 8, or 9, meaning that the compound will be a neutral molecule at neutral or acidic pH of a slurry, below 7.

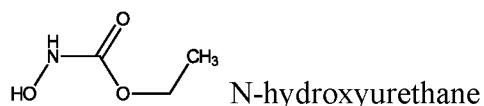
In certain embodiments the removal rate accelerator is a substituted hydroxamic acid wherein R is aromatic, such as phenyl (benzohydroxamic acid), 2-hydroxyphenyl

25 (salicylhydroxamic acid), and the like:

In certain other embodiments, the removal rate accelerator is a hydroxamic acid derivative having an alkyl or alkoxy substituent, preferably a lower alkyl group (C1 to C4) or an alkoxy made up of an oxygen and a lower alkyl group (C1 to C4). Examples include a methyl group (acetohydroxamic acid), a tert-butyl group (N-boc hydroxamine), 5 and a hydroxyethyl group (N-hydroxyurethane):



10



Hydroxamic acid and various substituted hydroxamic acids and hydroxamic acid derivatives are commercially available in forms (e.g., salt or acid) and purities useful in a 15 CMP slurry and CMP processing. Salicylhydroxamic acid (SHA) (aka SHAM, 2-Hydroxybenzenecarbohydroxamic acid, 2-Hydroxybenzohydroxamic acid, N,2-Dihydroxybenzamide) is commercially available at 99 percent purity from Sigma-Aldrich Co. LLC, St. Louis, MO.

The removal rate accelerator can be present in a slurry at any amount useful to 20 provide desired CMP processing performance, with preferred performance including a desirably high dielectric removal rate when polishing pattern dielectric, preferably also a desirably high planarization efficiency, and optionally one or more of a desirably low blanket removal rate, desirably low trench loss, and self-stopping behavior. Certain exemplary slurries can include from about 5 to about 3,000 parts per million (ppm) 25 removal rate accelerator (i.e., per convention, milligrams removal rate accelerator per liter slurry); for example from about 50 to about 2,000 ppm, from about 100 ppm to about 1,500 ppm, about 100 ppm to about 1,200 ppm, about 100 ppm to about 1,000 ppm,

about 100 ppm to about 800 ppm, about 100 ppm to about 750 ppm, about 100 ppm to about 650 ppm, about 100 ppm to about 500 ppm, about 250 ppm to about 1000 ppm, about 250 ppm to about 800 ppm, about 500 ppm to about 1000 ppm, or about 500 ppm to about 800 ppm.

5 A slurry as described can include any useful type or amount of abrasive particles. Preferred slurries include particles that are effective to polish or planarize a non-metal portion of a substrate such as pattern dielectric, e.g., a pattern oxide region of a substrate surface. Examples of preferred abrasive particles include particles of ceria (e.g. CeO₂) or zirconia (e.g. ZrO₂), silica (any of various forms) or a combination of these.

10 Because the slurries can be particularly useful in polishing pattern dielectric, the particles do not need to include, and can preferably exclude, any substantial amount of abrasive particles that are intended to remove a metal such as copper, silver, tungsten, or another metal, from a substrate surface. Accordingly, abrasive particles of preferred slurries can consist of or can consist essentially of ceria particles, zirconia particles, silica particles, or a combination of these, and can preferably exclude any more than an 15 insubstantial amount of particles useful to polish or planarize a metal substrate surface, such particles including certain types of metal oxides known to be useful for polishing a metal surface, e.g., alumina particles. Such a slurry may contain not more than 0.1 weight percent of abrasive particles other than ceria-based, silica-based, or zirconia-based 20 particles based on total weight slurry, e.g., less than 0.05 or 0.01 weight percent of abrasive particles other than ceria, silica, or zirconia-based particles based on total weight slurry. Alternately stated, such a slurry may contain not more than 0.5 weight percent of abrasive particles other than ceria-based, silica-based, or zirconia-based particles per total 25 weight abrasive particles in the slurry, e.g., less than 0.1, 0.05, or 0.01 weight percent of abrasive particles other than ceria-, silica-, or zirconia-based particles per total weight abrasive particles in the slurry.

30 Ceria particles useful for polishing dielectric materials are well known in the CMP arts and are commercially available. Examples include types referred to as wet-process ceria, calcined ceria, and metal-doped ceria, among others. Likewise, zirconia particles useful for polishing dielectric materials are well known in the CMP arts and are commercially available. Examples include metal-doped zirconia and non-metal-doped

zirconia, among others. Among metal doped zirconia are cerium-, calcium-, magnesium-, or yttrium-doped zirconia with dopant element weight percentage preferentially in a range from 0.1-25%.

Examples of suitable zirconia particles have been described in the patent

5 WO2012092361 (the entirety of which is incorporated herein), and references cited therein. Examples of zirconia particles suitable for use in a slurry as described this application include monoclinic phase, tetragonal phase, and cubic phase or a mixed phase. In terms of doping purity, the zirconia particle can be doped with up to 50% by weight of ceria, calcia, yittria, magnesia, or a combination of any of these. A preferred 10 metal oxide doping range is from 0.1% to 20% by weight. When yittria is used as a dopant, the zirconia is commonly called yittria stabilized zirconia. The zirconia particles will have a particle size distribution, e.g., with D50 (by weight average) of about 10-1000nm, such as from 30-250nm. The zirconia particles preferably exhibit positive zeta 15 potential at acidic pH (e.g. pH 4.0). Zirconia particle can be made from precipitating its chloride salt using a base, and calcination with or without a hydrothermal treatment. Or, it can be made directly from calcining the zirconia carbonate ($Zr(CO_3)(OH)_2$). Preferred calcination temperature lies in the range of 500C to 1700C, and most preferably in the 20 range of 750C to 1100C.

Certain preferred ceria particles for use in a slurry as described include those

20 described in Applicant's co-pending United States Provisional Patent Application Serial Number 14/639,564, filed March, 2015, entitled "Polishing Composition Containing Ceria Abrasive." A preferred polishing composition of the present description can contain abrasive particles as described in that provisional application, including wet-process ceria particles. Therein, slurries are described that may contain a single type of 25 abrasive particles or multiple different types of abrasive particles, based on size, composition, method of preparation, particle size distribution, or other mechanical or physical properties. That description and the present description refer to slurries that contain "first" abrasive particles, meaning that the slurry contains at least this "first" type of abrasive particles and may optionally contain (but is not required to contain) additional 30 abrasive particles that are different from the "first" abrasive particles.

Ceria abrasive particles can be made by a variety of different processes. For example, ceria abrasive particles can be precipitated ceria particles or condensation-polymerized ceria particles, including colloidal ceria particles.

As one more particular example, ceria abrasive particles (e.g., as the first abrasive particles) can be wet-process ceria particles made according to the following process. A first step in synthesizing wet-process ceria particles can be to dissolve a ceria precursor in water. The ceria precursor can be any suitable ceria precursor, and can include a ceria salt having a ceria ion of any suitable charge, e.g., Ce^{3+} or Ce^{4+} . Suitable ceria precursors include, for example, cerium III nitrate, cerium IV ammonium nitrate, cerium III carbonate, cerium IV sulfate, and cerium III chloride. Preferably, the ceria precursor is cerium III nitrate.

The pH of the ceria precursor solution can be increased to form amorphous $\text{Ce}(\text{OH})_3$. The pH of the solution can be increased to any suitable pH, for example to a pH of about 10 or more, e.g., a pH of about 10.5 or more, a pH of about 11 or more, or a pH of about 12 or more. Typically, the solution will have a pH of about 14 or less, e.g., a pH of about 13.5 or less, or a pH of about 13 or less. Any suitable base can be used to increase the pH of the solution. Suitable bases include, for example, KOH, NaOH, NH₄OH, and tetramethylammonium hydroxide. Organic bases such as ethanolamine and diethanolamine are also suitable. The solution will become white and cloudy as the pH increases and amorphous $\text{Ce}(\text{OH})_3$ is formed.

The ceria precursor solution typically is mixed for several hours, such as for about 1 hour or more, e.g., about 2 hours or more, about 4 hours or more, about 6 hours or more, about 8 hours or more, about 12 hours or more, about 16 hours or more, about 20 hours or more, or about 24 hours or more. Typically, the solution is mixed for about 1 hour to about 24 hours, e.g., about 2 hours, about 8 hours, or about 12 hours. When mixing is complete, the solution can be transferred to a pressurized vessel and heated.

The ceria precursor solution can then be heated to any suitable temperature. For example, the solution can be heated to a temperature of about 50° C or more, e.g., about 75° C or more, about 100° C or more, about 125° C or more, about 150° C or more, about 175° C or more, or about 200° C or more. Alternatively, or in addition, the solution can be heated to a temperature of about 500° C or less, e.g., about 450° C or less, about 400°

C or less, about 375° C or less, about 350° C or less, about 300° C or less, about 250° C or less, about 225° C, or about 200° C or less. Thus, the solution can be heated to a temperature within a range bounded by any two of the aforementioned endpoints. For example, the solution can be heated to a temperature of about 50° C to about 300° C, e.g.,

5 about 50° C to about 275° C, about 50° C to about 250° C, about 50° C to about 200° C, about 75° C to about 300° C, about 75° C to about 250° C, about 75° C to about 200° C, about 100° C to about 300° C, about 100° C to about 250° C, or about 100° C to about 225° C.

The ceria precursor solution typically is heated for several hours. For example,

10 the solution can be heated for about 1 hour or more, e.g., about 5 hours or more, about 10 hours or more, about 25 hours or more, about 50 hours or more, about 75 hours or more, about 100 hours or more, or about 110 hours or more. Alternately, or in addition, the solution can be heated for about 200 hours or less, e.g., about 180 hours or less, about 165 hours or less, about 150 hours or less, about 125 hours or less, about 115 hours or

15 less, or about 100 hours or less. Thus, the solution can be heated for a time period bounded by any two of the aforementioned endpoints. For example, the solution can be heated for about 1 hour to about 150 hours, e.g., about 5 hours to about 130 hours, about 10 hours to about 120 hours, about 15 hours to about 115 hours, or about 25 hours to about 100 hours.

20 After heating, the ceria precursor solution can be filtered to separate the precipitated ceria particles. The precipitated particles can be rinsed with excess water to remove unreacted ceria precursor. The mixture of precipitated particles and excess water can be filtered following each rinse step to remove impurities. Once adequately rinsed, the ceria particles can be dried for additional processing, e.g., sintering, or the ceria

25 particles can be directly redispersed.

The ceria particles optionally can be dried and sintered prior to redispersion. The terms “sintering” and “calcining” are used interchangeably herein to refer to the heating of the ceria particles under the conditions described below. Sintering the ceria particles impacts their resulting crystallinity. Without wishing to be bound by any particular

30 theory, it is believed that sintering the ceria particles at high temperatures and for extended periods of time reduces defects in the crystal lattice structure of the particles.

Any suitable method can be used to sinter the ceria particles. As an example, the ceria particles can be dried, and then can be sintered at an elevated temperature. Drying can be carried out at room temperature, or at an elevated temperature. In particular, drying can be carried out at a temperature of about 20° C to about 40° C, e.g., about 25° C, about 30° 5 C, or about 35° C. Alternatively, or in addition, drying can be carried out at an elevated temperature of about 80° C to about 150° C, e.g., about 85° C, about 100° C, about 115° C, about 125° C, or about 140° C. After the ceria particles have been dried, they can be ground to create a powder. Grinding can be carried out using any suitable grinding material, such as zirconia.

10 The ceria particles can be sintered in any suitable oven, and at any suitable temperature. For example, the ceria particles can be sintered at a temperature of about 200° C or more, e.g., about 215° C or more, about 225° C or more, about 250° C or more, about 275° C or more, about 300° C or more, about 350° C or more, or about 375° C or more. Alternatively, or in addition, the ceria particles can be sintered at a temperature of 15 about 1000° C or less, e.g., about 900° C or less, about 750° C or less, about 650° C or less, about 550° C or less, about 500° C or less, about 450° C or less, or about 400° C or less. Thus, the ceria particles can be sintered at a temperature bounded by any two of the aforementioned endpoints. For example, the ceria particles can be sintered at a temperature of about 200° C to about 1000° C, e.g., about 250° C to about 800° C, about 300° C to about 700° C, about 325° C to about 650° C, about 350° C to about 600° C, about 350° C to about 550° C, about 400° C to about 550° C, about 450° C to about 800° C, about 500° C to about 1000° C, or about 500° C to about 800° C.

20 The ceria particles can be sintered for any suitable length of time. For example, the ceria particles can be sintered for about 1 hour or more, e.g., about 2 hours or more, about 5 hours or more, or about 8 hours or more. Alternatively, or in addition, the ceria particles can be sintered for about 20 hours or less, e.g., about 18 hours or less, about 15 25 hours or less, about 12 hours or less, or about 10 hours or less. Thus, the ceria particles can be sintered for a time period bounded by any two of the aforementioned endpoints. For example, the ceria particles can be sintered for about 1 hour to about 20 hours, e.g., about 1 hour to about 15 hours, about 1 hour to about 10 hours, about 1 hour to about 5 30 hours, about 5 hours to about 20 hours, or about 10 hours to about 20 hours.

Ceria particles also can be sintered at various temperatures and for various lengths of time within the ranges described above. For example, the ceria particles can be sintered in a zone furnace, which exposes the ceria particles to one or more temperatures for various lengths of time. As an example, the ceria particles can be sintered at a 5 temperature of about 200° C to about 1000° C for about 1 hour or more, and then can be sintered at a different temperature that is within the range of about 200° C to about 1000° C for about 1 hour or more.

After drying, grinding, and optional sintering, etc., ceria particles can be 10 redispersed in a suitable liquid carrier, e.g., an aqueous carrier, particularly water. If the ceria particles are sintered, then the ceria particles are redispersed after the completion of sintering. Any suitable process can be used to redisperse the ceria particles. Typically, 15 the ceria particles are redispersed by lowering the pH of a mixture of the ceria particles and water using a suitable acid. As pH is lowered, the surfaces of ceria particles develop a cationic zeta potential. This cationic zeta potential creates repulsive forces between the ceria particles, which facilitates their redispersion. Any suitable acid can be used to lower the pH of the mixture. Examples of suitable acids include hydrochloric acid and 20 nitric acid. Organic acids that are highly water-soluble and have hydrophilic functional groups also are suitable. Suitable organic acids include, for example, acetic acid, among others. Acids with multivalent anions, such as H₃PO₄ and H₂SO₄, generally are not preferred. The mixture can be lowered to any suitable pH. For example, the pH of the mixture can be lowered to about 2 to about 5, e.g., about 2.5, about 3, about 3.5, about 4, or about 4.5. Typically, the pH of the mixture is not lowered to less than about 2.

The redispersed ceria particles typically are milled to reduce their particle size. 25 Preferably, ceria particles can be milled simultaneously with redispersion. Milling can be carried out using any suitable milling material, such as zirconia. Milling also can be carried out using sonication or wet-jet procedures. After milling, the ceria particles can be filtered to remove any remaining large particles. For example, the ceria particles can be filtered using a filter having a pore size of about 0.3 μm or more, e.g., about 0.4 μm or more, or about 0.5 μm or more.

30 Certain preferred abrasive particles (e.g., first abrasive particles) can have a median particle size of about 40 nm to about 100 nm. The particle size of a particle is the

diameter of the smallest sphere that encompasses the particle. Particle size can be measured using any of various known and suitable techniques. For example, particle size can be measured using a disc centrifuge, i.e., by differential centrifugal sedimentation (DCS). Suitable disc centrifuge particle size measurement instruments are commercially 5 available, such as from CPS Instruments (Prairieville, LA), e.g., CPS Disc Centrifuge Model DC24000UHR. Unless specified otherwise, the median particle size values reported and claimed herein are based on disc centrifuge measurements.

Preferred ceria abrasive particles (e.g., first abrasive particles) can have a median particle size of about 40 nm or more, e.g., about 45 nm or more, about 50 nm or more, 10 about 55 nm or more, about 60 nm or more, about 65 nm or more, about 70 nm or more, about 75 nm or more, or about 80 nm or more. Alternatively, or in addition, ceria abrasive particles can have a median particle size of about 100 nm or less, e.g., about 95 nm or less, about 90 nm or less, about 85 nm or less, about 80 nm or less, about 75 nm or less, about 70 nm or less, or about 65 nm or less. Thus, ceria abrasive particles can have 15 a median particle size within a range bounded by any two of the aforementioned endpoints. For example, ceria abrasive particles (e.g., first abrasive particles) can have a median particle size of about 40 nm to about 100 nm, e.g., about 40 nm to about 80 nm, about 40 nm to about 75 nm, about 40 nm to about 60 nm, about 50 nm to about 100 nm, about 50 nm to about 80 nm, about 50 nm to about 75 nm, about 50 nm to about 70 nm, 20 about 60 nm to about 100 nm, about 60 nm to about 80 nm, about 60 nm to about 85 nm, or about 65 nm to about 75 nm. Preferred abrasive particles (e.g., first abrasive particles) can have a median particle size of about 60 nm to about 80 nm, e.g., a median particle size of about 65 nm, a median particle size of about 70 nm, or a median particle size of about 75 nm.

25 Abrasive particles (e.g., first abrasive particles) can be present in a polishing composition at any useful concentration (e.g., per total weight of the concentration). An exemplary range of useful concentrations can be from about 0.005 to about 2 weight percent of the polishing composition. For example, first abrasive particles can be present in a polishing composition at a concentration of about 0.005 weight percent or more, e.g., about 0.0075 weight percent or more, about 0.01 weight percent or more, about 0.025 weight percent or more, about 0.05 weight percent or more, about 0.075 weight percent

or more, about 0.1 weight percent or more, or about 0.25 weight percent or more. Alternately, or in addition, first abrasive particles can be present in a polishing composition at a concentration of about 2 weight percent or less, e.g., about 1.75 weight percent or less, about 1.5 weight percent or less, about 1.25 weight percent or less, about 5 1 weight percent or less, about 0.75 weight percent or less, about 0.5 weight percent or less, or about 0.25 weight percent or less. Thus, abrasive particles (e.g., first abrasive particles) can be present in a polishing composition at a concentration within a range bounded by any two of the aforementioned endpoints. For example, abrasive particles (e.g., first abrasive particles) can be present in the polishing composition at a 10 concentration of about 0.005 weight percent to about 2 weight percent, e.g., about 0.005 weight percent to about 1.75 weight percent, about 0.005 weight percent to about 1.5 weight percent, about 0.005 weight percent to about 1.25 weight percent, about 0.005 weight percent to about 1 weight percent, about 0.01 weight percent to about 2 weight percent, about 0.01 weight percent to about 1.5 weight percent, about 0.05 weight percent 15 to about 2 weight percent, about 0.05 weight percent to about 1.5 weight percent, about 0.1 weight percent to about 2 weight percent, about 0.1 weight percent to about 1.5 weight percent, or about 0.1 weight percent to about 1 weight percent based on total weight slurry.

Certain preferred slurry types can contain first abrasive particles at a low end of 20 this range, such as from about 0.1 weight percent to about 0.5 weight percent based on total weight polishing composition, e.g., about 0.15 weight percent to about 0.4 weight percent, about 0.15 weight percent to about 0.35 weight percent, or about 0.2 weight percent to about 0.3 weight percent. More preferably, a slurry may contain first abrasive particles at a concentration of about 0.1 weight percent to about 0.3 weight percent, e.g., 25 about 0.1 weight percent, about 0.15 weight percent, about 0.2 weight percent, about 0.25 weight percent, about 0.28 weight percent, or about 0.29 weight percent based on total weight polishing composition.

Preferred first abrasive particles can have a particle size distribution of at least 30 about 300 nm. Particle size distribution refers to the difference between the particle size of the largest particle and the particle size of the smallest particle. For example, first abrasive particles can have a particle size distribution of at least about 315 nm, e.g., at

least about 320 nm, at least about 325 nm, at least about 330 nm, at least about 340 nm, at least about 350 nm, at least about 355 nm, at least about 360 nm, at least about 365 nm, at least about 370 nm, at least about 375 nm, or at least about 380 nm. Preferably, first abrasive particles have a particle size distribution of at least about 320 nm, e.g., at least 5 about 325 nm, at least about 335 nm, or at least about 350 nm. First abrasive particles can also preferably have a particle size distribution of about not greater than 500 nm, e.g., about 475 nm or less, about 450 nm or less, about 425 nm or less, or about 415 nm or less. Thus, abrasive particles (e.g., first abrasive particles) can have a particle size distribution within a range bounded by any two of the aforementioned endpoints. For 10 example, abrasive particles can have a particle size distribution of about 315 nm to about 500 nm, e.g., about 320 nm to about 480 nm, about 325 nm to about 475 nm, about 335 nm to about 460 nm, or about 340 nm to about 450 nm.

The first abrasive particles as described can have any suitable largest particle size and any suitable smallest particle size, with preferred particles having a particle size 15 distribution of is at least about 300 nm. For example, the abrasive particles can have a smallest particle size of about 1 nm to about 50 nm, e.g., about 1 nm to about 40 nm, about 1 nm to about 30 nm, about 1 nm to about 25 nm, about 1 nm to about 20 nm, about 5 nm to about 25 nm, or about 10 nm to about 25 nm. Preferably, the first abrasive particles have a smallest particle size of about 10 nm to about 30 nm, e.g., about 15 nm, 20 about 20 nm, or about 25 nm. Abrasive particles can have a largest particle size of about 250 nm to about 500 nm, e.g., about 250 nm to about 450 nm, about 250 nm to about 400 nm, about 300 nm to about 500 nm, or about 300 nm to about 400 nm. Preferably, the first abrasive particles have a largest particle size of about 350 nm to about 450 nm, e.g., about 375 nm, about 400 nm, or about 425 nm.

25 A polishing composition can optionally contain additional abrasive particles (e.g., second abrasive particles, third abrasive particles, etc.). Additional abrasive particles can be, for example, metal oxide abrasive particles of a different metal than the first abrasive particles, such as metal oxide abrasive particles of, titania (e.g., titanium dioxide), germania (e.g., germanium dioxide, germanium oxide), magnesia (e.g., magnesium oxide), nickel oxide, co-formed products thereof, or combinations thereof. The 30 additional abrasive particles also can be organic particles of gelatin, latex, cellulose,

polystyrene, or polyacrylate. Alternately, the polishing composition can contain first abrasive particles that are wet-process ceria particles having a median particle size of about 40 nm to about 100 nm and a particle size distribution of at least about 300 nm, wherein the polishing composition does not include any additional (second or third) 5 abrasive particles.

The additional abrasive particles also can be metal oxide abrasive particles of ceria (e.g., cerium oxide) that are a different type of ceria as compared to first abrasive particles of the polishing composition, i.e., ceria particles that are not wet-process ceria particles, such as fumed ceria particles or calcined ceria particles. Alternately, the 10 polishing composition can contain first abrasive particles that are wet-process ceria particles having a median particle size of about 40 nm to about 100 nm and a particle size distribution of at least about 300 nm, wherein the polishing composition does not include any additional ceria particles.

When the polishing composition includes additional abrasive particles (e.g., 15 second abrasive particles, third abrasive particles, etc.), the additional abrasive particles can have any suitable median particle size. For example, the polishing composition can include second abrasive particles having a median particle size of about 1 nm to about 60 nm, e.g., about 1 nm to about 55 nm, about 1 nm to about 50 nm, about 1 nm to about 40 nm, about 1 nm to about 35 nm, about 1 nm to about 30 nm, about 1 nm to about 25 nm, 20 about 1 nm to about 20 nm, about 5 nm to about 50 nm, about 5 nm to about 35 nm, or about 15 nm to about 30 nm. Alternately, second abrasive particles can have a median particle size of about 100 nm to about 350 nm, e.g., about 100 nm to about 300 nm, about 105 nm to about 350 nm, about 115 nm to about 350 nm, about 135 nm to about 325 nm, about 150 nm to about 315 nm, about 175 nm to about 300 nm, about 200 nm to about 250 nm, or about 225 nm to about 250 nm. Preferably, additional abrasive particles (e.g., 25 second abrasive particles, third abrasive particles, etc.) can have a median particle size of about 1 nm to about 35 nm, or a median particle size of about 125 nm to about 300 nm.

Additional abrasive particles (e.g., second abrasive particles, third abrasive particles, etc., in total) can be present in the polishing composition at any suitable 30 amount, in addition to first abrasive particles. In certain slurry embodiments, additional abrasive particles can be present at a concentration of about 0.005 weight percent to

about 2 weight percent based on total weight of the slurry. For example, additional abrasive particles can be present in a polishing composition at a concentration of about 0.005 weight percent or more, e.g., about 0.0075 weight percent or more, about 0.01 weight percent or more, about 0.025 weight percent or more, about 0.05 weight percent 5 or more, about 0.075 weight percent or more, about 0.1 weight percent or more, or about 0.25 weight percent or more. Alternately, or in addition, additional abrasive particles can be present in a polishing composition at a concentration of about 2 weight percent or less, e.g., about 1.75 weight percent or less, about 1.5 weight percent or less, about 1.25 weight percent or less, about 1 weight percent or less, about 0.75 weight percent or less, 10 about 0.5 weight percent or less, or about 0.25 weight percent or less based on total weight of the slurry. Thus, additional abrasive particles can be present in a polishing composition at a concentration within a range bounded by any two of the aforementioned endpoints. For example, a preferred polishing composition can include (in addition to an amount of first abrasive particles as described) second abrasive particles at a 15 concentration of about 0.005 weight percent to about 2 weight percent, e.g., about 0.005 weight percent to about 1.75 weight percent, about 0.005 weight percent to about 1.5 weight percent, about 0.005 weight percent to about 1.25 weight percent, about 0.005 weight percent to about 1 weight percent, about 0.01 weight percent to about 2 weight percent, about 0.01 weight percent to about 1.75 weight percent, about 0.01 weight 20 percent to about 1.5 weight percent, about 0.05 weight percent to about 2 weight percent, about 0.05 weight percent to about 1.5 weight percent, about 0.1 weight percent to about 2 weight percent, or about 0.1 weight percent to about 1.5 weight percent. More preferably, the additional abrasive particles can be present at a concentration of about 0.01 weight percent to about 0.5 weight percent, e.g., about 0.025 weight percent, about 25 0.05 weight percent, about 0.08 weight percent, about 0.1 weight percent, about 0.15 weight percent, about 0.2 weight percent, about 0.25 weight percent, about 0.3 weight percent, or about 0.4 weight percent, based on total weight of the slurry.

When a polishing composition contains additional abrasive particles (e.g., second abrasive particles, third abrasive particles, etc.), the polishing composition optionally can 30 exhibit a multimodal particle size distribution. As used herein, the term “multimodal” means that the polishing composition exhibits a particle size distribution having at least 2

maxima (e.g., 2 or more maxima, 3 or more maxima, 4 or more maxima, or 5 or more maxima). In particular, when the polishing composition contains second abrasive particles, the polishing composition can exhibit a bimodal particle size distribution, i.e., the polishing composition exhibits a particle size distribution having 2 median particle 5 size maxima. The terms “maximum” and “maxima” mean a peak or peaks in the particle size distribution. The peak or peaks correspond to the median particle sizes described herein for the first, second, and any additional abrasive particles. Thus, for example, when a polishing composition contains first abrasive particles and second abrasive particles, with no additional abrasive particles, a plot of the number of particles or 10 relative weight of the particles versus particle size can reflect a bimodal particle size distribution, with a first peak in the particle size range of about 40 nm to about 100 nm and a second peak in the particle size range of about 1 nm to about 35 nm.

The first abrasive particles and any additional abrasive particles present in the polishing composition desirably are suspended in the polishing composition, more 15 specifically in the aqueous carrier of the polishing composition. When the abrasive particles are suspended in the polishing composition, the abrasive particles preferably are colloidally stable. The term colloid refers to the suspension of abrasive particles in the aqueous carrier. Colloidal stability refers to the maintenance of that suspension over time. In the context of this invention, abrasive particles are considered colloidally stable 20 if, when the abrasive particles are placed in 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 25 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.

The polishing composition can exhibit a pH that is below about 7, e.g., from about 1 to about 6.5. Typically, the polishing composition has a pH of about 3 or greater. Also, the pH of the polishing composition typically is about 6 or less. For example, the 30 pH can be in the range of about 3.5 to about 6.5, e.g., a pH of about 3.5, a pH of about 4,

a pH of about 4.5, a pH of about 5, a pH of about 5.5, a pH of about 6, a pH of about 6.5, or a pH in a range defined by any two of these pH values.

Preferred polishing compositions further include a pH-adjusting agent, which can be any suitable pH-adjusting agent. For example, the pH-adjusting agent can be an alkyl 5 amine, an alcohol amine, quaternary amine hydroxide, ammonia, or a combination thereof. In particular, the pH-adjusting agent can be triethanolamine, tetramethylammonium hydroxide (TMAH or TMA-OH), or tetraethylammonium hydroxide (TEAH or TEA-OH). In certain preferred embodiments the pH-adjusting agent can be triethanolamine.

10 The pH-adjusting agent can be present in the polishing composition in any suitable concentration. Desirably, the pH-adjusting agent is present in an amount to achieve or maintain the pH of the polishing composition within a pH range set forth herein, e.g., below about 7, such as in the range of about 1 to about 6, or in the range of about 3.5 to about 5. For example, pH-adjusting agent can be present in the polishing 15 composition at a concentration of about 10 ppm to about 300 ppm, e.g., about 50 ppm to about 200 ppm, or about 100 ppm to about 150 ppm.

The polishing composition includes an aqueous carrier that contains water (e.g., deionized water) and may optionally contain one or more water-miscible organic solvents. Examples of organic solvents that can be used include alcohols such as 20 propenyl alcohol, isopropyl alcohol, ethanol, 1-propanol, methanol, 1-hexanol, and the like; aldehydes such as acetylaldehyde and the like; ketones such as acetone, diacetone alcohol, methyl ethyl ketone, and the like; esters such as ethyl formate, propyl formate, ethyl acetate, methyl acetate, methyl lactate, butyl lactate, ethyl lactate, and the like; ethers including sulfoxides such as dimethyl sulfoxide (DMSO), tetrahydrofuran, 25 dioxane, diglyme, and the like; amides such as N, N-dimethylformamide, dimethylimidazolidinone, N-methylpyrrolidone, and the like; polyhydric alcohols and derivatives of the same such as ethylene glycol, glycerol, diethylene glycol, diethylene glycol monomethyl ether, and the like; and nitrogen-containing organic compounds such as acetonitrile, amines, isopropylamine, imidazole, dimethylamine, and the like.

30 Preferably, the aqueous carrier is water alone without the presence of organic solvent or

with only an insignificant amount of organic solvent, such as less than 0.1, 0.05, 0.01, or 0.005 weight percent organic solvent.

The polishing composition can include additional ingredients as additives. One example of optional additive is an anionic copolymer derived from monomers that 5 include: a carboxylic acid monomer, a sulfonated monomer or a phosphonated monomer, and an acrylate monomer. Other examples include other polymers (e.g., nonionic polymers) including polyvinylpyrrolidones, polyethylene glycols (e.g., polyethylene glycol), and a polyvinylalcohols (e.g., a copolymer of 2-hydroxyethylmethacrylic acid and methacrylic acid). Still other optional additives include silanes such as amino 10 silanes, ureido silanes, and a glycidyl silanes. And still other optional additives include: an N-oxide of a functionalized pyridine (e.g., picolinic acid N-oxide); a starch; a cyclodextrin (e.g., alpha-cyclodextrin or beta-cyclodextrin); or combinations of two or more of these.

15 Polyvinylpyrrolidone can be useful as an additive, and can have any suitable molecular weight. For example, polyvinylpyrrolidone as an additive can have a molecular weight about 10,000 grams per mole (g/mol) to about 1,000,000 g/mol, e.g., up to or about 20,000 g/mol, 30,000 g/mol, 40,000 g/mol, 50,000 g/mol, or 60,000 g/mol.

20 When a slurry includes nonionic polymer as an additive, and when the nonionic polymer is polyethylene glycol, the polyethylene glycol can have any suitable molecular weight. For example, the polyethylene glycol can have a molecular weight of about 200 g/mol to about 200,000 g/mol, e.g., about 8000 g/mol, about 100,000 g/mol.

25 When a slurry includes silane as an additive, the silane can be any suitable amino silane, ureido silane, or glycidyl silane. Some specific examples include 3-aminopropyltrimethoxysilane, 3-aminopropylsilanetriol, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilanetriol, (N,N-dimethyl-3-aminopropyl)trimethoxysilane, N-phenyl-3-aminopropyltrimethoxysilane, ureidopropyltriethoxysilane, and 3-glycidopropyldimethylethoxysilane.

30 Certain particularly preferred additives in a polishing composition include copolymers of 2-hydroxyethylmethacrylic acid and methacrylic acid;

polyvinylpyrrolidone; aminopropylsilanetriol; picolinic acid N-oxide; picolinic acid, starch; alpha-cyclodextrin; beta-cyclodextrin; and combinations thereof.

An additive or additives (e.g., the anionic copolymer of a carboxylic acid monomer, a sulfonated monomer, or a phosphonated monomer, and an acrylate, a 5 polyvinylpyrrolidone, or a polyvinylalcohol; the silane; the N-oxide of a functionalized pyridine; picolinic acid; the starch; the cyclodextrin; or a combination thereof, in total) can be present in a polishing composition as described at any suitable concentration. Preferably, additive or additives are present in the polishing composition at a concentration of about 1 ppm to about 500 ppm, e.g., about 5 ppm to about 400 ppm, 10 about 10 ppm to about 400 ppm, about 15 ppm to about 400 ppm, about 20 ppm to about 400 ppm, about 25 ppm to about 400 ppm, about 10 ppm to about 300 ppm, about 10 ppm to about 250 ppm, about 30 ppm to about 350 ppm, about 30 ppm to about 275 ppm, about 50 ppm to about 350 ppm, or about 100 ppm to about 300 ppm. More preferably, additive or additives are present in the polishing composition at a concentration of about 15 1 ppm to about 300 ppm, e.g., about 1 ppm to about 275 ppm, about 1 ppm to about 250 ppm, about 1 ppm to about 100 ppm, about 1 ppm to about 50 ppm, about 10 ppm to about 250 ppm, about 10 ppm to about 100 ppm, or about 35 ppm to about 250 ppm.

In particular embodiments, picolinic acid can be included in the slurry. The amount of picolinic acid may be any desired amount, such as an amount in a range from 1 20 ppm to 1,000 ppm, e.g., from 100 ppm to about 800 ppm, such as from 250 ppm to 750 ppm. As used herein, ppm relates to parts per million on a weight to weight basis. That is, 1,000 ppm would be equivalent to 0.1 weight percent. Relative to the removal rate accelerator, an exemplary range of picolinic acid can be from about 5 to 80 weight percent picolinic acid based on the weight of the removal rate accelerator, e.g., from 20 to 25 60 weight percent picolinic acid based on the weight of the removal rate accelerator.

A polishing composition as described may also optionally include cationic polymer. The cationic polymer is selected from a quaternary amine, a cationic polyvinyl alcohol, a cationic cellulose, and combinations thereof. The polishing composition 30 optionally can include a cationic polymer selected from a quaternary amine, a cationic polyvinyl alcohol, a cationic cellulose, and combinations thereof, in addition to one or more of the additives described above, i.e., one or more of an anionic copolymer of a

carboxylic acid monomer, sulfonated monomer or a phosphonated monomer, and an acrylate; a polyvinylpyrrolidone or a polyvinylalcohol; polyethylene glycol; a nonionic polymer; a silane; an N-oxide of a functionalized pyridine; a starch; and a cyclodextrin. Alternatively, the polishing composition can include a cationic polymer without one or

5 more of these additives described above.

A cationic polymer can be a polymer containing a quaternary amine group or made of quaternary amine monomers. For example, a cationic polymer can be a selected from poly(vinylimidazolium), a poly(methacryloyloxyethyltrimethylammonium) halide such as poly(methacryloyloxyethyltrimethylammonium) chloride (polyMADQUAT), a 10 poly(diallyldimethylammonium) halide such as poly(diallyldimethylammonium) chloride (polyDADMAC), and polyquaternium-2. Preferably, when the cationic polymer is a quaternary amine polymer, the cationic polymer is poly(vinylimidazolium).

Alternately, a cationic polymer can be any suitable cationic polyvinyl alcohol or cationic cellulose. Preferably, the cationic polymer is a cationic polyvinyl alcohol. For 15 example, the cationic polyvinyl alcohol can be the Nippon Gosei GOHSEFIMER K210TM polyvinyl alcohol product.

A cationic polymer (e.g., quaternary amine polymer, the cationic polyvinyl alcohol, the cationic cellulose, or a combination thereof, in total) can be present in a polishing composition at any suitable concentration, for example at a concentration of 20 about 1 ppm to about 250 ppm, e.g., about 1 ppm to about 100 ppm, about 1 ppm to about 50 ppm, about 1 ppm to about 40 ppm, about 1 ppm to about 25 ppm, about 5 ppm to about 225 ppm, about 5 ppm to about 100 ppm, about 5 ppm to about 50 ppm, about 10 ppm to about 215 ppm, about 10 ppm to about 100 ppm, about 15 ppm to about 200 ppm, about 25 ppm to about 175 ppm, about 25 ppm to about 100 ppm, or about 30 ppm to 25 about 150 ppm.

When the cationic polymer is poly(vinylimidazolium), the cationic polymer can preferably be present in a polishing composition at a concentration of about 1 ppm to about 10 ppm, e.g., about 2 ppm, about 5 ppm, about 6 ppm, about 7 ppm, about 8 ppm, or about 9 ppm. More preferably, when the cationic polymer is poly(vinylimidazolium), 30 the cationic polymer can preferably be present in the polishing composition at a

concentration of about 1 ppm to about 5 ppm, e.g., about 2 ppm, about 3 ppm, or about 4 ppm.

The polishing composition can also, optionally, include a carboxylic acid. The carboxylic acid can be any suitable carboxylic acid, e.g., having a pKa of about 1 to about 6, e.g., from about 2 to about 6, such as from about 3.5 to about 5. Examples of useful carboxylic acids include acetic acid, propionic acid, and butanoic acid.

A carboxylic acid can be present in the polishing composition at any suitable concentration. Preferably, the carboxylic acid is present in the polishing composition at a concentration of about 10 ppm to about 1000 ppm, e.g., about 10 ppm to about 500 ppm, about 10 ppm to about 250 ppm, about 25 ppm to about 750 ppm, about 25 ppm to about 500 ppm, about 25 ppm to about 250 ppm, about 30 ppm to about 250 ppm, about 35 ppm to about 350 ppm, about 50 ppm to about 425 ppm, about 55 ppm to about 400 ppm, or about 75 ppm to about 350 ppm. More preferably, the carboxylic acid can be present in the polishing composition at a concentration of about 25 ppm to about 150 ppm, e.g. about 40 ppm, about 50 ppm, about 60 ppm, about 75 ppm, about 100 ppm, or about 125 ppm.

Desirably, the pH of the polishing composition can be within about 2 units of the pKa of the carboxylic acid. As an example, if the pH of the polishing composition is about 3.5, the pKa of the carboxylic acid preferably is about 1.5 to about 5.5.

When the polishing composition includes cationic polymer, and when the cationic polymer is a quaternary amine polymer, the polishing composition preferably also includes a carboxylic acid. When the polishing composition includes cationic polymer, and the cationic polymer is selected from a cationic polyvinyl alcohol and a cationic cellulose, the polishing composition optionally further includes a carboxylic acid.

A polishing composition may optionally include one or more other additives such as a surfactant or rheological control agent, including viscosity enhancing agents and coagulants (e.g., polymeric rheological control agents, such as, for example, urethane polymers), a dispersant, a biocide (e.g., KATHON™ LX), or the like. Suitable surfactants include, for example, cationic surfactants, anionic surfactants, anionic polyelectrolytes, nonionic surfactants, amphoteric surfactants, fluorinated surfactants, mixtures thereof.

Preferred polishing compositions of the present description are designed to be used for CMP processing of dielectric materials, e.g., pattern dielectric. The polishing compositions, for this purpose, are not designed for and are not required to be effective in processing a metal surface of a substrate. Accordingly, these preferred polishing

5 compositions can exclude abrasive and chemical ingredients of CMP compositions designed and effective for processing a metal surface, examples of such chemical ingredients being metal passivating agents and metal chelating agents. These preferred slurries do not require and can preferably exclude chemical ingredients that are intended to act as metal passivating agents or as metal chelating agents during CMP processing.

10 This of course does not require that all slurries of this description exclude any form of ingredient that may exhibit some level of metal passivating or metal chelating behavior, especially to the extent that the presently-described slurries may be expressed as containing chemistry that might exhibit either metal passivating (e.g., salicylhydroxamic acid) or metal chelating behavior, if present in a slurry used for processing a metal-

15 containing substrate. Instead, a slurry embodiment can be useful without requiring an ingredient (different from ingredients specifically described herein, such as specific removal rate accelerators) that is either intended or effective to cause metal passivation or metal chelation. Not including ingredients specifically described as useful in the present slurries that may exhibit some level of metal passivating (e.g., salicylhydroxamic acid or

20 other removal rate accelerators) or metal chelating activity, some slurry embodiments can include not more than an insubstantial amount of ingredients that are metal passivating or metal chelating materials, e.g., less than 0.001, 0.0005, or 0.0001 weight percent metal passivating agent based on total slurry weight; e.g., less than 0.01, 0.005, or 0.001 weight percent metal chelating compound based on total slurry weight.

25 Examples of specific metal passivating agents that are not required in, and that may be specifically excluded from, a slurry of the present description are identified as “secondary film-forming metal-passivating agents” of compositions of United States patent 8,435,421 (the entirety of which is incorporated herein by reference) (see column 6, lines 29-67). These agents include compounds having the general formula (II): $Z-X^2(Y^2R^5)(Y^3R^6)$, as well as salts or other chemical (e.g., base or acid) forms of compounds of formula (II), and partially neutralized forms of formula (II).

In formula (II), Z is NH₂ or OH; X² is P=O or C; Y² and Y³ are each independently N, NH, or O; and R⁵ and R⁶ can each independently be R⁷-(OCH₂CH₂)_n-, wherein R⁷ can be H, C₁-C₂₀-alkyl, phenyl, or C₁-C₂₀-alkyl-substituted phenyl, and wherein "n" has an average value in the range of about 2 to about 1000, or when Y² and Y³ each independently are N or NH, then R⁵ and R⁶ each independently can be N, NH, or CH, and together form a five-membered ring heterocycle with X², Y² and Y³. Preferably, R⁷ is C₁-C₂₀-alkyl, phenyl, or C₁-C₂₀-alkyl-substituted phenyl. In some preferred embodiments, R⁷ is C₁-C₂₀-alkyl-substituted phenyl, particularly nonylphenyl.

Non-limiting examples of compounds of formula (II) include heterocycles (e.g., 10 5-aminotetrazole, 5-amino-1,2,-4-triazole, and the like), and phosphate esters such as bis-pegylated phosphate esters, particularly phosphate esters that include poly(oxyethylene) chains attached to two oxygens of the phosphate group, wherein the poly(oxyethylene) chains are terminated by an aryl ether group (e.g., phenyl), an alkyl ether group (e.g., a C₁-C₂₀-alkyl, such as lauryl or stearyl), or an alkylaryl ether group (e.g., C₁-C₂₀-15 alkylphenyl, such as nonylphenyl). The term "poly(oxyethylene)" refers to a polymer or oligomer having an average of 2 to about 1000 oxyethylene (-OCH₂CH₂-) monomer units, preferably 2 to 100 (e.g., 5, 10, 20, 30, 40, 50, 60, 70, 80, or 90) oxyethylene units per poly(oxyethylene) chain. One specific example of a phosphate ester-type passivating agent is a bis-(nonylphenylpoly(oxyethylene)) phosphate ester (NPPOP), which is 20 commercially available under the trade name SURFONIC™ PE 1198, from Huntsman.

Examples of specific metal chelating agents that are not required in, and that may be specifically excluded from, a slurry of the present description are identified in United States patent 8,435,421 at column 7, lines 17-51. These include oxalic acid, amino-substituted carboxylic acids (e.g., amino polycarboxylates, such as iminodiacetic acid 25 (IDA), ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDS), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), as well as alpha-amino acids, such as glycine, beta-amino acids, and the like); hydroxyl-substituted carboxylic acids (e.g., glycolic acid and lactic acid, as well as hydroxyl polycarboxylic acids, such as malic acid, citric acid, tartaric acid, and the like); phosphonocarboxylic 30 acids; aminophosphonic acids; salts of any of the foregoing; combinations of two or more of the foregoing; and the like.

A polishing composition can be prepared in any useful manner, many examples of which are known to those of skill. The polishing composition can be prepared in a batch or continuous process. Generally, the polishing composition can be prepared by combining its components in any order, with suitable mixing, to produce a uniform 5 mixture (slurry) of the components. The term “component” as used herein includes individual ingredients (e.g., first abrasive particles, hydroxamic acid, or substituted hydroxamic acid, pH-adjusting agent, etc.) as well as any combination of ingredients.

For example, removal rate accelerator can be added to water at a desired concentration. The pH of the resultant aqueous solution can then be adjusted (as desired) 10 and abrasive particles (e.g., first abrasive particles) can be added to the solution at a desired concentration. Other ingredients can also be incorporated into the solution at a time to allow uniform incorporation of the ingredients.

A polishing composition can be prepared soon or immediately prior to its use in a CMP process, with one or more components added to the polishing composition soon or 15 shortly before use (e.g., within about 1 minute before use, or within about 1 hour before use, or within about 7 days before use). A polishing composition also can be prepared by mixing the components at the surface of the substrate during a CMP polishing operation or immediately before applying the slurry to a substrate.

In alternate embodiments, a polishing composition can be provided as a 20 concentrate that is designed to be transported or stored commercially, then diluted for use with an appropriate amount of aqueous carrier, particularly water, at a time shortly before use. In these embodiments, the polishing composition concentrate can include first abrasive particles, removal rate accelerator, pH-adjusting agent, and water, in amounts such that, upon dilution of the concentrate with an appropriate amount of water, each 25 component of the polishing composition will be present in the diluted polishing composition in an amount within the a range specified hereinabove for a polishing composition. Furthermore, the concentrate can contain a fraction of the aqueous carrier (e.g., water) present in the polishing composition during use, to ensure that other components are at least partially or fully dissolved in the concentrate.

30 While a polishing composition can be prepared well before, or even shortly before, use, the polishing composition also can be produced by mixing the components of

the polishing composition at or near a point-of-use. As used herein, the term “point-of-use” refers to the point at which the polishing composition is applied to a substrate surface (e.g., the polishing pad or the substrate surface itself). When the polishing composition is to be prepared by point-of-use mixing, the components of the polishing
5 composition are separately stored in two or more storage devices.

To mix components contained in storage devices to produce a polishing composition at or near a point-of-use, the storage devices typically are provided with one or more flow lines leading from each storage device to the point-of-use of the polishing composition (e.g., the platen, the polishing pad, or the substrate surface). The term “flow
10 line” refers a path of flow from an individual storage container to the point-of-use of the component stored therein. The one or more flow lines can each lead directly to the point-of-use, or, in the situation where more than one flow line is used, two or more of the flow lines can be combined at any point into a single flow line that leads to the point-of-use.
15 Furthermore, any of the one or more flow lines (e.g., the individual flow lines or a combined flow line) can first lead to one or more of the other devices (e.g., pumping device, measuring device, mixing device, etc.) prior to reaching the point-of-use of the component(s).

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

When two or more components of a polishing composition are combined prior to reaching a point-of-use, the components can be combined in the flow line and delivered to the point-of-use without the use of a mixing device. Alternatively, one or more of the flow lines can lead into a mixing device to facilitate the combination of two or more of 5 the components. Any suitable mixing device can be used. For example, the mixing device can be a nozzle or jet (e.g., a high pressure nozzle or jet) through which two or more of the components flow. Alternately, a mixing device can be a container-type mixing device that includes one or more inlets by which two or more components of the polishing composition are introduced to the container-type mixing device, and at least 10 one outlet through which mixed components exit to be delivered to the point-of-use, either directly or via other elements of the apparatus (e.g., via one or more flow lines). A mixing device may include a single chamber or more than one chamber, each chamber having at least one inlet and at least one outlet, wherein two or more components are combined in each chamber. If a container-type mixing device is used, the mixing device 15 preferably includes a mixing mechanism to uniformly agitate and combine the components, preferably without producing undue foam or air entrapment. Mixing mechanisms are generally known in the art and include stirrers, blenders, agitators, paddled baffles, gas sparger systems, vibrators, etc.

A polishing composition as described may be useful for polishing any suitable 20 substrate, and can be particularly useful for polishing a substrate that includes a dielectric-containing (e.g., silicon oxide-containing) surface, especially one having a region of pattern dielectric that includes raised dielectric areas separated by trench areas of dielectric material. Exemplary substrates include those being processed for use as a component of a flat panel display, integrated circuit, memory or rigid disk, inter-layer 25 dielectric (ILD) device, microelectromechanical system (MEMS), 3D NAND device, or the like.

The polishing composition is particularly well suited for planarizing or polishing 30 a substrate that has undergone shallow trench isolation (STI) or a similar process, whereby dielectric is coated over a structured lower layer to produce regions of pattern dielectric material. For a substrate that has undergone shallow trench isolation, typical step heights can be in a range from 1,000 angstroms to 7,000 angstroms.

Certain embodiments of the described polishing composition are also useful for planarizing or polishing a substrate that is an in-process 3D NAND flash memory device. In such substrates, a lower layer that is made of semiconductor layer that includes trenches, holes, or other structures that have a high aspect ratio, such as an aspect ratio of 5 at least 10:1, 30:1, 60:1 or 80:1. When a surface having structures of such high aspect ratios is coated by dielectric material, the resultant pattern dielectric will exhibit a high step height, such as a step height that is substantially greater than 7,000 angstroms, e.g., greater than 10,000, 20,000, 30,000, or 40,000 angstroms, or more.

The dielectric layer of any of the devices described herein may comprise, consist 10 essentially of, or consist of any suitable dielectric material, many of which are well known, including various forms of silicon oxide and silicon oxide-based dielectric materials. For example, a dielectric layer that includes silicon oxide or silicon oxide-based dielectric layer can comprise, consist of, or consist essentially of any one or more of: tetraethoxysilane (TEOS), high density plasma (HDP) oxide, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), high aspect ratio process (HARP) oxide, spin 15 on dielectric (SOD) oxide, chemical vapor deposition (CVD) oxide, plasma-enhanced tetraethyl ortho silicate (PETEOS), thermal oxide, or undoped silicate glass.

According to processes of the present description, a substrate may include a silicon nitride liner located at locations of intended ends of a dielectric polishing and 20 removal step. In other embodiments, a substrate does not require and can optionally and preferably exclude a silicon nitride “liner” or “cap” disposed at locations of an end a step of removing dielectric from an active area.

According to these and other embodiments of substrates that may be processed by methods, using slurries, as described, a substrate may also include a silicon nitride layer, 25 e.g., over a dielectric layer. When processing dielectric substrates having raised (12) and lower (e.g., trench, 14) features, a layer of silicon nitride (not shown) may be placed over the raised and lowered dielectric material to protect the trench areas and improve planarization efficiency during CMP processing.

A substrate can be planarized or polished with the polishing composition 30 described herein by any suitable technique, especially CMP processing using chemical-mechanical polishing (CMP) equipment. Typically, the CMP apparatus includes a platen,

which, when in use, is in motion and has a velocity that results from orbital, linear, or circular motion; a polishing pad in contact with the platen and moving with the platen when in motion; and a carrier that holds a substrate to be polished by contacting and moving relative to the surface of the polishing pad. Polishing takes place by the substrate 5 being placed in contact with a polishing composition as described, and typically a polishing pad, then removing at least a portion of the surface of the substrate, e.g., pattern dielectric material. Any suitable polishing conditions can be used.

A substrate can be planarized or polished with the chemical-mechanical polishing composition in conjunction with any suitable polishing pad (e.g., polishing surface).
10 Suitable polishing pads include, for example, woven and non-woven polishing pads. Moreover, suitable polishing pads can include 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, 15 polyamide, polyurethane, polystyrene, polypropylene, coformed products thereof, and mixtures thereof.

Optionally, the CMP apparatus includes 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 20 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 25 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.

Depending on the substrate being processed, an initial step height may be at least 1,000, 2,000, or 5,000 angstroms, and may be substantially greater, such as greater than 30 7,000 angstroms, or at least 10,000, 20,000, 30,000, or 40,000 angstroms, measured before beginning a step of CMP processing.

Figure 1 schematically shows an initial step height, h_0 , and an initial trench thickness, t_0 , of a substrate, before polishing. After polishing, step height is reduced to h_1 and trench thickness is reduced to t_1 . Referring to figure 1, illustrated is an exemplary substrate having an initial step height h_0 and an initial trench thickness is t_0 . The 5 material of the step height can be mostly dielectric such as TEOS, BPSG, or other amorphous silica-containing materials. The key step in 3D NAND dielectric (and other bulk oxide removal) processing is to reduce step height, h_1 , to a low number (e.g., <1000 or < 900 angstroms) at a trench loss (t_0-t_1) as low as possible. Trench loss refers to the difference between a thickness of a trench (t_0) before CMP processing, less the thickness 10 of the trench after CMP processing (t_1); trench loss equals t_0-t_1 (for a given amount of processing). For good planarization efficiency (PE), the final step height must be achieved at a reasonable trench loss. This requires a slurry with a higher removal rate on the active (raised) areas than at the trench area.

15 Removal rate of dielectric material at raised (active) areas is referred to as a removal rate of pattern material (e.g., pattern oxide) or “pattern removal rate” or “active removal rate.” The pattern removal rate achieved using a process and slurry as described can be any useful rate, and for any given process and substrate will depend in great part on the dimensions (e.g., width) of the raised areas and process conditions such as the amount of pressure between a polishing pad and a substrate. According to preferred 20 processes, a removal rate of pattern dielectric material can be at least 2,000 angstroms per minute, preferably at least 4,000 angstroms per minute, such as at least about 5,000 or 6,000 angstroms per minute, optionally even up to 10,000, 14,000, or 15,000 angstroms per minute.

25 According to preferred processes of CMP planarization of substrates described herein, the pattern dielectric can be processed to a planarized surface by CMP processing of the pattern dielectric for a time that is less than 5 minutes, e.g., less than 3, 2, or 1 minute. This can be accomplished for a substrate with pattern dielectric that includes an initial step height of at least 7,000 or 10,000, e.g., 20,000, 30,000, or 40,000 angstroms. The surface is considered to be effectively planarized upon achieving a reduced (by 30 polishing) step height (i.e., a “remaining” step height) of less than 1,000 angstroms, e.g., less than 900 angstroms, 500 angstroms, 300 angstroms, or 250 angstroms.

According to certain processes and slurries as described, a removal rate of dielectric material (e.g., pattern rate of silicon oxide), planarization efficiency, or both, can be improved by use of a removal rate accelerator of Formula 1 (in a CMP slurry) as compared to an otherwise identical process that does not use a removal rate accelerator of

5 Formula 1. According to certain particularly preferred processes and slurries, removal rate of dielectric material (e.g., pattern rate of silicon oxide) can be increased and planarization efficiency can at the same time be improved, by use of a removal rate accelerator of Formula 1. Both high active removal rate and good planarization efficiency are desired in a CMP slurry and process. Each is separately desirable, but

10 improvement to both of the two performance properties in a single CMP process is understood to be not easily achieved and of especially high commercial value.

As described herein an improvement in active removal rate, planarization efficiency, or both, as well as improvements in trench loss, self-stopping behavior etc., is measured relative to an otherwise identical CMP process using an otherwise identical

15 slurry, except that the otherwise identical slurry does not contain removal rate accelerator of Formula 1. The otherwise identical slurry may contain no chemical that is comparable to a rate accelerator of Formula 1, or may contain an amount of a chemical compound that is in some respects similar to a rate accelerator of Formula 1 but that still falls outside of the structural definition of Formula 1. For example, chemical compounds that

20 in some respects are similar to rate accelerators of Formula 1 but still fall outside of the definition of Formula 1 include chemical compounds that are similar to Formula 1 but have a different R groups. Other comparable compounds may differ from Formula 1 in other respects but may still be a chemical compound of comparable molecular weight that includes an amine group (-NH₂) adjacent to a carboxyl (-C(O)-) group, the compound

25 also containing a hydroxide (-OH) group either attached to the amine group (i.e., -NH(OH)), or elsewhere. Examples of compounds that are comparable in these respects to removal rate accelerators of Formula 1, but chemically outside of the definition of Formula 1, include 4-hydroxybenzamide, hydroxyurea, salicylamide, and benzamide. (See figures 2 through 4).

30

EXAMPLES

Figure 2 shows comparative removal rates of blanket dielectric material using equipment and conditions as shown, including an IC1010 pad, 1 percent zirconia abrasive particles in a CMP polishing slurry, a pad pressure of 5 psi, a slurry pH of 5.5, and 300 ppm of each of the different compounds shown. Some compounds are removal rate accelerators of Formula 1, and others are chemical compounds (not necessarily in the prior art) that contain chemical groups in common with the removal rate accelerators of Formula 1 (e.g., amine, amide, hydroxy, carboxyl, and aromatic or substituted aromatic groups) but that fall outside of the definition of Formula 1. The first bar in the graph represents salicylhydroxamic acid (SHA) with a yttrium-doped zirconia particle. The data show a higher removal rate by use of removal rate accelerators of Formula 1, as compared to some chemically similar non-Formula 1 compounds present in the same amount, and as compared to a slurry containing no removal rate accelerator.

Figure 3 shows comparative removal rates of blanket dielectric material using equipment and conditions as shown, including an IC1010 pad, 0.286 percent ceria abrasive particles in a CMP polishing slurry, a pad pressure of 3 psi, a slurry pH of 5.5, and 250 ppm of each of the different compounds shown. Some compounds are removal rate accelerators of Formula 1, and others are chemical compounds (not necessarily in the prior art) that contain chemical groups in common with the removal rate accelerators of Formula 1 (e.g., amine, amide, hydroxy, carboxyl, and aromatic or substituted aromatic groups) but that fall outside of the definition of Formula 1. The data show a higher removal rate by use of removal rate accelerators of Formula 1 as compared to some chemically similar non-Formula 1 compounds present in the same amount, and as compared to a slurry containing no removal rate accelerator.

Figure 4 shows comparative removal rates (as angstroms per minute) of blanket silicon oxide dielectric material using a comparative slurry and an inventive slurry containing salicylhydroxamic acid (SHA) as a removal rate accelerator. The comparative slurry in this example is a ceria containing slurry that has exhibited high polishing rates for silicon oxide. Equipment and conditions used were a Reflexion LK CMP tool, an IC1010 pad, and pad downforce pressures of 3 or 4 psi. The comparative abrasive slurries (A through D) contained 5 weight percent ceria abrasive particles, 500 ppm picolinic acid, no removal rate accelerator of Formula 1, and the ceria particles were of a

D50 particles size of 100 nanometers. The inventive slurries (E through H) contained 5 weight percent zirconia abrasive particles (St.Gobain ZrO₂-180), 600 ppm salicylhydroxamic acid (SHA) as a removal rate accelerator, and had a slurry pH of 5.5. Slurries A, B, E and F were evaluated at 3 psi downforce pressure, while slurries C, D, G and H were at 4 psi. All polishing conditions and materials were the same other than the different slurries and downforce pressures as indicated. The data show advantageously high removal rates by use of the zirconia plus a removal rate accelerator of Formula 1 (SHA), with the removal rates being equivalent to the comparative slurry.

In addition to the illustrated oxide removal rate, a silicon nitride removal rate is also relevant here, as silicon nitride is often used in 3D NAND fabrication as a liner to protect a trench area (for improved planarization efficiency). Using such process steps, the silicon nitride liner on the pattern active area must be removed first (without unduly affecting the trench area) with relative fast speed. For the same slurries in Figure 4, the inventive slurry containing zirconia and removal rate accelerator of Formula 1 (SHA) exhibited a silicon nitride removal rate of 2100A/min, and the comparative slurry with ceria and picolinic acid exhibited a silicon nitride removal rate of less than 200A/min.

Claims:

1. A method of polishing a dielectric-containing surface of a substrate, the method comprising:

providing a substrate comprising a surface that includes dielectric

5 material,

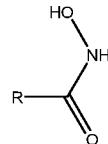
providing a polishing pad,

providing a chemical-mechanical polishing composition comprising:

an aqueous medium,

abrasive particles dispersed in the aqueous medium, and

removal rate accelerator having the formula:



wherein R is selected from : straight or branched alkyl, aryl, substituted aryl, alkoxy, straight or branched halogen-substituted alkyl, halogen-substituted aryl, and halogen-substituted alkoxy,

15 the slurry having a pH of below about 7,

contacting the substrate with the polishing pad and the chemical-mechanical polishing composition; and

moving the polishing pad and the chemical-mechanical polishing composition relative to the substrate to abrade at least a portion of the dielectric layer on
20 a surface of the substrate to polish the substrate.

2. The method of claim 1 wherein the abrasive particles comprise ceria, zirconia, or a mixture thereof.

25 3. The method of claim 1, wherein particle is zirconia and the slurry pH is about 3.5 to about 6.5.

4. The method of claim 3, wherein the zirconia comprises metal-doped zirconia, non-metal-doped zirconia, or a combination thereof.

5. The method of claim 1 wherein R is selected from methyl, phenyl, 2-hydroxyphenyl, methoxy ethoxy, or butoxy.

6. The method of claim 1 wherein the substrate comprises a surface that includes
5 pattern dielectric material comprising raised areas of the dielectric material and trench areas of the dielectric material, a difference between a height of the raised areas and a height of the trench areas being step height.

7. The method of claim 1 wherein the removal rate accelerator is selected from the
10 group consisting of acetohydroxamic acid, benzhydroxamic acid, salicylhydroxamic acid, N-hydroxyurethane, N-boc hydroxylamine and combinations thereof.

8. The method of claim 1 wherein the composition further comprises picolinic acid.

15 9. The method of claim 8 wherein the picolinic acid is in an amount in a range from 5 to 80 weight percent based on the weight of the removal rate accelerator.

10. The method of claim 1 wherein the removal rate accelerator is salicylhydroxamic acid.

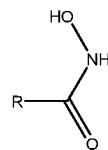
20 11. The method of claim 1 wherein removal rate accelerator is present in the polishing composition at a concentration of about 5 to about 3,000 parts per million.

12. The method of claim 1 wherein the pattern dielectric consists of dielectric
25 material selected from silicon oxide, tetraethoxysilane, phosphosilicate glass, or borophosphosilicate glass.

13. A chemical-mechanical polishing composition useful for polishing a dielectric-containing substrate, the composition comprising:

30 aqueous medium,
abrasive particles dispersed in the aqueous medium, and

removal rate accelerator having the formula:



wherein R is selected from; a straight or branched alkyl, aryl, substituted aryl, alkoxy,

5 straight or branched halogen-substituted alkyl, halogen-substituted aryl, and halogen-substituted alkoxy,

and the slurry has a pH of below about 7.

10 14. The composition of claim 13 wherein R is methyl, phenyl, 2-hydroxyphenyl, methoxy ethoxy, or butoxy.

15. The composition of claim 13 wherein the removal rate accelerator is selected from the group consisting of acetohydroxamic acid, benzhydroxamic acid,

15 salicylhydroxamic acid, N-hydroxyurethane, and N-boc hydroxylamine, and combinations thereof.

16. The composition of claim 13 further comprising picolinic acid.

20 17. The composition of claim 16 wherein the picolinic acid is in an amount in a range from 5 to 80 weight percent based on the weight of the removal rate accelerator.

18. The composition of claim 13 wherein the removal rate accelerator is salicylhydroxamic acid.

25

19. The composition of claim 13 wherein removal rate accelerator is present in the polishing composition at a concentration of about 5 to about 3,000 parts per million, based upon the weight of the composition.

20. The composition of claim 13 wherein the abrasive particles comprise ceria, zirconia, or a mixture thereof.

21. The composition of claim 20 wherein the abrasive particles are wet-process ceria 5 particles, calcined ceria particles, metal-doped ceria particles, zirconia particles, metal-doped zirconia particles, or a combination thereof.

22. The composition of claim 21 wherein the abrasive particles are wet-process ceria particles having a median particle size of about 40 to about 100 nanometers, are present 10 in the polishing composition at a concentration of about 0.005 weight percent to about 2 weight percent, and have a particle size distribution of at least about 300 nanometer.

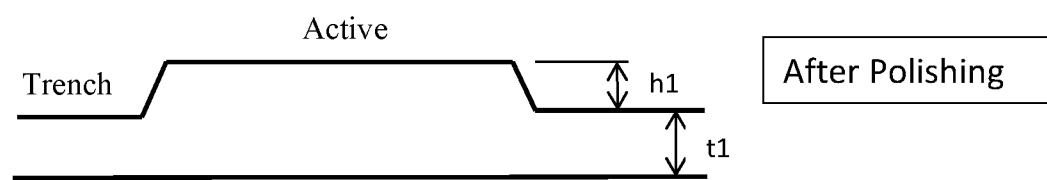
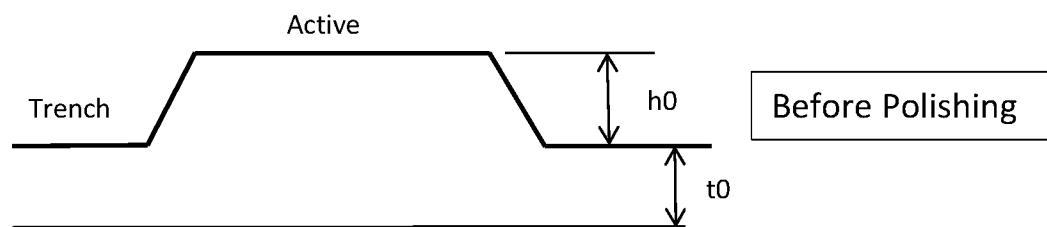
23. The composition of claim 19 wherein the abrasive particles are present in the polishing composition at a concentration of about 0.1 weight percent to about 15 weight 15 percent.

24. The composition of claim 13 wherein the pH of the polishing composition is about 1 to about 6.

25. The composition of claim 13 further comprising not greater than 0.001 weight 20 percent of a metal passivating agent.

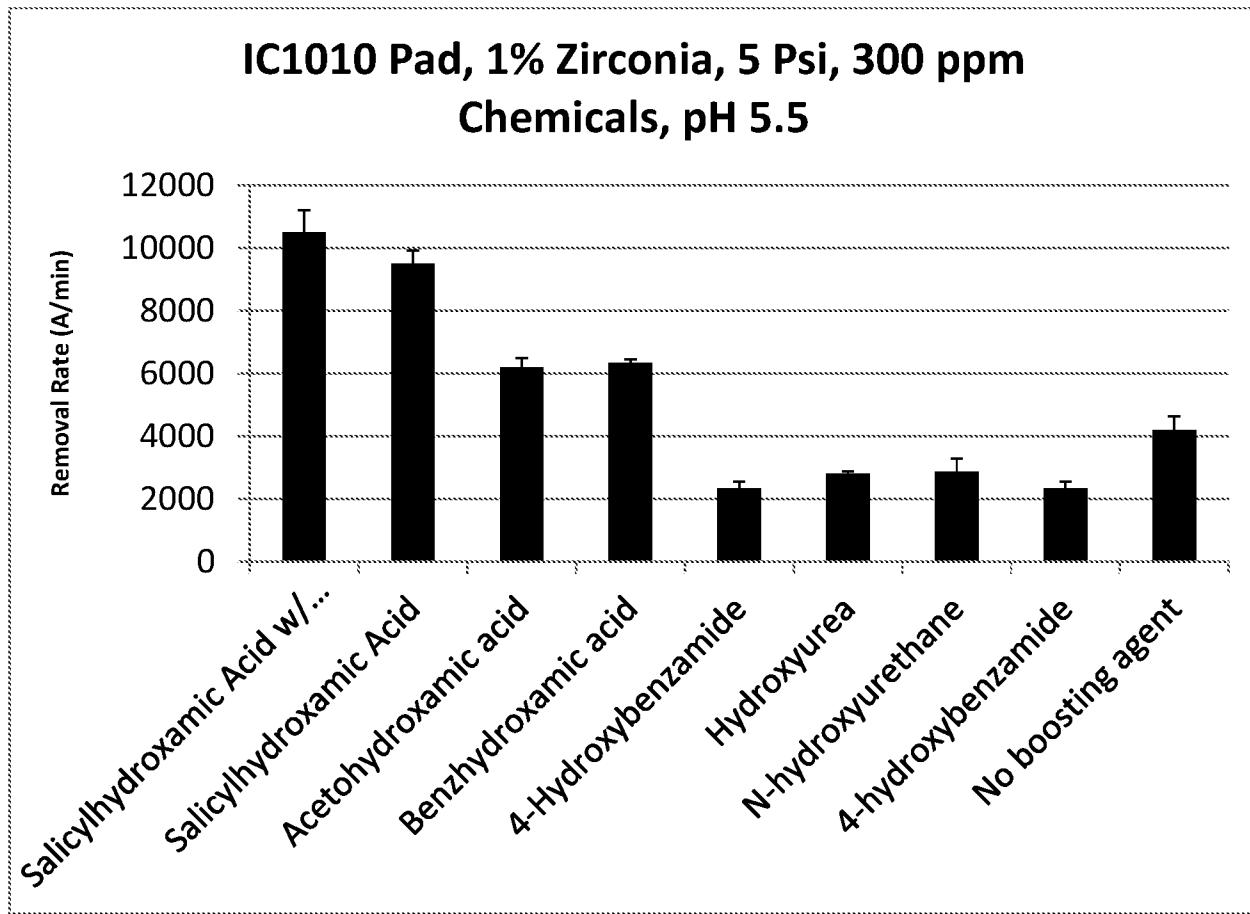
1/4

Figure 1



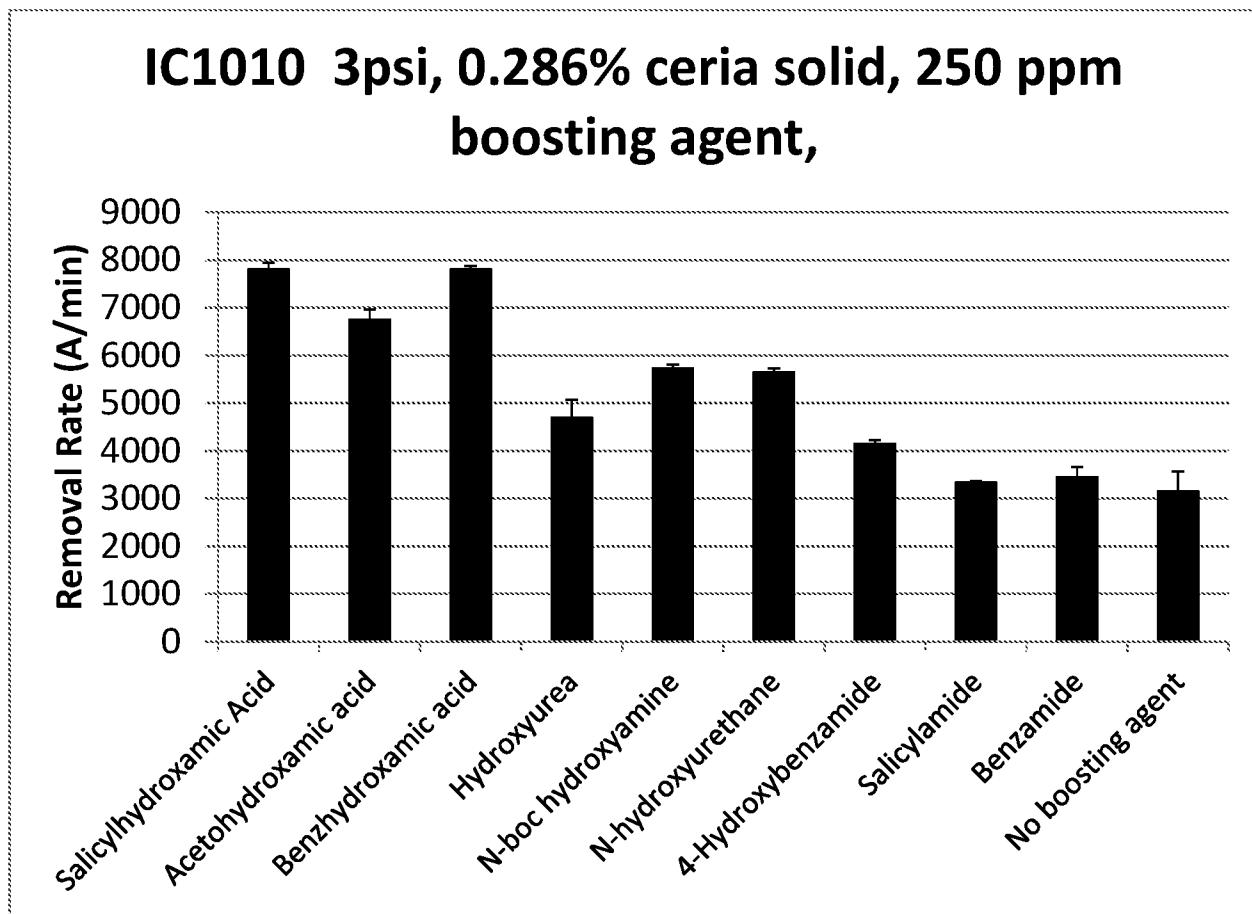
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Figure 2



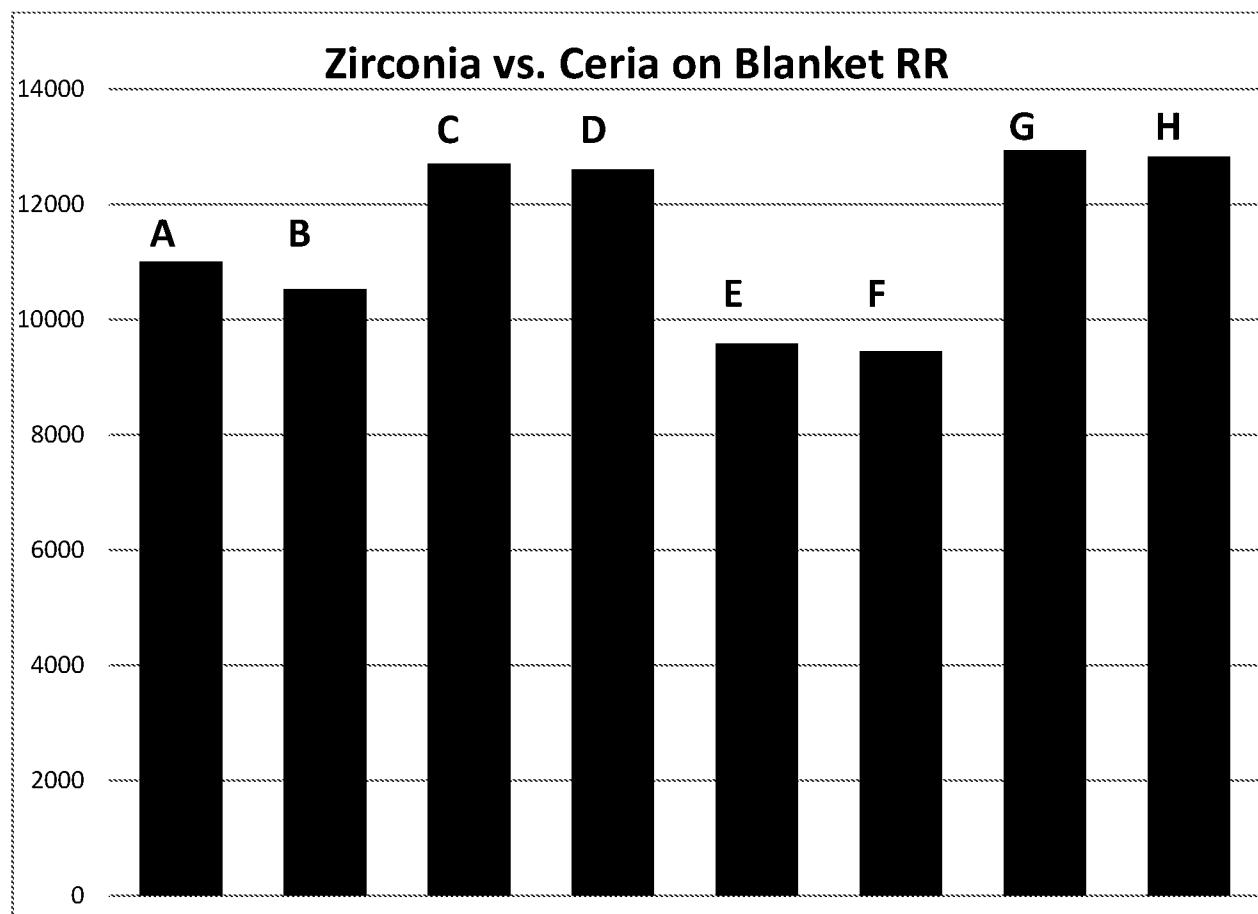
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Figure 3



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Figure 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/049563

A. CLASSIFICATION OF SUBJECT MATTER

C09G 1/02(2006.01)i, C09K 3/14(2006.01)i, H01L 21/306(2006.01)i, H01L 21/321(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)

C09G 1/02; H01L 21/304; C09K 13/06; C09K 13/00; C23F 1/18; C09K 3/14; C23F 3/06; B44C 1/22; H01L 21/306; H01L 21/321

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
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: dielectric, surface, substrate, polishing pad, CMP composition, abrasive particle, removal rate accelerator, salicylhydroxamic acid, metal passivating agent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013-0313225 A1 (JIN, W. et al.) 28 November 2013 See paragraphs [0008]–[0027], [0035], [0036] and [0048]; claims 1–25; and Table 3.	1–9, 11–17, 19–25
A	US 2014-0014872 A1 (TAMADA, S. et al.) 16 January 2014 See paragraphs [0028] and [0040]–[0048]; and claims 1–19.	10, 18
A	US 2012-0280170 A1 (DE REGE THESAURO, F. et al.) 08 November 2012 See paragraphs [0020]–[0026] and [0047]–[0049]; Example 1; and claims 1–4.	1–25
A	WO 2013-100447 A1 (CHEIL INDUSTRIES INC.) 04 July 2013 See claims 1–9.	1–25
A	US 2005-0279733 A1 (CARTER, P. W. et al.) 22 December 2005 See paragraphs [0002] and [0003]; and claims 1–33.	1–25

 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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 23 November 2016 (23.11.2016)	Date of mailing of the international search report 23 November 2016 (23.11.2016)
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer KIM, Dong Seok Telephone No. +82-42-481-5405

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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