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POLISHING**(52) **U.S. Cl.**
CPC **C23F 1/16** (2013.01); **C23F 3/00** (2013.01)(71) Applicant: **Cabot Microelectronics Corporation,**
Aurora, IL (US)(72) Inventors: **Chih-Pin TSAI**, Kaohsiung (TW);
Ming-Chih Yeh, Taipei (TW); **Glenn
Whitener**, Batavia, IL (US); **Lung-Tai
Lu**, Tainan (TW)(21) Appl. No.: **14/308,587**(22) Filed: **Aug. 22, 2014****Publication Classification**(51) **Int. Cl.**
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C23F 3/00 (2006.01)(57) **ABSTRACT**

A method of planarizing/polishing germanium is described. The method comprises the step of abrading the surface of a substrate comprising germanium with an aqueous chemical mechanical polishing (CMP) composition comprising an oxidizing agent, a particulate abrasive, and a germanium etching inhibitor. The germanium etching inhibitor is selected from the group consisting of a water-soluble polymer, an amino acid having a non-acidic side chain, a bis-pyridine compound, and a combination of two or more thereof. The polymer can be a cationic or nonionic polymer that comprises basic nitrogen groups, amide groups, or a combination thereof.

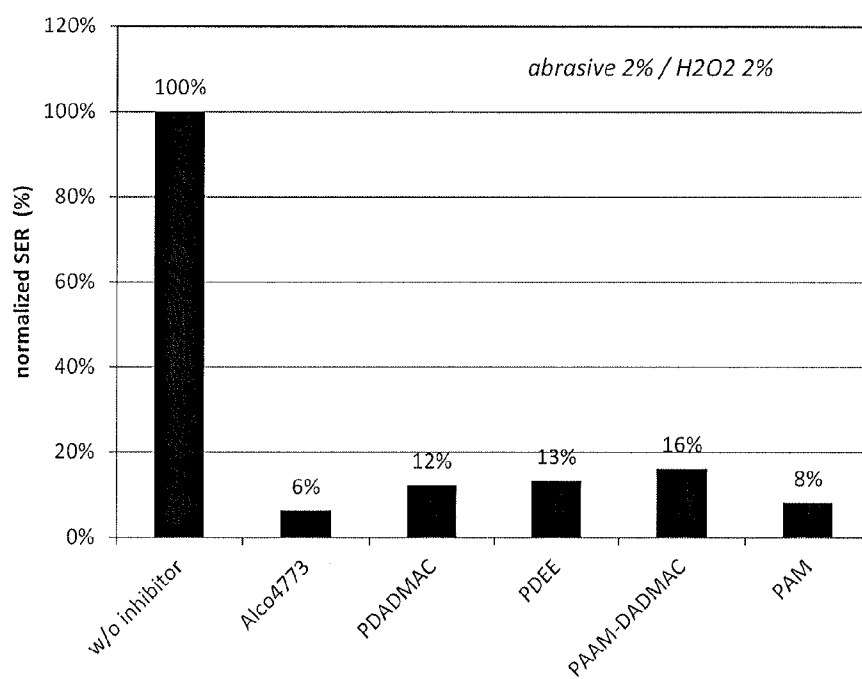


FIG. 1

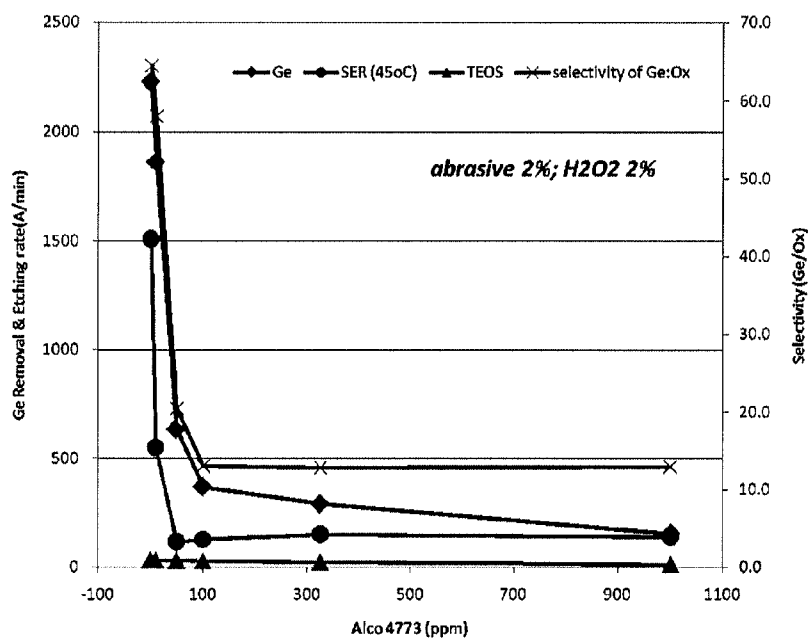
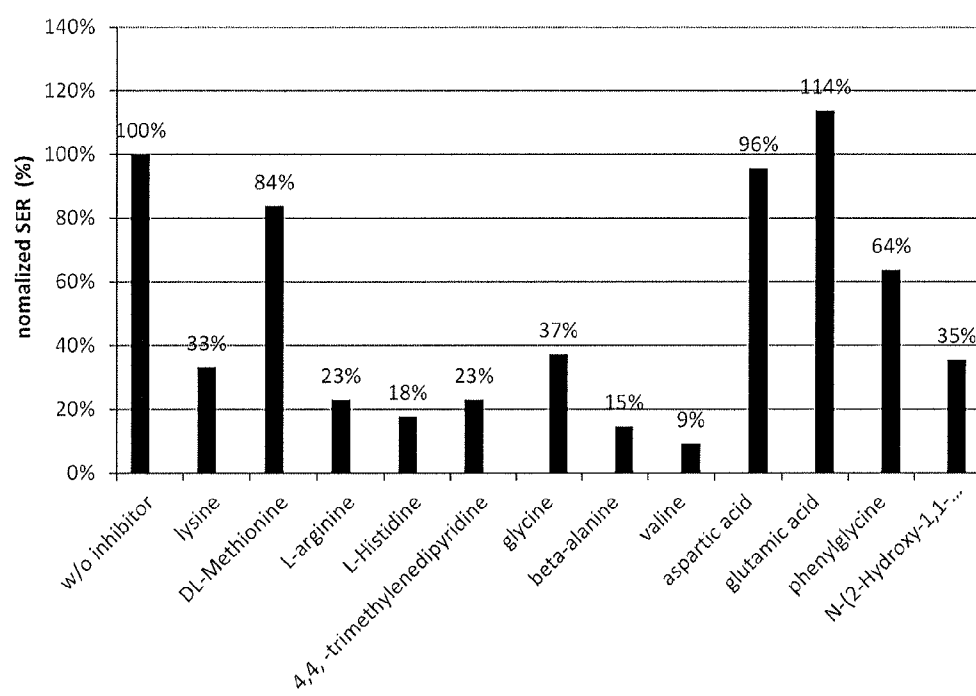


FIG. 2

**FIG. 3**

GERMANIUM CHEMICAL MECHANICAL POLISHING

FIELD OF THE INVENTION

[0001] This invention relates to chemical mechanical polishing (CMP) compositions and methods. More particularly, this invention relates to a method for CMP removal of germanium.

BACKGROUND

[0002] Compositions and methods for CMP of the surface of a substrate are well known in the art. Compositions for chemical mechanical polishing/planarizing various substrates (also known as polishing slurries, CMP slurries, and CMP compositions), e.g., semiconductor substrates in integrated circuit manufacture, typically contain an abrasive, various additive compounds, and the like.

[0003] In conventional CMP techniques, a substrate carrier or polishing head is mounted on a carrier assembly and positioned in contact with a polishing pad in a CMP apparatus. The carrier assembly provides a controllable pressure to the substrate, urging the substrate against the polishing pad. The pad and carrier, with its attached substrate, are moved relative to one another. The relative movement of the pad and substrate serves to abrade the surface of the substrate to remove a portion of the material from the substrate surface, thereby polishing the substrate. The polishing of the substrate surface typically is further aided by the chemical activity of the polishing composition (e.g., by oxidizing agents, acids, bases, or other additives present in the CMP composition) and/or the mechanical activity of an abrasive suspended in the polishing composition. Typical abrasive materials include silicon dioxide, cerium oxide, aluminum oxide, zirconium oxide, and tin oxide.

[0004] Germanium is a useful semiconductor material in advanced metal oxide semiconductor (MOS) transistor structures for integrated circuits (IC), e.g., in designs utilizing shallow trench isolation (STI) techniques, due to the higher electron mobility and hole mobility of germanium relative to silicon. Planarization of germanium under oxidative conditions is required to prepare acceptable MOS structures under current integrated circuit design parameters. Unfortunately, germanium oxides are highly soluble, resulting in high static etching rates (SER) in the presence of oxidants such as hydrogen peroxide. The high SER, in turn leads to dishing problems when germanium is planarized using CMP compositions comprising hydrogen peroxide or other oxidants, which can severely limit options for advanced IC design using germanium. Cationic surfactants have been evaluated in the past as germanium etching inhibitors; however, such materials lead to foaming problems during CMP, which severely limits their practical usefulness.

[0005] The methods described herein address the etching and dishing problems associated with germanium CMP by utilizing certain germanium etching inhibitor materials in the CMP slurries, which do not suffer from the foaming problems of cationic surfactants and which provide suitably low roughness surfaces for advanced germanium IC applications with minimal dishing.

SUMMARY

[0006] A method of planarizing/polishing germanium is described. The method comprises the step of abrading the

surface of a substrate comprising germanium with an aqueous CMP composition comprising an oxidizing agent (e.g., about 0.5 to about 4 percent by weight (wt %) hydrogen peroxide), a particulate abrasive such as colloidal silica (e.g., at a concentration in the range of about 0.1 to about 5 wt %, preferably about 0.5 to about 3 wt %), and a germanium etching inhibitor. The germanium etching inhibitor is selected from the group consisting of a water-soluble polymer, an amino acid having a non-acidic side chain, a bis-pyridine compound, and a combination of two or more thereof.

[0007] The water-soluble polymer can be a cationic or non-ionic polymer that comprises basic nitrogen groups, amide groups, or a combination thereof. These groups can be substituents situated along the polymer backbone (e.g., a hydrocarbon, ester, amide, or ether backbone), can form part of the polymer backbone (e.g., as in some polyimides), or both. In some embodiments, the polymer comprises basic nitrogen groups selected from primary amino groups, secondary amino groups, tertiary amino groups, quaternary amino groups, and a combination of two or more thereof, and/or basic nitrogen heterocyclic groups, such as pyridine, imidazole, or quaternized versions thereof. In some other embodiments, the polymer comprises amide groups selected from the group consisting of —C(=O)NH_2 , —C(=O)NHR , —C(=O)NR_2 , and a combination of two or more thereof, typically as substituents on a hydrocarbon (e.g., “polyvinyl” or “polyolefin”) backbone, e.g., polyacrylamide compounds, wherein each R independently is a hydrocarbon moiety (e.g., lower alkyl, such as methyl, ethyl, propyl, etc.). In yet other embodiments, the polymer can comprise amide groups and basic nitrogen groups.

[0008] Polyacrylamide-type nonionic polymers bearing —C(=O)NH_2 and/or —C(=O)NHR amide groups are preferred non-ionic polymers for use in the compositions and methods described herein. Non-limiting examples of such materials include; polyacrylamide (PAM), poly(N-isopropylacrylamide) (PNIPAM), PAM copolymers, and the like.

[0009] Useful cationic polymers include one or more polymers selected from the group consisting of a poly(diallyldimethylammonium)halide such as poly(diallyldimethylammonium)chloride (polyDADMAC), a poly(methacryloyloxyethyltrimethylammonium)halide such as poly(methacryloyloxyethyltrimethylammonium)chloride (polyMADQUAT), poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (polyDEE), and the like. In some embodiments, the cationic polymer can comprise both amide groups and basic nitrogen groups, e.g., as in a copolymer of acrylamide (AAm) and DADMAC, such as polyAAm-co-DADMAC. In some preferred embodiments, the polymer is present in the CMP composition at a concentration in the range of about 10 to about 2000 parts-per-million (ppm).

[0010] The amino acid-based germanium etching inhibitors are amino acids that have non-acidic side chain. In some cases, the amino acids preferably have a basic side chain, a hydrophobic side chain, and/or have an isoelectric point of 6 or greater. Non-limiting examples of such amino acids include lysine, arginine, histidine, glycine, beta-alanine, valine, and N-(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)glycine also known as tricine. Preferably, the amino acid is present in the composition at a concentration in the range of about 50 to about 5000 ppm.

[0011] Bis-pyridine-type Ge etching inhibitors are compounds comprising two pyridine groups linked together via a covalent bond (i.e., bipyridyl compounds) or through a 1 to 3

carbon linking group. In some embodiments, the Ge etching inhibitor comprises at least one compound selected from the group consisting of 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl)ethane, 2,2'-bipyridyl, and 1,2-bis(2-pyridyl)ethylene. Preferably, the bis-pyridine compound, if utilized, is present in the composition at a concentration in the range of about 50 to about 5000 ppm.

[0012] In one embodiment, the particulate abrasive, e.g., colloidal silica, is present in the CMP composition at a concentration in the range of about 0.5 to about 3 wt %, and the polymer is present at a concentration of about 10 to about 1000 ppm. In other embodiments, the CMP composition comprises about 0.5 to about 3 wt % of the abrasive (e.g., colloidal silica), and about 50 to about 5000 ppm of the amino acid. In yet other embodiments, the CMP composition comprises about 0.5 to about 3 wt % of the abrasive (e.g., colloidal silica), about 10 to about 1000 ppm of the polymer, and about 50 to about 5000 ppm of the amino acid.

[0013] The methods described herein are suitable for planarizing Ge and $\text{Si}_x\text{Ge}_{(1-x)}$ (for x =about 0.1 to about 0.9) materials and provide surprisingly good germanium removal rates without significant dishing due to germanium etching and low surface roughness, without creating foaming problems during the CMP process.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 provides a graph comparing the Ge static etch rate (SER) observed for CMP compositions containing various polymer-type Ge etching inhibitor compounds.

[0015] FIG. 2 provides graphs of Ge SER, as well as removal rates for Ge and silicon oxide (Ox), and selectivity for Ge/Ox observed for CMP compositions comprising various concentrations of polyMADQUAT (ALCO 4773).

[0016] FIG. 3 provides a graph comparing the Ge static etch rate (SER) observed for CMP compositions containing various amino acid and pyridine Ge etching inhibitor compounds.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0017] The CMP compositions useful in the methods described herein include an oxidant (e.g., hydrogen peroxide), a particulate abrasive (e.g., colloidal silica and the like), and a germanium etching inhibitor (e.g., a water soluble non-ionic polymer, a water-soluble cationic polymer, and amino acid, a bis-pyridine compound, or a combination of two or more thereof) in an aqueous carrier.

[0018] Oxidizing agents useful in compositions and methods described herein include, e.g., hydrogen peroxide, ammonium persulfate, potassium permanganate, and the like. Hydrogen peroxide is the preferred oxidizing agent. Preferably, the oxidizing agent, e.g. hydrogen peroxide, is present in the composition at a concentration in the range of about 0.1 to about 4 wt %, more preferably about 0.5 to about 3.5 wt %, at the point of use (i.e., diluted for use in the polishing process).

[0019] The term “water-soluble” as used herein, refers to polymers that dissolve in water, or are dispersible in water, to form substantially clear, transparent dispersions. The water-soluble polymer can be a cationic or nonionic polymer that comprises basic nitrogen groups, imide groups, or a combination thereof. In some embodiments, the polymer comprises basic nitrogen groups selected from primary amino groups, secondary amino groups, tertiary amino groups, quaternary

amino groups, and a combination of two or more thereof, and/or basic nitrogen heterocyclic groups, such as pyridine, imidazole, or quaternized versions thereof. In some other embodiments, the polymer comprises amide groups selected from the group consisting of $-\text{C}(=\text{O})\text{NH}_2$, $-\text{C}(=\text{O})\text{NHR}$, $-\text{C}(=\text{O})\text{NR}_2$, and a combination of two or more thereof, typically as substituents on a hydrocarbon (e.g., “polyvinyl” or “polyolefin”) backbone, e.g., polyacrylamide compounds, wherein each R independently is as hydrocarbon moiety (e.g., lower alkyl, such as methyl, ethyl, propyl, etc.). In yet other embodiments, the polymer can comprise carbonamide groups and basic nitrogen groups.

[0020] Polyacrylamide-type nonionic polymers bearing $-\text{C}(=\text{O})\text{NH}_2$ and/or $-\text{C}(=\text{O})\text{NHR}$ amide groups are preferred non-ionic water-soluble polymers for use in the compositions and methods described herein. Non-limiting examples of such materials include, polyacrylamide (PAM), poly(N-isopropylacrylamide) (PNIPAM, PAM copolymers, and the like.

[0021] Cationic polymers useful as germanium etching inhibitors in the compositions and methods described herein include homopolymers of cationic monomers, e.g., a poly(diallyldimethylammonium)halide such as poly(diallyldimethylammonium)chloride (polyDADMACH), 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-DADMACH), and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (polyDEE). Some other non-limiting examples of such cationic polymer include polyethyleneimine, ethoxylated polyethyleneimine, poly(diallyldimethylammonium)halide, poly(amidoamine), poly(methacryloyloxyethyltrimethylammonium)chloride, poly(vinylpyrrolidone), poly(vinylimidazole), poly(vinylpyridine), and poly(vinylamine). A preferred cationic polymer for use in the CMP compositions of the invention is a poly(methacryloyloxyethyltrimethylammonium)halide (e.g., the chloride), also known as polyMADQUAT, such as ALCO 4773, which is commercially available from Alco Chemical Inc.

[0022] 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 any 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-alkylpyridinium)polymer, a poly(4-vinyl-N-

alkylpyridinium)polymer, a vinyl-N-alkylpyridinium copolymer, a poly(N1-vinyl-N3-alkylimidazolium)polymer, and the like.

[0023] The polymer preferably is present in the CMP composition at a concentration of about 10 to about 2000 ppm (more preferably about 10 to about 1000), at point of use in a polishing method as described herein.

[0024] The molecular weight of the polymer is not limited, but typically, the polymer has a weight average molecular weight of about 5 kDa or more (e.g., about 10 kDa or more, about 20 kDa or more, about 30 kDa or more, about 40 kDa or more, about 50 kDa or more, or about 60 kDa or more) cationic polymer. The polishing composition preferably comprises a polymer having a molecular weight of about 100 kDa or less (e.g., about 80 kDa or less, about 70 kDa or less, about 60 kDa or less, or about 50 kDa or less). Preferably, the polishing composition comprises a polymer having a molecular weight of about 5 kDa to about 100 kDa (e.g., about 10 kDa to about 80 kDa, about 10 kDa to about 70 kDa, or about 15 kDa to about 70 kDa).

[0025] Amino acids useful as germanium etching inhibitors in the compositions and methods described herein include amino acids that have non-acidic side chains. In some preferred embodiments, the amino acid comprises a basic side chain, such as e.g., lysine, arginine, and histidine. In other embodiments, the amino acid has a hydrophobic side chain (e.g., alanine, leucine, isoleucine, valine, phenylglycine). In yet other embodiments, the amino acid is selected from amino acids having an isoelectric point of 6 or greater (e.g., lysine, arginine, histidine, glycine, beta-alanine, valine, and the like). Preferably, the amino acid does not include a sulfur-containing side chain (e.g., methionine, cysteine, or cystine). Examples of some preferred amino acids include, e.g., lysine, arginine, histidine, glycine, beta-alanine, tryptophan, and valine. Preferably, the amino acid is present in the composition at a concentration in the range of about 50 to about 5000 ppm.

[0026] Bis-pyridine-type Ge etching inhibitors are compounds comprising two pyridine groups linked together via a covalent bond (i.e., bipyridyl compounds) or through a 1 to 3 carbon linking group, e.g., compounds of the formula Pyr-R'-Pyr, in which Pyr is a pyridine group, which can be substituted (e.g., with an alkyl group) or unsubstituted. Each Pyr independently is attached to R' at the 2, 3, or 4 position of the pyridine ring. R' can be a covalent bond (in which case the compounds are bipyridyl compounds), $(CH_2)_n$, or $CH=CH$, wherein n is 1, 2, or 3. When R' is $CH=CH$, the Pyr groups can be attached to $CH=CH$ in the E or Z orientation. Non-limiting examples of bis-pyridine-type Ge etching inhibitors include, e.g., 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl) ethane, 2,2'-bipyridyl, 1,2-bis(2-pyridyl)ethylene, and the like. Preferably, the bis-pyridine compound, if utilized, is present in the composition at a concentration in the range of about 50 to about 5000 ppm.

[0027] The particulate abrasive can comprise any abrasive material suitable for use in CMP of semiconductor and integrated circuit materials. Examples of such materials include, e.g., silica, ceria, zirconia, and titania. A preferred particulate abrasive is silica (e.g., colloidal silica). Preferably, the particulate abrasive has a mean particle size of about 20 to about 200 nm. Preferred colloidal silica has a mean particle size of about 60 to about 150 nm (e.g., about 120 nm). Preferably, the abrasive (e.g., colloidal silica) is present in the CMP composition at a concentration of about 0.2 to about 3 wt % (e.g.,

about 0.4 to about 2 wt %), at point of use. The colloidal silica particles can have any shape. In some embodiments the colloidal silica particles are generally spherical, cocoon-shaped, or a combination thereof. Optionally, the colloidal silica can include additional cationic materials (e.g., quaternary amines) on the surface of the silica particles to impart a positive zeta potential to the surface.

[0028] The CMP compositions of the present invention can have any pH, but preferably have a pH in the range of about 1.5 to about 9 (e.g., about 2 to about 5). The pH of the composition can be achieved and/or maintained by inclusion of a buffering material, as is well known to those of ordinary skill in the chemical arts.

[0029] The polishing compositions of the invention optionally also can include suitable amounts of one or more other additive materials commonly included in polishing compositions, such as metal complexing agents, dispersants, corrosion inhibitors, viscosity modifying agents, biocides, inorganic salts, and the like. For example, the composition can include a biocide such as KATHON, KORDEK, or NEOLONE biocides; a complexing agent such as acetic acid, picolinic acid, tartaric acid, iminodiacetic acid, benzoic acid, nitrilotriacetic acid (NTA), and the like; and/or a corrosion inhibitor such as benzotriazole (BTA), 1,2,3-triazole, 1,2,4-triazole, a tetrazole, 5-aminotetrazole, 3-amino-1,2,4-triazole, phenylphosphonic acid, methylphosphonic acid; and the like.

[0030] The aqueous carrier can be any aqueous solvent, e.g., water, aqueous methanol, aqueous ethanol, a combination thereof, and the like. Preferably, the aqueous carrier comprises predominately deionized water.

[0031] The polishing compositions used in the methods described herein can be prepared by any suitable technique, many of which are known to those skilled in the art. The polishing composition can be prepared in a batch or continuous process. Generally, the polishing composition can be prepared by combining the components thereof in any order. The term "component" as used herein includes individual ingredients (e.g., abrasive, polymer, amino acid, buffers, and the like), as well as any combination of ingredients. For example, the abrasive can be dispersed in water, combined with the etching inhibitor components, and mixed by any method that is capable of incorporating the components into the polishing composition. Typically, the oxidizing agent is not added to the polishing composition until the composition is ready for use in a CMP process. For example, the oxidizing agent can be added just prior to initiation of polishing. The pH can be further adjusted at any suitable time by addition of an acid, base, or buffer, as needed.

[0032] The polishing compositions of the present invention also can be provided as a concentrate, which is intended to be diluted with an appropriate amount of aqueous solvent (e.g., water) prior to use. In such an embodiment, the polishing composition concentrate can include the various components dispersed or dissolved in aqueous solvent in amounts such that, upon dilution of the concentrate with an appropriate amount of aqueous solvent, each component of the polishing composition will be present in the polishing composition in an amount within the appropriate range for use.

[0033] The compositions and methods of the invention surprisingly provide low surface roughness and significant reductions in SER (e.g., 80% or greater reductions in SER) compared to similar CMP slurry formulations that do not contain the etching inhibitor materials.

[0034] The CMP methods of the invention preferably are achieved using a chemical-mechanical polishing apparatus. Typically, the CMP apparatus comprises a platen, which, when in use, is in motion and has a velocity that results from orbital, linear, and/or circular motion, a polishing pad in contact with the platen and moving relative to the platen when in motion, and a carrier that holds a substrate to be polished by contacting and moving relative to the surface of the polishing pad. The polishing of the substrate takes place by the substrate being placed in contact with the polishing pad and a polishing composition of the invention and then moving the polishing pad relative to the substrate, so as to abrade at least a portion of the substrate to polish the substrate.

[0035] The following examples further illustrate certain aspects of the invention but, of course, should not be construed as in any way limiting its scope. As used herein and in the following examples and claims, concentrations reported as parts-per-million (ppm) or percent by weight (wt %) are based on the weight of the active component of interest divided by the weight of the composition, and are on a point of use basis.

EXAMPLE 1

[0036] This example illustrates the effect of selected cationic and nonionic polymers on Ge SER and removal rates.

[0037] Ge blanket wafers with (100) preferred orientation were planarized with aqueous CMP slurries (at a pH of about 2.3) comprising about 2 wt % colloidal silica, 2 wt % hydrogen peroxide, and various polymer additives at a concentration of 100 ppm. The Ge removal rates (RR) and static etch rates (SER) were evaluated. Planarization was accomplished on a POLI 500 brand polisher using an IC1010 brand polishing pad at a platen speed of about 60 rpm, a carrier speed of about 63 rpm, a down force of about 1.5 psi, and a slurry flow rate of about 100 mL/minute; polishing time: 60 seconds. SER was determined by dipping the wafers in 35° C. and 45° C. slurries with oxidizer present, for two minutes.

[0038] In one evaluation, the effects of various polymers on Ge SER was determined. The characteristics of the slurries are described in Table 1 along with SER values, and the SER results are provided in FIG. 1, reported as normalized SER as a percentage of the SER obtained with a slurry that did not include any polymer additive. The normalized SER was set at 100% for the composition that did not contain any etching inhibitor component.

TABLE 1

Slurry	SER (Å/min)	Polymer
1	105	polyMADQUAT (ALCO 4773)
2	206	polyDEE (PDEE)
3	223	polyDADMAC (PDADMAC)
4	271	polyAAm-DADMAC (PAAM-DADMAC)
5	137	PAM

[0039] As is evident from FIG. 1, the polymers all provided surprising reductions in Ge SER in the range of about 84 to 94%.

[0040] In another evaluation, Ge removal rates and SER were evaluated for slurries comprising 2 wt % of commercially available colloidal silica (cocoon-shaped particles, primary particle size of about 30 to 35 nm, secondary particle size of about 70 nm, cationic surface-modified), 2 wt % hydrogen peroxide, and 0 to 1000 ppm of polyMADQUAT. In

addition, the slurries were evaluated for PETEOS silicon oxide removal rates, and for the selectivity of Ge:Ox (Ge removal versus silicon oxide removal). Planarization was accomplished, on a POLI 500 brand polisher using an IC1010 brand polishing pad at a platen speed of about 60 rpm, a carrier speed of about 63 rpm, a down force of about 1.5 psi, and a slurry flow rate of about 100 mL/minute; polishing time: 60 seconds. SER was determined, by dipping the wafers in 35° C. and 45° C. slurries with oxidizer present, for two minutes. The results are shown in FIG. 2.

[0041] The results in FIG. 2 indicate that the effects of the polyMADQUAT leveled off after about 100 ppm polymer concentration, and that there was a significant selectivity for Ge removal versus oxide removal of >12 at polymer concentrations in the range of 100 to 1000 ppm.

EXAMPLE 2

[0042] This example illustrates the effects of various amino acids and a pyridine compound on Ge SER.

[0043] Ge blanket wafers with (100) preferred orientation were planarized with CMP slurries comprising 2 wt % commercially available colloidal silica (cocoon-shaped particles, primary particle size of about 30 to 35 nm, secondary particle size of about 70 nm, cationic surface-modified), 2 wt % hydrogen peroxide, and various amino acid and pyridine additives, i.e., 1000 ppm of lysine, D,L-methionine, arginine, histidine, and 4,4'-trimethylenedipyridine; and 100 ppm of glycine, beta-alanine, valine, aspartic acid, glutamic acid, phenylalanine, and N-(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)glycine (also known as tricine). Planarization was accomplished on a POLI 500 brand polisher using an IC1010 brand polishing pad at a platen speed of about 60 rpm, a carrier speed of about 63 rpm, a down force of about 1.5 psi, and a slurry flow rate of about 100 mL/minute; polishing time: 60 seconds. SER was determined by dipping the wafers in 35° C. and 45° C. slurries with oxidizer present, for two minutes. The SER results are provided in FIG. 3, reported as normalized SER as a percentage of the SER obtained using a slurry without any polymer additive.

[0044] The data in FIG. 3 clearly indicate that the pyridine compound and amino acids with non-acidic side chains provided significant Ge SER reductions. Acidic amino acids such as aspartic acid and glutamic acid were ineffective, while methionine and phenylglycine provided some suppression of SER, but were significantly less effective than the other non-acidic amino acids. Lysine, arginine, histidine, glycine, beta-alanine, and valine all reportedly have an isoelectric point, pI, of 6 or greater, whereas methionine, phenylglycine the acidic amino acids have a pI of less than 6. Consequently, in some embodiments, the preferred amino acid-type Ge etching inhibitors have an isoelectric point of 6 or greater.

EXAMPLE 3

[0045] This example illustrates the effects of lysine, arginine and polyMADQUAT on Ge removal (RR) and Ge SER.

[0046] Ge blanket wafers with (100) preferred orientation were planarized with aqueous CMP slurries (at a pH of about 2.3) comprising colloidal silica, hydrogen peroxide, and various combinations of polyMADQUAT (ALCO 4773), lysine and arginine. The Ge removal rates (RR) and static etch rates (SER) were evaluated. Planarization was accomplished on a POLI 500 brand polisher using an IC1010 brand polishing pad at a platen speed of about 60 rpm, a carrier speed of about

63 rpm, a down force of about 1.5 psi, and a slurry flow rate of about 100 mL/minute; polishing time: 60 seconds. SER was determined by dipping the wafers in 35° C. and 45° C. slurries with oxidizer present, for two minutes. Table 2 provides a summary of the colloidal silica materials used and silica concentrations, the amino acids and concentration thereof, the polymer concentration, and the hydrogen peroxide concentration, as well as the observed, germanium SER and RR. Preferred target SER and RR are <100 Å/min and 200-2000 Å/min, respectively.

TABLE 2

Sam- ple	Silica Wt % (PS*)	Amino acid, (Conc. ppm)	Alco4773 (Conc. ppm)	H ₂ O ₂ Wt %	SER (Å/min) @35° C.	Ge RR (Å/min)
A	2% (30)	0	0	2.0%	~1500	~2250
B	2% (30)	0	100	2.0%	~150	~400
C	2% (30)	0	325	2.0%	291	149
D	2% (30)	0	1000	2.0%	154	139
E	2% (50)	Lys (1000)	0	2.0%	270.4	849.7
F	2% (50)	Lys (5000)	0	2.0%	199.3	745.1
G	2% (50)	Arg (1000)	0	2.0%	207.1	1847.2
H	2% (50)	Arg (5000)	0	2.0%	261.3	2120.1
I	2% (50)	Lys (5000)	325	2.0%	94	260
J	1% (50)	Arg (1000)	10	2.0%	102	1555
K	1% (50)	Arg (1000)	10	1.0%	99	1633
L	1% (50)	Arg (1000)	10	0.5%	14	1196
M	1% (50)	Arg (1000)	25	2.0%	103.9	671.3
N	1% (50)	Arg (1000)	50	2.0%	97.9	493.7
O	1% (50)	Arg (5000)	10	2.0%	87.0	1231.5
P	1% (50)	Arg (5000)	50	2.0%	85.7	529.7

*PS = nominal primary particle size of cationic surface-modified colloidal silica, in nm

[0047] As is evident from the data in Table 2, the combinations of amino acid plus polyMADQUAT generally provided SER values within or very close to the preferred range of <100 Å/min while also maintaining the Ge removal rates within the desire target range of 200 to 2000 Å/min.

[0048] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0049] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. The terms “consisting of” and “consists of” are to be construed as closed terms, which limit any compositions or methods to the specified components or steps, respectively, that are listed in a given claim or portion of the specification. In addition, and because of its open nature, the term “comprising” broadly encompasses compositions and methods that “consist essentially of” or “consist of” specified components or steps, in addition to compositions and methods that include other components or steps beyond those listed in the given claim or portion of the specification. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated, into the specification as if it were individually recited herein. All numerical values

obtained by measurement (e.g., weight, concentration, physical dimensions, removal rates, flow rates, and the like) are not to be construed as absolutely precise numbers, and should be considered to encompass values within the known limits of the measurement techniques commonly used in the art, regardless of whether or not the term “about” is explicitly stated. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate certain aspects of the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention. **[0050]** Preferred embodiments of this invention are described herein, including, the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

1. A method of polishing germanium comprising the step of abrading the surface of a substrate comprising germanium with an aqueous chemical mechanical polishing (CMP) composition comprising an oxidizing agent, a particulate abrasive, and a germanium etching inhibitor comprising a cationic polymer selected from the group consisting of poly(diallyldimethylammonium)chloride (polyDADMAC), poly(methacryloyloxyethyltrimethylammonium)chloride (polyMADQUAT), poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) (polyDEE), and a copolymer of acrylamide and DADMAC, plus an amino acid selected from the group consisting of lysine, arginine, histidine, glycine, beta-alanine, tricine, and valine.

2.-10. (canceled)

11. A method of polishing germanium comprising the step of abrading the surface of a substrate comprising germanium with an aqueous chemical mechanical polishing (CMP) composition comprising an oxidizing agent, a particulate abrasive, and a germanium etching inhibitor comprising a bis-pyridine compound of formula Pyr-R'-Pyr, wherein each Pyr independently is a pyridine group attached to R' at the 2, 3, or 4 position of the pyridine group; R' is a covalent bond, (CH₂)_n, or CH=CH; and n is 1, 2, or 3.

12. The method of claim 11 wherein the bis-pyridine compound comprises at least one compound selected from the group consisting of 4,4'-trimethylenedipyridine, 1,2-bis(4-pyridyl)ethane, 2,2'-bipyridyl, and 1,2-bis(2-pyridyl)ethylene.

13. The method of claim 1 wherein the amino acid is present in the composition at a concentration in the range of about 50 to about 5000 parts-per-million (ppm).

14. The method of claim 1 wherein the water-soluble polymer is present in the CMP composition at a concentration in the range of about 10 to about 2000 ppm.

15. The method of claim 1 wherein the bis-pyridine compound is present in the composition at a concentration in the range of about 50 to about 5000 ppm.

16. The method of claim 1 wherein the particulate abrasive comprises colloidal silica at a concentration in the range of about 0.5 to about 3.5 percent by weight (wt %).

17. The method of claim 1 wherein the CMP composition comprises about 0.5 to about 3.5 wt % of the colloidal silica, and about 10 to about 2000 ppm of the water soluble polymer.

18. The method of claim 1 wherein the CMP composition comprises about 0.5 to about 3.5 wt % of the colloidal silica, and about 50 to about 5000 ppm of the amino acid.

19. The method of claim 1 wherein the CMP composition comprises about 0.5 to about 3.5 wt % of the colloidal silica, about 10 to about 2000 ppm of the polymer, and about 50 to about 5000 ppm of the amino acid.

20. The method of claim 1 wherein the oxidizing agent comprises hydrogen peroxide at a concentration in the range of about 0.5 to about 4 wt %.

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