80 mV or less. Thus, the colloidal silica particles can have a permanent positive charge (i.e., zeta potential) bounded by any two of the aforementioned endpoints. Preferably, the colloidal silica particles have a permanent positive charge (i.e., zeta potential) of about 20 mV to about 100 mV (e.g., about 20 mV to about 75 mV, about 25 mV to about 100 mV, about 25 mV to about 75 mV, or about 25 mV to about 50 mV) over a suitable pH range (e.g., a pH of less than or equal to about 4).

[0013] The permanent positive charge on the colloidal silica particles can be determined using any suitable method and is not particularly limited. For example, dialysis techniques can be used to characterize the charge of colloidal silica particles. In addition, ultrafiltration methods can also be used. An exemplary three-step ultrafiltration method is described herein. The skilled artisan will recognize that the parameters of the conditions of the ultrafiltration method described herein are illustrative and should not be construed as limiting in any manner.

[0014] A volume of the polishing composition (e.g., 200 mL) is passed through a Millipore ULTRACELL™ regenerated cellulose ultrafiltration disk (e.g., having a molecular weight cutoff of 100,000 Daltons and a pore size of 6.3 nm.) The remaining dispersion (the dispersion that is retained by the ultrafiltration disk) is collected and replenished to the original volume with pH adjusted deionized water. The deionized water is pH adjusted to the original pH of the polishing composition using a suitable inorganic acid such as nitric acid. This procedure is repeated for a total of three ultrafiltration cycles (each of which includes an ultrafiltration step and a replenishing step). The zeta-potential of the triply ultra-filtered and replenished polishing composition is then measured and compared with the zeta potential of the original polishing composition.

[0015] While not wishing to be bound by any particular theory, it is believed that the dispersion retained by the ultrafiltration disk (the retained dispersion) includes the colloidal silica particles and any chemical compounds (e.g., cationic compounds) that may be associated with the surface of the particles (e.g., bonded or attached to or electrostatically interacting with the particle surface). At least a portion of the liquid carrier (e.g., water) and the chemical compounds dissolved therein pass through the ultrafiltration disk. Replenishing the retained dispersion to the original volume is believed to upset the equilibrium in the original polishing composition such that the chemical compounds associated with the particle surface may tend towards a new equilibrium. Compounds that are strongly associated (e.g., covalently bonded) with the particle surface remain on the surface such that there tends to be

potential bound by any of the aforementioned endpoints. In a preferred embodiment, the pH of the polishing composition is about 4 and the colloidal silica particles have a zeta potential of about 40 mV to about 50 mV (e.g., about 45 mV).

[0022] In other embodiments, wherein the pH of the polishing composition is about 4.5, the cationically modified colloidal silica particles can have a zeta potential of about 100 mV or less (e.g., about 95 mV or less, about 90 mV or less, about 85 mV or less, about 80 mV or less, about 75 mV or less, about 70 mV or less, about 65 mV or less, about 60 mV or less, or about 55 mV or less). Alternatively, or in addition, the cationically modified colloidal silica particles can have a zeta potential of about 20 mV or more (e.g., about 25 mV or more, about 30 mV or more, about 35 mV or more, about 40 mV or more, about 45 mV or more, or about 50 mV or more). Thus, the cationically modified colloidal silica particles can have a zeta potential bound by any of the aforementioned endpoints. In a preferred embodiment, the pH of the polishing composition is about 4.5 and the colloidal silica particles have a zeta potential of about 40 mV to about 45 mV (e.g., about 42 mV).

[0023] The cationically modified colloidal silica particles of the first abrasive can be prepared using any suitable method. An exemplary method includes treating colloidal silica particles with at least one cationic compound, for example, an aminosilane compound. Suitable aminosilane compounds include primary aminosilanes, secondary aminosilanes, tertiary aminosilanes, quaternary aminosilanes, and multi-podal (e.g., dipodal) aminosilanes. The aminosilane compound can be any suitable aminosilane, such as bis(2-hydroxyethyl)-3-aminopropyl trialkoxysilane, diethylaminomethyltrialkoxysilane, (N,N-diethyl-3-aminopropyl)trialkoxysilane), 3-(N-styrylmethyl-2-aminoethylaminopropyl trialkoxysilane, aminopropyl trialkoxysilane, (2-N-benzylaminoethyl)-3-aminopropyl trialkoxysilane), trialkoxysilyl propyl-N,N,N-trimethyl ammonium chloride, N-(trialkoxysilylethyl)benzyl-N,N,N-trimethyl ammonium chloride, bis(methyldialkoxysilylpropyl)-N-methyl amine, bis(trialkoxysilylpropyl)urea, bis(3-(trialkoxysilyl)propyl)-ethylenediamine, bis(trialkoxysilylpropyl)amine, bis(trialkoxysilylpropyl)amine, and mixtures thereof.

[0024] Any suitable method of treating the colloidal silica particles can be employed. For example, the colloidal silica particles may be treated with the aminosilane compound before mixing with the other components of the polishing composition or the aminosilane and the colloidal silica particles may be added simultaneously to the other components of the polishing composition.

particles and a second abrasive having a Mohs hardness, of about 5.5 or more, are particularly suitable for polishing a substrate comprising tungsten, titanium, titanium nitride, or a combination thereof. In keeping with an aspect of the invention, the second abrasive particles are harder, as measured by the Mohs hardness of the bulk material, than the first abrasive comprising cationically modified colloidal silica particles.

[0027] The second abrasive can have Mohs hardness of about 5.5 or more, e.g., about 6 or more, about 6.5 or more, about 7 or more, about 7.5 or more, about 8 or more, about 8.5 or more, about 9 or more, about 9.5 or more, or about 10. Alternatively, or in addition, the second abrasive can have a Mohs hardness of about 10 or less, e.g., about 9.5 or less, about 9 or less, about 8.5 or less, or about 8 or less. Thus, the second abrasive can have a Mohs hardness bounded by any two of the aforementioned endpoints. For example, the second abrasive can have a Mohs hardness of about 5.5 to about 10, e.g., about 6 to about 9.5, about 6.5 to about 9, about 7 to about 8.5, or about 7.5 to about 8. In an embodiment, the second abrasive has a Mohs hardness of about 9.

[0028] The second abrasive can comprise more than one type of particle having a Mohs hardness of about 5.5 or more. In an embodiment, the second abrasive is selected from α-alumina particles, zirconia particles, diamond particles, and combinations thereof.

[0029] In a preferred embodiment, the second abrasive comprises α-alumina particles. In another preferred embodiment, the second abrasive consists of α-alumina particles.

[0030] A suitable alumina is α-alumina commercially available from Saint-Gobain (Worcester, MA).

[0031] In an embodiment, the polishing composition contains cationically modified colloidal silica particles as the first abrasive and α-alumina particles as the second abrasive.

[0032] The abrasive particles (i.e., the first abrasive comprising cationically modified colloidal silica particles and second abrasive having a Mohs hardness of about 5.5 or more) can have any suitable size (e.g., primary particle size, average particle diameter, etc.). As used herein, average particle size refers to the weight average particle size (D_w), as will be understood by those of ordinary skill in the art. The average particle size of the abrasive particles can be measured using any suitable technique, for example, using laser diffraction techniques. Suitable particle size measurement instruments are available from, e.g., Malvern Instruments (Malvern, UK). If the average particle size of the abrasive particles is too small, the polishing composition may not exhibit sufficient removal rate. In contrast, if the average particle size of the abrasive particles is too large, the polishing composition may exhibit

undesirable polishing performance such as, for example, poor substrate defectivity. Accordingly, the abrasive particles can have an average particle size of about 10 nm or more, for example, about 15 nm or more, about 20 nm or more, about 30 nm or more, about 40 nm or more, about 50 nm or more, about 60 nm or more, about 70 nm or more, about 80 nm or more, about 90 nm or more, or about 100 nm or more. Alternatively, or in addition, the abrasive particles can have an average particle size of about 1,000 nm or less, for example, about 750 nm or less, about 500 nm or less, about 400 nm or less, about 300 nm or less, or about 200 nm or less. Thus, the abrasive particles can have an average particle size bounded by any two of the aforementioned endpoints. For example, the abrasive particles can have an average particle size of about 10 nm to about 1,000 nm, about 20 nm to about 750 nm, about 30 nm to about 500 nm, about 40 nm to about 400 nm, about 50 nm to about 300 nm, about 60 nm to about 300 nm, about 70 nm to about 300 nm, about 80 nm to about 300 nm, about 90 nm to about 300 nm, or about 100 nm to about 200 nm.

[0033] In a preferred embodiment, the first abrasive comprising cationically modified colloidal silica particles have an average particle size of about 110 nm.

[0034] In another preferred embodiment, the second abrasive particles having a Mohs hardness of about 5.5 or more have an average particle size of about 70 nm to about 110 nm.

[0035] In an embodiment, the cationically modified colloidal silica particles have an average particle size of about 50 nm to about 200 nm, for example, about 55 nm, about 60 nm, about 65 nm, about 70 nm, about 75 nm, about 80 nm, about 85 nm, about 90 nm, about 95 nm, about 100 nm, about 105 nm, about 110 nm, about 115 nm, about 120 nm, about 125 nm, about 130 nm, about 135 nm, about 140 nm, about 145 nm, about 150 nm, about 155 nm, about 160 nm, about 165 nm, about 170 nm, about 175 nm, about 180 nm, about 185 nm, about 190 nm, or about 195 nm.

[0036] In another embodiment, the cationically modified colloidal silica particles have an average particle size of about 100 nm to about 140 nm.

[0037] The polishing composition can comprise any suitable amount of abrasive (i.e., first abrasive comprising cationically modified colloidal silica particles and second abrasive having a Mohs hardness of about 5.5 or more). If the polishing composition of the invention comprises too little abrasive, the composition may not exhibit sufficient removal rate. In contrast, if the polishing composition comprises too much abrasive, the composition may exhibit undesirable polishing performance, may cause surface defects such as scratches, may not be cost effective, and/or may lack stability. The polishing composition can comprise

about 10 wt.% or less of abrasive, for example, about 9 wt.% or less, about 8 wt.% or less, about 7 wt.% or less, about 6 wt.% or less, or about 5 wt.% or less. Alternatively, or in addition, the polishing composition can comprise about 0.01 wt.% or more of abrasive, for example, about 0.05 wt.% or more, about 0.1 wt.% or more, about 0.2 wt.% or more, about 0.3 wt.% or more, about 0.4 wt.% or more, about 0.5 wt.% or more, or about 1 wt.% or more. Thus, the polishing composition can comprise abrasive in an amount bounded by any two of the aforementioned endpoints. For example, the polishing composition can comprise about 0.01 wt.% to about 10 wt.% of abrasive, e.g., about 0.05 wt.% to about 9.5 wt.% of abrasive, about 0.1 wt.% to about 9 wt.% of abrasive, about 0.1 wt.% to about 8 wt.% of abrasive, about 0.1 wt.% to about 7 wt.% of abrasive, about 0.1 wt.% to about 6 wt.% of abrasive, about 0.1 wt.% to about 5 wt.% of abrasive, about 0.2 wt.% to about 5 wt.% of abrasive, about 0.3 wt.% to about 5 wt.% of abrasive, about 0.4 wt.% to about 5 wt.% of abrasive, about 0.5 wt.% to about 5 wt.% of abrasive, about 0.6 wt.% to about 5 wt.% of abrasive, about 0.7 wt.% to about 5 wt.% of abrasive, about 0.8 wt.% to about 5 wt.% of abrasive, about 0.9 wt.% to about 5 wt.% of abrasive, or about 1 wt.% to about 5 wt.% of abrasive.

[0038] In an embodiment, the polishing composition comprises about 0.05 wt.% to about 5 wt.% of abrasive. In another embodiment, the polishing composition comprises about 0.15 wt.% to about 2 wt.% of abrasive.

[0039] The first abrasive can be present in the polishing composition in any suitable amount. In an embodiment, the cationically modified colloidal silica particles are present in the polishing composition in an amount of about 0.05 wt.% to about 5 wt.%.

[0040] In an embodiment, the cationically modified colloidal silica particles are present in the polishing composition in an amount of about 1 wt.%.

[0041] The second abrasive can be present in the polishing composition in any suitable amount. Without wishing to be bound to a particular theory, if too little second abrasive is present, the polishing composition may not exhibit suitable barrier layer removal rates. If too much second abrasive is present, an additional increase in barrier layer removal rates may not be observed and the polishing composition may not be cost effective. Typically, the second abrasive is present in the polishing composition in a lower amount than the first abrasive. For example, in an embodiment, the second abrasive is present in the polishing composition in an amount of about 25 ppm on a weight basis (i.e., about 0.0025 wt.%) or higher, for example, about 30 ppm, about 35 ppm, about 40 ppm, about 45 ppm, about 50 ppm, about 55 ppm,

comprising a cationic polymer provides suitable barrier layer (i.e., film) removal rates in bulk tungsten polishing.

[0046] The cationic polymer can comprise, consist essentially of, or consist of any suitable cationic polymer. Exemplary cationic polymers include polymers comprising quaternary ammonium groups, including copolymers of quaternary ammonium containing monomers/polymers and acrylamide monomers/polymers (e.g., amino acrylate polymers). Exemplary cationic polymers also include homopolymers of cationic monomers, e.g., a poly(diallyldimethylammonium)halide such as poly(diallyldimethylammonium)chloride (polyDADMAC), a poly(methacryloyloxyethyltrimethylammonium)halide such as poly(methacryloyloxyethyltrimethylammonium)chloride (polyMADQUAT), and the like. In addition, the cationic polymer can be a copolymer of cationic and nonionic monomers (e.g., alkylacrylates, alkylmethacrylates, acrylamide, styrene, and the like), such as poly(acrylamide-co-diallyldimethylammonium)chloride (polyAAm-DADMAC), and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (polyDEE). Some other non-limiting examples of suitable cationic polymers include polyethyleneimine, ethoxylated polyethyleneimine, poly(diallyldimethylammonium)halide, poly(amidoamine), poly(methacryloyloxyethyldimethylammonium)chloride, poly(vinylpyrrolidone), poly(vinylimidazole), poly(vinylpyridine), and poly(vinylamine). In a preferred embodiment, the cationic polymer is polyDADMAC. In another preferred embodiment, the cationic polymer is polyMADQUAT. In yet another preferred embodiment, the cationic polymer is polylysine.

[0047] Alternatively, or in addition, the cationic polymer can include nitrogen-heteroaryl or quaternized nitrogen-heteroaryl groups, i.e., heteroaromatic compounds comprising at least one nitrogen in an aromatic ring, optionally having at least one of the nitrogen atoms in the ring alkylated to impart a formal positive charge on the heteroaryl ring (e.g., on a nitrogen in the ring). Preferably, the heteroaryl group is attached to the backbone of the polymer through a carbon-carbon bond (e.g., as in a quaternized poly(vinylpyridine)polymer) or a carbon-nitrogen bond (e.g., as in a quaternized poly(vinylimidazole)polymer) either directly to the aromatic ring or through an alkylene spacer group (e.g., methylene (CH_2) or ethylene (CH_2CH_2) group). The positive charge on the quaternized nitrogen is balanced by a counter anion, which can be, e.g., a halide (e.g., chloride), nitrate, methylsulfate, or a combination of anions. In some embodiments, the cationic polymer comprises, consists essentially of, or consists of a poly(vinyl-N-alkylpyridinium)polymer, such as a poly(2-vinyl-N-

less, for example, about 95 kDa or less, about 90 kDa or less, about 85 kDa or less, about 80 kDa or less, about 75 kDa or less, about 70 kDa or less, about 65 kDa or less, about 60 kDa or less, about 55 kDa or less, about 50 kDa or less, about 45 kDa or less, about 40 kDa or less, about 35 kDa or less, about 30 kDa or less, about 25 kDa or less, or about 20 kDa or less.

[0052] Thus, the cationic polymer can have an average molecular weight of about 500 g/mol or more, for example, about 1,000 g/mol or more, about 1,500 g/mol or more, about 2,000 g/mol or more, about 2,500 g/mol or more, about 3,000 g/mol or more, about 3,500 g/mol or more, about 4,000 g/mol or more, about 4,500 g/mol or more, about 5,000 g/mol or more, about 5,500 g/mol or more, about 6,000 g/mol or more, about 6,500 g/mol or more, about 7,000 g/mol or more, about 7,500 g/mol or more, about 8,000 g/mol or more, about 8,500 g/mol or more, about 9,000 g/mol or more, about 9,500 g/mol or more, or about 10,000 g/mol or more. Alternatively, or in addition, the cationic polymer can have an average molecular weight of about 15,000 g/mol or less, for example, about 14,500 g/mol or less, about 14,000 g/mol or less, about 13,500 g/mol or less, for example, about 13,000 g/mol or less, about 12,500 g/mol or less, about 12,000 g/mol or less, about 11,500 g/mol or less, about 11,000 g/mol or less, or about 10,500 g/mol or less. Thus, the cationic polymer can have an average molecular weight bounded by any two of the aforementioned endpoints. For example, the cationic polymer can have an average molecular weight of about 500 g/mol to about 15,000 g/mol, about 1,000 g/mol to about 14, 500 g/mol, about 1,500 g/mol to about 14,000 g/mol, about 2,000 g/mol to about 13,500 g/mol, about 2,500 g/mol to about 13,000 g/mol, about 3,000 g/mol to about 12,500 g/mol, about 3,500 g/mol to about 12,000 g/mol, about 4,000 g/mol to about 11,500 g/mol, about 4,500 g/mol to about 11,000 g/mol, about 5,000 g/mol to about 10,500 g/mol, about 5,500 g/mol to about 10,000 g/mol, about 6,000 g/mol to about 9,500 g/mol, about 6,500 g/mol to about 9,000 g/mol, about 7,000 g/mol to about 8,500 g/mol, or about 7,500 g/mol to about 8,000 g/mol.

[0053] In a preferred embodiment, the cationic polymer has a molecular weight of about 2,000 g/mol to about 15,000 g/mol.

[0054] In another preferred embodiment, the cationic polymer has a molecular weight of about 8,500 g/mol.

[0055] The polishing composition can comprise any suitable amount of the cationic polymer. Without wishing to be bound to a particular theory, it is believed that typically there is an inverse relationship between the average molecular weight of the cationic polymer

activator, the tungsten removal rate may not be suitable. In contrast, if the polishing composition contains too much iron containing activator, the polishing composition may be unstable or not cost effective. The iron-containing activator can be present in the polishing composition in an amount of about 10 ppm (on a weight basis) or more, for example, about 25 ppm or more, about 50 ppm or more, about 75 ppm or more, about 100 ppm or more, about 125 ppm or more, about 150 ppm or more, about 175 ppm or more, about 200 ppm or more, about 225 ppm or more, about 250 ppm or more, about 275 ppm or more, about 300 ppm or more, about 325 ppm or more, or about 350 ppm or more. Alternatively, or in addition, the iron-containing activator can be present in the polishing composition in an amount of 1,000 ppm or less, for example, about 975 ppm or less, about 950 ppm or less, about 925 ppm or less, about 900 ppm or less, about 875 ppm or less, about 850 ppm or less, about 825 ppm or less, about 800 ppm or less, about 775 ppm or less, about 750 ppm or less, about 725 ppm or less, about 700 ppm or less, about 675 ppm or less, about 650 ppm or less, about 625 ppm or less, about 600 ppm or less, about 575 ppm or less, about 550 ppm or less, about 525 ppm or less, about 500 ppm or less, about 475 ppm or less, about 450 ppm or less, about 425 ppm or less, about 400 ppm or less, or about 375 ppm or less. Thus, the iron-containing activator can be present in the polishing composition in an amount bounded by any two of the aforementioned endpoints. For example, the iron containing activator can be present in the polishing composition in an amount of about 10 ppm to about 1,000 ppm, e.g., about 25 ppm to about 975 ppm, about 50 ppm to about 950 ppm, about 75 ppm to about 925 ppm, or about 100 ppm to about 900 ppm.

[0060] In an embodiment, the iron from the iron-containing activator is present in the polishing composition in an amount of about 1 ppm to about 100 ppm (on a weight basis). In another embodiment, the iron from iron-containing activator is present in the polishing composition in an amount of about 50 ppm. In another embodiment, the iron from the iron-containing activator is present in the polishing composition in an amount of about 60 ppm.

[0061] In some embodiments, the polishing composition comprising an iron-containing activator can further include a stabilizer. Without wishing to be bound to any particular theory, it is believed that the stabilizer prevents the iron-containing activator from degrading the oxidizing agent over time. It is believed that the addition of a stabilizer can reduce the effectiveness of the iron-containing activator, such that the choice of the type and amount of stabilizer may impact on CMP performance. More specifically, it is believed that the

addition of a stabilizer may lead to the formation of a stabilizer/activator complex (e.g., the stabilizer binds to the soluble iron salt) that inhibits the activator from reacting with the oxidizing agent while at the same time allowing the activator to remain sufficiently active so as to promote (e.g., facilitate) rapid tungsten polishing rates. In an embodiment, the stabilizer is selected from phosphoric acid, phthalic acid, citric acid, adipic acid, oxalic acid, malonic acid, aspartic acid, succinic acid, glutaric acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, glutaconic acid, muconic acid, ethylenediaminetetraacetic acid, propylenediaminetetraacetic acid, and combinations thereof.

[0062] In a preferred embodiment, the stabilizer comprises malonic acid.

[0063] The polishing composition can comprise any suitable amount of stabilizer. If the polishing composition contains too little stabilizer, then the iron containing activator may degrade too quickly and the polishing performance of the polishing composition may not be suitable. In contrast, if the polishing composition contains too much stabilizer, then the polishing composition may be unstable and may not be cost effective. Typically, the stabilizer is present in the polishing composition in an amount of about 20 ppm or more (on a weight basis), for example, about 50 ppm or more, about 100 ppm or more, about 150 ppm or more, about 200 ppm or more, about 250 ppm or more, about 300 ppm or more, about 350 ppm or more, about 400 ppm or more, about 450 ppm or more, about 500 ppm or more, about 550 ppm or more, about 600 ppm or more, about 650 ppm or more, about 700 ppm or more, about 750 ppm or more, about 800 ppm or more, about 850 ppm or more, about 900 ppm or more, about 950 ppm or more, or about 1,000 ppm or more. Alternatively, or in addition, the stabilizer can be present in the polishing composition in an amount of about 2,000 ppm or less, about 1,950 ppm or less, about 1,900 ppm or less, about 1,850 ppm or less, about 1,800 ppm or less, about 1,750 ppm or less, about 1,700 ppm or less, about 1,650 ppm or less, about 1,600 ppm or less, about 1,550 ppm or less, about 1,500 ppm or less, about 1,450 ppm or less, about 1,400 ppm or less, about 1,350 ppm or less, about 1,300 ppm or less, about 1,250 ppm or less, about 1,200 ppm or less, about 1,150 ppm or less, about 1,100 ppm or less, or about 1,050 ppm or less. Thus, the stabilizer can be present in the polishing composition in an amount bounded by any two of the aforementioned endpoints. For example, the stabilizer can be present in the polishing composition in an amount of about 50 ppm to about 2,000 ppm, about 100 ppm to about 1,950 ppm, about 150 ppm to about 1,900 ppm, about 200 ppm to about 1,850 ppm, about 250 ppm to about 1,800 ppm, about 300 ppm to about 1,750 ppm, about 350 ppm to about 1,700 ppm, about

titanium (Ti) and/or titanium nitride (TiN). The dielectric layer may be a metal oxide such as a silicon oxide layer derived from tetraethylorthosilicate (TEOS), porous metal oxide, porous or non-porous carbon doped silicon oxide, fluorine-doped silicon oxide, glass, organic polymer, fluorinated organic polymer, or any other suitable high or low-k insulating layer.

[0087] In a preferred embodiment, the substrate comprises a titanium layer on a surface of the substrate, wherein at least a portion of the titanium layer is abraded to polish the substrate.

[0088] In another preferred embodiment, the substrate comprises a nitride layer on a surface of the substrate, wherein at least a portion of the nitride layer is abraded to polish the substrate.

[0089] In a preferred embodiment, the nitride layer is selected from titanium nitride, silicon nitride, and combinations thereof.

[0090] In another preferred embodiment, the substrate comprises a silicon oxide layer on a surface of the substrate, wherein at least a portion of the silicon oxide layer is abraded to polish the substrate.

[0091] In a preferred embodiment, the silicon oxide layer comprises TEOS.

[0092] In another preferred embodiment, the substrate comprises a tungsten layer on a surface of the substrate, wherein at least a portion of the tungsten layer is abraded to polish the substrate.

[0093] In another preferred embodiment, the substrate comprises both a tungsten layer and a titanium nitride layer on a surface of the substrate, wherein both the tungsten layer and the titanium nitride layer are abraded to polish the substrate.

[0094] The chemical-mechanical polishing composition and method of the invention are particularly suited for use in conjunction with a chemical-mechanical polishing apparatus. Typically, the apparatus comprises a platen, which, when in use, is in motion and has a velocity that results from orbital, linear, or circular motion, a polishing pad in contact with the platen and moving with the platen when in motion, and a carrier that holds a substrate to be polished by contacting and moving the substrate relative to the surface of the polishing pad. The polishing of the substrate takes place by the substrate being placed in contact with the polishing pad and the polishing composition of the invention, and then the polishing pad moving relative to the substrate, so as to abrade at least a portion of the substrate to polish the substrate.

[0095] A substrate can be polished with the chemical-mechanical polishing composition using any suitable polishing pad (e.g., polishing surface). Suitable polishing pads include, for example, woven and non-woven polishing pads. Moreover, suitable polishing pads can comprise any suitable polymer of varying density, hardness, thickness, compressibility, ability to rebound upon compression, and compression modulus. Suitable polymers include, for example, polyvinylchloride, polyvinylfluoride, nylon, fluorocarbon, polycarbonate, polyester, polyacrylate, polyether, polyethylene, polyamide, polyurethane, polystyrene, polypropylene, co-formed products thereof, and mixtures thereof. Soft polyurethane polishing pads are particularly useful in conjunction with the inventive polishing method. Typical pads include but are not limited to SURFIN™ 000, SURFIN™ SSW1, SPM3100 (Eminess Technologies), POLITEX™ commercially available from Dow Chemical Company (Newark, DE), and POLYPAS™ 27 commercially available from Fujibo (Osaka, JP), and EPIC™ D100 pads or NEXPLANAR™ E6088 commercially available from Cabot Microelectronics (Aurora, IL). A preferred polishing pad is the rigid, microporous polyurethane pad (IC1010 ™) commercially available from Dow Chemical.

[0096] Desirably, the chemical-mechanical polishing apparatus further comprises an in situ polishing endpoint detection system, many of which are known in the art. Techniques for inspecting and monitoring the polishing process by analyzing light or other radiation reflected from a surface of the substrate being polished are known in the art. Such methods are described, for example, in U.S. Patent 5,196,353, U.S. Patent 5,433,651, U.S. Patent 5,609,511, U.S. Patent 5,643,046, U.S. Patent 5,658,183, U.S. Patent 5,730,642, U.S. Patent 5,838,447, U.S. Patent 5,872,633, U.S. Patent 5,893,796, U.S. Patent 5,949,927, and U.S. Patent 5,964,643. Desirably, the inspection or monitoring of the progress of the polishing process with respect to a substrate being polished enables the determination of the polishing end-point, i.e., the determination of when to terminate the polishing process with respect to a particular substrate.

EMBODIMENTS

[0097] (1) In embodiment (1) is presented a chemical-mechanical polishing composition comprising (a) a first abrasive comprising cationically modified colloidal silica particles, (b) a second abrasive having a Mohs hardness of about 5.5 or more, (c) a cationic polymer, (d) an iron containing activator, (e) an oxidizing agent, and (f) water.

[0142] (46) In embodiment (46) is presented the method of any one of embodiments (22)-(45), wherein the substrate comprises a silicon oxide layer on a surface of the substrate, and wherein at least a portion of the silicon oxide layer is abraded to polish the substrate.

[0143] (47) In embodiment (47) is presented the method of embodiment (46), wherein the silicon oxide layer comprises TEOS.

[0144] (48) In embodiment (48) is presented the method of any one of embodiments (22)-(47), wherein the substrate comprises a tungsten layer on a surface of the substrate, and wherein at least a portion of the tungsten layer is abraded to polish the substrate.

[0145] (49) In embodiment (49) is presented the method of any one of embodiments (22)-(48), wherein the substrate comprises both a tungsten layer and a titanium nitride layer on a surface of the substrate, and wherein both the tungsten layer and the titanium nitride layer are abraded to polish the substrate.

EXAMPLES

[0146] The following examples further illustrate the invention but, of course, should not be construed as in any way limiting its scope.

[0147] The following abbreviations are used herein: W refers to tungsten; Ti refers to titanium; TiN refers to titanium nitride; TEOS refers to tetraethylorthosilicate; MW refers to molecular weight, and RR refers to removal rate.

EXAMPLE 1

[0148] This example demonstrates the effect of a second abrasive having a Mohs hardness of about 5.5 or more on removal rates and polishing performance for polishing compositions according to the invention.

[0149] Substrates comprising blankets of TiN, Ti, W, and TEOS were polished with two polishing compositions (i.e., Polishing Compositions 1A and 1B). The polishing compositions contained the following components (3x concentrate): 1.0 wt.% of cationically modified colloidal silica as a first abrasive, 1,335 ppm malonic acid as a stabilizer, 618 ppm of ferric nitrate as an iron-containing activator; 75-150 ppm of polyDADMAC (MW of 8,500 g/mol) as a cationic polymer, 2 wt.% of hydrogen peroxide as an oxidizing agent, and 15 ppm of KATHON™ LX as a biocide. The pH of the polishing compositions was adjusted to 2.15.

[0150] Polishing Compositions 1A and 1B were identical except that polishing composition 1B further comprised 150 ppm of α-alumina as a second abrasive.

[0151] Substrates were polished using a MIRRA™ polisher (Applied Materials, Santa Clara, CA) and a NEXPLANAR™ E6088 polishing pad (Cabot Microelectronics, Aurora, IL) using 2 psi of downforce.

[0152] The polishing results are set forth in Table 1.

TABLE 1. Removal Rates as a Function of Second Abrasive

Composition	**W RR (Å/min)**	**TiN RR (Å/min)**	**Ti RR (Å/min)**	**TEOS RR (Å/min)**
1A (control)	1,984	355	118	30
1B (inventive)	1,923	769	469	20

[0153] As is apparent from the results set forth in Table 1, inventive Polishing Composition 1B exhibited increased removal rates for the TiN and Ti barrier films while maintaining a comparable tungsten and TEOS removal rate as compared to control Polishing Composition 1A. In addition, the tungsten and TEOS removal rates of control Polishing Composition 1A and inventive Polishing Composition 1B were similar with no significant differences. Thus, these results show the beneficial impact of a second abrasive particle having a Mohs hardness of about 5.5 or more on polishing compositions according to the invention.