

TITLE

CMP Formulations and Methods for Polishing Polysilicon Films

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States Provisional Patent Application No. 63/601,119, filed on November 20, 2023, which is herein incorporated in its entirety.

BACKGROUND

[0002] This disclosure relates to the chemical mechanical planarization (CMP) compositions that are useful for polishing films containing polysilicon.

[0003] In semiconductor device manufacturing, hardmasks are used for etching deep, high aspect ratio (HAR) features that conventional photoresists cannot withstand. For advanced logic and memories, including DRAM and vertical NAND, the hardmask requirements include very high etch selectivity, low stress, and good mechanical strength. It also needs to be removable when etching is completed. For advanced devices with very high aspect ratios, hardmask thickness needed is pretty large. As a result, CMP is considered a method a suitable technology for removing hard masks.

[0004] Polycrystalline silicon (polysilicon or poly-Si) containing films are used in various IC applications. Components comprising polysilicon films may be gate electrodes, damascene interconnects, and structural components.

[0005] Polysilicon films may be deposited over a stop layer comprising films such as silicon oxide (SiO₂) or silicon nitride (SiN). Selectivity is characteristically expressed as the ratio of the polysilicon film polish or removal rate to the stop layer polish or removal rate. For certain applications, a high selectivity of polysilicon films over stop layer film is desired to protect the stop layer.

SUMMARY

[0006] The present disclosure provides CMP polishing compositions for polishing films comprising polysilicon.

[0007] In a first main aspect, the a chemical mechanical polishing composition is provided. The chemical mechanical polishing composition comprising: an abrasive comprising silica particles; 0.01 wt.% to 10.0% wt.%, preferably 0.025 wt.% to 1.0 wt.%, or most preferably 0.05 wt.% to 0.5 wt.% of a first chemical additive, wherein the first chemical additive comprises a molecule comprising a quaternary ammonium compound; between 0.005 wt.% and 1.0 wt.% or preferably between 0.01 and 0.5 wt.% of a second chemical additive, wherein the second chemical additive comprises a sulfonic acid compound; a water soluble solvent; and optionally a biocide; and pH adjusters; wherein the chemical mechanical polishing composition has a pH of preferably 8 to 12, more preferably 9 to 11, and most preferably 9.5 to 10.5.

[0008] In a further aspect of the first main aspect, the quaternary ammonium compound is chosen from the group consisting of ethyltrimethylammonium hydroxide (ETMAH), ethyltrimethylammonium bromide, ethyltrimethylammonium chloride, benzalkonium hydroxide, benzalkonium bromide, benzalkonium chloride, cetyltrimethylammonium hydroxide, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride, lauryltrimethylammonium hydroxide, lauryltrimethylammonium bromide, lauryltrimethylammonium chloride (LTAC), stearyltrimethylammonium hydroxide, stearyltrimethylammonium bromide, stearyltrimethylammonium chloride, hexadecylpyridinium hydroxide, hexadecylpyridinium bromide, hexadecylpyridinium chloride (Cetylpyridinium chloride), poly(dimethyldiallylammonium hydroxide), poly(dimethyldiallylammonium bromide), poly(dimethyldiallylammonium chloride) (PDMDAAC), trimethylstearyltrimethylammonium hydroxide, trimethylstearyltrimethylammonium bromide, trimethylstearyltrimethylammonium chloride, dimethyldioctadecyltrimethylammonium hydroxide, dimethyldioctadecyltrimethylammonium bromide, dimethyldioctadecyltrimethylammonium chloride, tetraalkyltrimethylammonium hydroxides, tetraalkyltrimethylammonium bromides, tetraalkyltrimethylammonium chlorides, tetramethyltrimethylammonium hydroxide (TMAH), tetramethyltrimethylammonium bromide, tetramethyltrimethylammonium chloride, tetraethyltrimethylammonium hydroxide, tetraethyltrimethylammonium bromide, tetraethyltrimethylammonium chloride, tetrapropyltrimethylammonium hydroxide, tetrapropyltrimethylammonium bromide, tetrapropyltrimethylammonium chloride, tetrabutyltrimethylammonium hydroxide, tetrabutyltrimethylammonium bromide, tetrabutyltrimethylammonium chloride, ethyltrimethylammonium hydroxide, ethyltrimethylammonium bromide, ethyltrimethylammonium chloride, diethyldimethyltrimethylammonium hydroxide, diethyldimethyltrimethylammonium bromide, diethyldimethyltrimethylammonium chloride, methyltriethyltrimethylammonium hydroxide, methyltriethyltrimethylammonium bromide, methyltriethyltrimethylammonium chloride, choline

hydroxide, choline bromide, choline chloride, choline bicarbonate, choline bitartrate, and other choline salts.

[0009] In a further aspect of the first main aspect, the second chemical additive is chosen from the group consisting of methanesulfonic acid (MSA), benzenesulfonic acid (BSA), toluenesulfonic acid, p-toluenesulfonic acid, 2-naphthalenesulfonic acid, naphthalene-1-sulfonic acid, dodecylbenzenesulfonic acid (DDBSA), camphorsulfonic acid, lignosulfonic acid, and poly(styrenesulfonic acid) (PSSA), ethane disulfonic acid, naphthalene - 2 - sulfonic acid, naphthalene disulfonic acid.

[0010] In a further aspect of the first main aspect, the first chemical additive comprises ethyltrimethylammonium hydroxide. In a further aspect of the first main aspect, the second chemical additive comprises benzenesulfonic acid. In a further aspect of the first main aspect, further comprising an amino acid.

[0011] In a further aspect of the first main aspect, wherein the amino acid is glycine.

[0012] In a further aspect of the first main aspect, the first chemical additive comprises ethyltrimethylammonium hydroxide, and the second chemical additive comprises benzenesulfonic acid.

[0013] In a further aspect of the first main aspect, wherein a ratio of the first chemical additive to the second chemical additive is between about 4:1 and about 1:4, preferably between about 3:1 and about 1:3, and most preferably about 2:1 to about 1:2.

[0014] In a second main aspect, a method of chemical mechanical polishing (CMP) a semiconductor substrate having at least one surface comprising a film containing polysilicon and silicon nitride is provided. The method comprising: providing the semiconductor substrate; providing a polishing pad; providing the chemical mechanical polishing (CMP) composition in any of claims 1 to 9; contacting the surface of the semiconductor substrate with the polishing pad and the chemical mechanical polishing composition; and polishing the least one surface.

[0015] In a further aspect of the second main aspect, a selectivity of polysilicon removal rate to silicon nitride removal rate is greater than about 50, preferably greater than about 70, and more preferably greater than about 80.

[0016] In a further aspect of the second main aspect, a removal rate of polysilicon is greater than about 5000 Å/min, preferably greater than about 6000 Å/min, most preferably greater than about 6500 Å/min.

[0017] In a third main aspect, a system of chemical mechanical polishing (CMP) a semiconductor substrate having at least one surface comprising a film containing polysilicon is provided. The system comprising: a. the semiconductor substrate; b. the chemical mechanical polishing (CMP) composition in any one of claims 1 to 9; and c. a polishing pad; wherein the at least one surface comprising polysilicon is in contact with the polishing pad and the chemical mechanical polishing composition.

[0018] In a further aspect of the third main aspect, the semiconductor substrate further comprises a silicon oxide film, wherein the silicon oxide film is selected from the group consisting of Chemical vapor deposition (CVD), Plasma Enhance CVD (PECVD), High Density Deposition CVD (HDP), or spin on silicon oxide film.

[0019] In a further aspect of the third main aspect, the semiconductor substrate further comprises a silicon nitride film.

[0020] In a further aspect of the third main aspect, a selectivity of polysilicon removal rate to silicon nitride removal rate is greater than about 50, preferably greater than about 70, and more preferably greater than about 80.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0021] FIG. 1. A graph is provided showing removal rate and selectivity of CMP compositions of example 1 of the instant disclosure;

[0022] FIG. 2. A graph is provided showing removal rate and selectivity of CMP compositions of example 2 of the instant disclosure; and

[0023] FIG. 3. A graph is provided showing silicon nitride removal rates of CMP compositions of example 2 of the instant disclosure.

DETAILED DESCRIPTION

[0024] Semiconductor device manufacturing includes processes to form intricately patterned films on the substrate. Producing the patterned films involves several deposition, etching, and polishing (CMP) steps. Hardmasks are often used to protect underlying films during the etching process. CMP is one of the processes that is used to remove hardmasks after the etching processes has been completed.

[0025] Polysilicon based films are widely being used due to their superior chemical and mechanical properties.

[0026] The polished polysilicon films may include more than 50% of polycrystalline silicon in terms of atomic percentage. The polished polysilicon films may also additionally include other elements such as but not limited to silicon, germanium, carbon, nitrogen, phosphorous, oxygen and hydrogen.

[0027] This disclosure relates to the Chemical mechanical polishing (CMP) compositions for polishing polysilicon containing films.

[0028] More specifically, the disclosed chemical mechanical polishing (CMP) composition for polysilicon containing films have a unique combination of using silica particles and the suitable chemical additives for boosting removal rates of polysilicon containing films and for reducing removal rates of silicon nitride containing films.

[0029] The first type of chemical additive is a polysilicon removal rate booster.

[0030] Preferably, the first chemical additive comprises a molecule comprising a quaternary ammonium compound.

[0031] Preferably, the quaternary ammonium compound is chosen from the group consisting of ethyltrimethylammonium hydroxide (ETMAH), ethyltrimethylammonium bromide, ethyltrimethylammonium chloride, benzalkonium hydroxide, benzalkonium bromide, benzalkonium chloride, cetyltrimethylammonium hydroxide, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride, lauryltrimethylammonium hydroxide, lauryltrimethylammonium bromide, lauryltrimethylammonium chloride (LTAC), stearyltrimethylammonium hydroxide, stearyltrimethylammonium bromide, stearyltrimethylammonium chloride, hexadecylpyridinium hydroxide, hexadecylpyridinium bromide, hexadecylpyridinium chloride (Cetylpyridinium chloride), poly(dimethyldiallylammonium hydroxide), poly(dimethyldiallylammonium bromide), poly(dimethyldiallylammonium chloride) (PDMDAAC), trimethylstearyltrimethylammonium hydroxide, trimethylstearyltrimethylammonium bromide, trimethylstearyltrimethylammonium chloride, dimethyldioctadecyltrimethylammonium hydroxide, dimethyldioctadecyltrimethylammonium bromide, dimethyldioctadecyltrimethylammonium chloride, tetraalkyltrimethylammonium hydroxides, tetraalkyltrimethylammonium bromides, tetraalkyltrimethylammonium chlorides, tetramethyltrimethylammonium hydroxide (TMAH), tetramethyltrimethylammonium bromide, tetramethyltrimethylammonium chloride, tetraethyltrimethylammonium hydroxide, tetraethyltrimethylammonium bromide, tetraethyltrimethylammonium chloride, tetrapropyltrimethylammonium hydroxide, tetrapropyltrimethylammonium bromide, tetrapropyltrimethylammonium chloride, tetrabutyltrimethylammonium hydroxide, tetrabutyltrimethylammonium bromide, tetrabutyltrimethylammonium chloride, ethyltrimethylammonium hydroxide, ethyltrimethylammonium bromide, ethyltrimethylammonium chloride,

diethyldimethylammonium hydroxide, diethyldimethylammonium bromide, diethyldimethylammonium chloride, methyltriethylammonium hydroxide, methyltriethylammonium bromide, methyltriethylammonium chloride, choline hydroxide, choline bromide, choline chloride, choline bicarbonate, choline bitartrate, and other choline salts.

[0032] More preferably, the CMP composition comprises 0.01 wt.% to 10.0% wt.%, preferably 0.025 wt.% to 1.0 wt.%, or most preferably 0.05 wt.% to 0.5 wt.% of a first chemical additive

[0033] Preferably, the first chemical additive comprises ethyltrimethylammonium hydroxide.

[0034] The second type of chemical additive is a silicon nitride removal rate suppressor. Preferably, the second chemical additive comprises a sulfonic acid compound.

[0035] Preferably, the sulfonic acid compound is chosen from the group consisting of methanesulfonic acid (MSA), benzenesulfonic acid (BSA), toluenesulfonic acid, p-toluenesulfonic acid, 2-naphthalenesulfonic acid, naphthalene-1-sulfonic acid, dodecylbenzenesulfonic acid (DDBSA), camphorsulfonic acid, lignosulfonic acid, and poly(styrenesulfonic acid) (PSSA), ethane disulfonic acid, naphthalene - 2 - sulfonic acid, naphthalene disulfonic acid.

[0036] More preferably, the CMP composition comprises between 0.005 wt.% and 1.0 wt.% or preferably between 0.01 and 0.5 wt.% of a second chemical additive.

[0037] Preferably, the second chemical additive comprises benzenesulfonic acid.

[0038] The particle sizes of the silica particles disclosed herein range from 5 nm to 1,000nm as measured by dynamic light scattering (DLS). The preferred mean particle sizes range from 20nm to 500nm, the more preferred mean particle sizes range from 20nm to 100nm.

[0039] Silica particles may be modified using any suitable methods to provide positive surface charge. One of the ways could be incorporating a cationic compound in the formulation itself. Alternatively, silica particles could be modified to yield positive surface zeta potential prior to incorporation into the slurry formulation.

[0040] Examples of suitable methods of modifying the surface charge of the particles include but not limited to treatment of particles or precursors to the particles

with nitrogen or phosphorous compounds. Several such methods are known in publications such as U.S. Patent No. 9,499,721, U.S. Patent Publication No. 20030209522, U.S. Patent Publication No. 20050079718, and U.S. Patent Publication No. 20090081927. Treated particles may contain nitrogen or phosphorous compounds on the surface of the particles or be internal to the outer surface of the particle or form a shell on the core particle. Aminosilane compounds are the most preferred nitrogen-containing compound. Such aminosilane compounds may include primary aminosilanes, secondary aminosilanes, tertiary aminosilanes, quaternary aminosilanes, and multi-podal (e.g., dipodal) aminosilanes. The aminosilane compound may include substantially any suitable aminosilane, for example, a propyl group containing aminosilane, or an aminosilane compound including a propyl amine. Examples of suitable aminosilanes may include 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, N-(trialkoxysilylethyl)benzyl-N,N,N-trimethyl ammonium, (bis(methyldialkoxysilylpropyl)-N-methyl amine, bis(trialkoxysilylpropyl)urea, bis(3-(trialkoxysilyl)propyl)-ethylenediamine, bis(trialkoxysilylpropyl)amine, bis(trialkoxysilylpropyl)amine, 3-aminopropyltrialkoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldialkoxysilane, N-(2-aminoethyl)-3-aminopropyltrialkoxysilane, 3-aminopropylmethyldialkoxysilane, 3-aminopropyltrialkoxysilane, (N-trialkoxysilylpropyl)polyethyleneimine, trialkoxysilylpropyldiethylenetriamine, N-phenyl-3-aminopropyltrialkoxysilane, N-(vinylbenzyl)-2-aminoethyl-3-aminopropyltrialkoxysilane, 4-aminobutyltrialkoxysilane, and mixtures thereof.

[0041] Silica can be any of precipitated silica, fumed silica, silica fumed, pyrogenic silica, colloidal silica, high purity colloidal silica, silica doped with one or more adjuvants, or any other silica-based compound. In an alternate embodiment the silica can be produced, for example, by a process selected from the group consisting of a sol-gel process, a hydrothermal process, a plasma process, a fuming process, a precipitation process, and any combination thereof. Silica may also be modified by incorporating various metals or metallic compounds in the bulk or the surface of the particles.

[0042] Particles may have various shapes including but not limited to spherical, cocoon or chain like structures. Preferred particle shape is cocoon. Cocoon shaped particles are characterized by aggregate ratio which is the ratio of mean particle size

measured by DLS to primary particle diameter calculated based on specific surface area assuming nonporous spherical particles. Preferred aggregate ratio of cocoon shaped particles is >1.7 or more preferably between 1.7 and 2.3.

[0043] The concentrations of these silica particles range from 0.01 wt.% to 20 wt.%, the preferred concentrations range from 0.05 wt.% to 2 wt.%, the more preferred concentrations range from 0.1 wt.% to 1 wt.%.

[0044] The water soluble solvent includes but is not limited to deionized (DI) water, distilled water, and alcoholic organic solvents. The preferred water soluble solvent is DI water.

[0045] The polysilicon polishing CMP composition may contain biocide from 0.0001 wt.% to 0.05 wt.%; preferably from 0.0005 wt.% to 0.025 wt.%, and more preferably from 0.001 wt.% to 0.01 wt.%.

[0046] The biocide includes, but is not limited to, Kathon™, Kathon™ CG/ICP II, from Dupont/Dow Chemical Co. Bioban from Dupont/Dow Chemical Co. They have active ingredients of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one.

[0047] The polysilicon CMP composition may contain a pH adjusting agent.

[0048] An acidic or basic pH adjusting agent can be used to adjust the polysilicon polishing compositions to the optimized pH value.

[0049] The pH adjusting agents include, but are not limited to nitric acid, hydrochloric acid, sulfuric acid, phosphoric acid, other inorganic or organic acids, and mixtures thereof.

[0050] pH adjusting agents also include the basic pH adjusting agents, such as sodium hydride, potassium hydroxide, ammonium hydroxide, tetraalkyl ammonium hydroxide, organic quaternary ammonium hydroxide compounds, organic amines, and other chemical reagents that can be used to adjust pH towards the more alkaline direction.

[0051] The polysilicon CMP composition contains 0 wt.% to 1 wt.%; preferably 0.01 wt.% to 0.5 wt.%; more preferably 0.02 wt.% to 0.25 wt.% pH adjusting agent.

[0052] The polysilicon CMP composition contains 0.01 wt.% to 10.0% wt.%, preferably 0.025 wt.% to 1.0 wt.%, or most preferably 0.05 wt.% to 0.5 wt.% of a first

chemical additive, wherein the first chemical additive comprises a molecule comprising a quaternary ammonium compound.

[0053] The polysilicon CMP composition contains between 0.005 wt.% and 1.0 wt.% or preferably between 0.01 and 0.5 wt.% of a second chemical additive, wherein the second chemical additive comprises a sulfonic acid compound

[0054] Preferably, the first chemical additive comprises ethyltrimethylammonium hydroxide, and the second chemical additive comprises benzenesulfonic acid.

[0055] Concentration of second chemical additive (Si booster compound) can be between 0.01 and 0.2 wt.% or preferably between 0.01 and 0.05 wt.%.

[0056] In certain embodiments, the CMP formulation has a ratio of the first chemical additive to the second chemical additive is between about 4:1 and about 1:4, preferably between about 3:1 and about 1:3, and most preferably about 2:1 to about 1:2.

[0057] The formulations may be shipped in the concentrate form and diluted at the point of use with the addition of water. Component concentrations in a concentrate would be increased as per the dilution factor at point of use. In the illustrated embodiment, the dilution factor is between about 2x and about 10x, preferably between about 3x and about 8x.

[0058] In certain embodiments, the formulation is provided as a single pack of concentrated slurry with excellent particle stability defined by measuring particle size change over an aging period of at least 10 days at 50 degrees Celsius. The slurry is deemed stable when the particle size change over at least 10 days is less than 5 nm, or preferably less than 3 nm or most preferably less than 2nm

[0059] In another embodiment, the slurry may be made in multiple packs, where in one of the packs may be rich in abrasive particles, another pack may be rich in chemical additives; and the different packs are combined at point of use along with dilution of water and optionally oxidizer for the polishing purposes.

[0060] Polysilicon film polish removal rates are preferably greater than 5000 Å/min or more preferably greater than 6000 Å/min or most preferably greater than 7000 Å/min

[0061] The substrate disclosed above can further comprises a dielectric film. The dielectric film may be any suitable film such as silicon nitride or silicon oxide or any film comprising silicon, carbon and oxygen elements in various component concentration.

[0062] Silicon oxide films may be deposited by many different techniques. Typically, silicon oxide films are deposited using Tetraethyl orthosilicate precursor using chemical vapor deposition techniques, referred to as TEOS films. Other types of silicon oxide films commonly used are HDP (High density Plasma) oxides and thermal oxides.

[0063] In preferred embodiments, the removal selectivity of polysilicon film removal rate: silicon nitride film removal rate is greater than 50, preferably greater than 70, and more preferably greater than 80, wherein the dielectric films may be a silicon oxide or a silicon nitride film.

[0064] The following non-limiting examples are presented to further illustrate the subject matter of the present disclosure.

CMP Methodology

[0065] In the examples presented below, CMP experiments were run using the procedures and experimental conditions given below.

Metrology

[0066] Films were measured with KLA FX5 ellipsometric measurement system. Forty-nine-point diameter scan at 5mm edge exclusion for film was taken before and after polishing to measure the removal rates of polysilicon films, TEOS films and SiN films.

CMP Tool

[0067] The CMP tool that was used is 300mm Ebara Frex 300X. An IC1010 pad supplied by Dupont, Inc, 451 Bellevue Rd., Newark, DE 19713 was used for polishing wafers.

Polishing Experiments

[0068] The tool baseline conditions were: table speed; 103rpm, head speed: 97 rpm, membrane pressure; 2.5 psi downforce, composition flow; 250 ml/min. The polishing pad used for testing was IC1070 pad which was supplied by Dupont . In situ conditioning with Saesol conditioning disk (Part# AM02B8031C7) at 3.2 psi down-force was used for the testing.

Wafers

[0069] In the examples presented below, CMP experiments were run using the procedures and experimental conditions given below.

Components

[0070] High purity colloidal silica: used as abrasive having a mean particle size ranged from about 40 nm to 120 nm supplied by FUSO CHEMICAL Co., LTD in Japan.

[0071] Chemical additives, such as benzenesulfonic acid (BSA) was supplied by Sigma-Aldrich, St Louis, Mo. Ethyltrimethylammonium Hydroxide (ETMAH) was supplied by Sachem, Woodward St. Austin, Texas. KOH used as a pH adjustor was supplied by Samchun. in Korea.

[0072] Polishing Pad: Polishing pad, IC1070 and other pads were used during CMP, supplied by Dupont.

[0073] Conditioners were used during CMP, supplied by Saesol Inc. Seonggok-dong, Ansan, in Korea

1. Slurry preparation for test

[0074] For polish test, slurry was prepared, mixing abrasive, chemicals sequentially and adjusted pH with KOH.

2. CMP tool

[0075] The CMP tool that was used is a 300mm Ebara manufactured by Ebara Technologies, Inc. 51 Main Avenue Sacramento, CA 95838. An IC1070 pad supplied by DOW, Inc 451 Bellevue Rd., Newark, Del. 19713 was used for blanket and pattern wafer studies. The IC1070 pad or other pad was break-in by conditioning the pad for 30 mins at 9lbf and 10min at 5lbf with DIW.

3. Wafers

[0076] Polishing experiments were conducted using PECVD or LPCVD or HD TEOS wafers purchased from Advantech (ADV) Co., Ltd, Hibiya-Kokusai, Chiyoda-ku, Tokyo in Japan. LP-SiN and polysilicon wafers were purchased from ADV Co., Ltd, Hibiya-Kokusai, Chiyoda-ku, Tokyo in Japan.

4. Polishing experiment

[0077] In blanket wafer studies, oxide blanket wafers, and SiN blanket wafers were polished at baseline conditions. The tool baseline conditions were: table speed; 103 rpm; head speed; 97 rpm; polish down force; 2.5psi; slurry flow speed; 250ml/min.

[0078] These wafers were measured thickness by F5X from KLA-Tencor corporation 1 Technology Drive Milpitas, CA 95035.

Working Examples

[0079] Tables 1 and 2 shows the polishing performance and the removal rates corresponding to the tested formulations. Polysilicon (Poly-Si) removal rate, SiN removal rate, and TEOS removal rate data was collected. Abrasive 1 has a mean particle size of 80 nm, Abrasive 2 has a mean particle size of 40 nm, and Abrasive 3 has a mean particle size of 120 nm. Slurry pH was adjusted to 10.5. The water soluble solvent was deionized (DI) water.

Example 1. Effect of Comparison of Poly-Si:SiN selectivity using various additives and abrasives.

[0080] In Example 1, silicon nitride, TEOS and polysilicon removal rate were checked different formulation based on piperidine and ETMAH. pH range was 8 to 12. Different sized abrasives were tested.

[0081] Table 1 Film Removal rates and Poly-Si:SiN Selectivity

CMP Comp.	1 (Ref.)	2	3	4	5	6	7	8
Poly-Si RR (Å/min.)	7305	8148	5415	5577	5175	6078	7338	7158
SiN RR (Å/min.)	24	15	12	10.5	10.5	63	46.5	58.5
TEOS RR (Å/min.)	22.5	19.5	10.5	13.5	16.5	168	57	117
Poly-Si: SiN Selectivity	304.3	543.2	451.2	531.1	492.8	96.4	157.8	122.3
Glycine (wt.%)	0.2	0.2	0.1	0.1	0.1	0.1	0.2	0.1
Piperidine (wt.%)	0.1600	0.2500						
ETMAH (wt.%)			0.2	0.24	0.2	0.24	0.15	0.15
BSA (wt.%)						0.3		0.3
Abrasive 1 (wt.%)	2	4					3	3

Abrasive 2 (wt.%)			3.5	3.5		3.5		
Abrasive 3 (wt.%)					3.5			
pH adjustor (wt.%) (base to pH 10.5)	0.13	0.090				0.165	0.127	0.165
pH adjustor (wt.%) (acid to pH 10.5)				0.006	0.03			

[0082] As results shown Table 1, a higher amount of ETMAH in formulation shows lower SiN removal rate than piperidine formulation. Also in case of examples 3 and 4, an increased amount of ETMAH from 0.2 to 0.24% shows decreased SiN rate 12 Å/min to 10.5 Å/min and it makes high Poly-Si:SiN selectivity (451.2 to 531.1).

Example 2. Comparison of Poly-Si:SiN selectivity according to the type and concentration of acid

[0083] In Example 2, This is an example of decreasing the SiN removal rate while maintaining the Poly-Si removal rate at an appropriate level (>6000 Å/min). In each formulation, 3 wt% of silica abrasive, 0.1 to 0.3% of acid additive (acid) and 0.09 to 0.5 wt% of pH adjustor were used. The test results were listed in Table 2.

[0084] Table 2. Film Removal Rates with acid additive

Film	1	2	3	4	5
Poly-Si RR (Å/min.)	6774	6360	6636	6684	6581
SiN RR (Å/min.)	79.5	94.5	85.5	108	97.6
TEOS RR (Å/min.)	78	97	129	113	155
Poly-Si: SiN Selectivity	85.21	67.30	77.61	61.89	67.43
Glycine (wt.%)	0.3	0.3	0.3	0.3	0.3
ETMAH (wt.%)	0.15	0.15	0.15	0.15	0.15
PEG 8000					
BSA (wt.%)	0.1	0.3			
Etidronic acid (wt.%)			0.1	0.3	
Nicotinic acid (wt.%)					0.1
Abrasive 3 (wt.%)	3	3	3	3	3

pH adjustor (base)	0.211	0.245	0.337	0.297	0.475
-----------------------	-------	-------	-------	-------	-------

[0085] As the results shown in Table 2 illustrate, the 0.1% Benzenesulfonic acid containing formulation (number one) shows low SiN removal rate as 79.5Å/min and high Poly-Si:SiN selectivity than other formulations as < 85 with highest poly-Si removal rate 6774 Å/min.

[0086] Table 2 shows the polishing performance and the removal rates corresponding to those formulations. Polysilicon removal rate, SiN removal rate, and TEOS removal rate data was collected.

[0087] By optimizing the abrasive concentration and the additive concentrations, a combination of high polysilicon film rates and low silicon nitride removal rates were achieved. Polysilicon to nitride selectively of greater than 80 was achieved with a ratio of the first chemical additive (ETMAH) to the second chemical additive (BSA) of about 1:1 to about 1:2.

[0088] The embodiments listed above, including the working example, are exemplary of numerous embodiments that may be made of this disclosure. It is contemplated that numerous other configurations of the process may be used, and the materials used in the process may be elected from numerous materials other than those specifically disclosed.

CLAIMS

We claim:

1. A chemical mechanical polishing composition comprising:
 - an abrasive comprising silica particles;
 - 0.01 wt.% to 10.0% wt.%, preferably 0.025 wt.% to 1.0 wt.%, or most preferably 0.05 wt.% to 0.5 wt.% of a first chemical additive, wherein the first chemical additive comprises a molecule comprising a quaternary ammonium compound;
 - between 0.005 wt.% and 1.0 wt.% or preferably between 0.01 and 0.5 wt.% of a second chemical additive, wherein the second chemical additive comprises a sulfonic acid compound;
 - a water soluble solvent; and
 - optionally
 - a biocide; and
 - pH adjusters;
 - wherein the chemical mechanical polishing composition has a pH of preferably 8 to 12, more preferably 9 to 11, and most preferably 9.5 to 10.5.
2. The chemical mechanical polishing composition of claim 1, wherein the quaternary ammonium compound is chosen from the group consisting of ethyltrimethylammonium hydroxide (ETMAH), ethyltrimethylammonium bromide, ethyltrimethylammonium chloride, benzalkonium hydroxide, benzalkonium bromide, benzalkonium chloride, cetyltrimethylammonium hydroxide, cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride, lauryltrimethylammonium hydroxide, lauryltrimethylammonium bromide, lauryltrimethylammonium chloride (LTAC), stearyltrimethylammonium hydroxide, stearyltrimethylammonium bromide, stearyltrimethylammonium chloride, hexadecylpyridinium hydroxide, hexadecylpyridinium bromide, hexadecylpyridinium chloride (Cetylpyridinium chloride), poly(dimethyldiallylammonium hydroxide), poly(dimethyldiallylammonium bromide), poly(dimethyldiallylammonium chloride) (PDMDAAC), trimethylstearyltrimethylammonium hydroxide, trimethylstearyltrimethylammonium bromide, trimethylstearyltrimethylammonium chloride, dimethyldioctadecylammonium hydroxide, dimethyldioctadecylammonium bromide, dimethyldioctadecylammonium chloride, tetraalkylammonium hydroxides, tetraalkylammonium bromides, tetraalkylammonium chlorides,

tetramethylammonium hydroxide (TMAH), tetramethylammonium bromide, tetramethylammonium chloride, tetraethylammonium hydroxide, tetraethylammonium bromide, tetraethylammonium chloride, tetrapropylammonium hydroxide, tetrapropylammonium bromide, tetrapropylammonium chloride, tetrabutylammonium hydroxide, tetrabutylammonium bromide, tetrabutylammonium chloride, ethyltrimethylammonium hydroxide, ethyltrimethylammonium bromide, ethyltrimethylammonium chloride, diethyldimethylammonium hydroxide, diethyldimethylammonium bromide, diethyldimethylammonium chloride, methyltriethylammonium hydroxide, methyltriethylammonium bromide, methyltriethylammonium chloride, choline hydroxide, choline bromide, choline chloride, choline bicarbonate, choline bitartrate, and other choline salts.

3. The chemical mechanical polishing composition of claim 1, wherein the second chemical additive is chosen from the group consisting of methanesulfonic acid (MSA), benzenesulfonic acid (BSA), toluenesulfonic acid, p-toluenesulfonic acid, 2-naphthalenesulfonic acid, naphthalene-1-sulfonic acid, dodecylbenzenesulfonic acid (DDBSA), camphorsulfonic acid, lignosulfonic acid, and poly(styrenesulfonic acid) (PSSA), ethane disulfonic acid, naphthalene - 2 - sulfonic acid, naphthalene disulfonic acid.
4. The chemical mechanical polishing composition of claim 2, wherein the first chemical additive comprises ethyltrimethylammonium hydroxide.
5. The chemical mechanical polishing composition of claim 3, wherein the second chemical additive comprises benzenesulfonic acid.
6. The chemical mechanical polishing composition of claim 1, further comprising an amino acid.
7. The chemical mechanical polishing composition of claim 6, wherein the amino acid is glycine.

8. The chemical mechanical polishing composition of claim 1, wherein the first chemical additive comprises ethyltrimethylammonium hydroxide, and the second chemical additive comprises benzenesulfonic acid.
9. The chemical mechanical polishing composition of claim 1, wherein a ratio of the first chemical additive to the second chemical additive is between about 4:1 and about 1:4, preferably between about 3:1 and about 1:3, and most preferably about 2:1 to about 1:2.
10. A method of chemical mechanical polishing (CMP) a semiconductor substrate having at least one surface comprising a film containing polysilicon and silicon nitride, comprising:
 - providing the semiconductor substrate;
 - providing a polishing pad;
 - providing the chemical mechanical polishing (CMP) composition of claim 1;
 - contacting the surface of the semiconductor substrate with the polishing pad and the chemical mechanical polishing composition; and
 - polishing the least one surface.
11. The method of claim 10, wherein a selectivity of polysilicon removal rate to silicon nitride removal rate is greater than about 50, preferably greater than about 70, and more preferably greater than about 80.
12. The method of claim 10, wherein a removal rate of polysilicon is greater than about 5000 Å/min, preferably greater than about 6000 Å/min, most preferably greater than about 6500 Å/min.
13. A system of chemical mechanical polishing (CMP) a semiconductor substrate having at least one surface comprising a film containing polysilicon, comprising:
 - a. the semiconductor substrate;
 - b. the chemical mechanical polishing (CMP) composition of claim 1; and
 - c. a polishing pad;wherein the at least one surface comprising polysilicon is in contact with the polishing pad and the chemical mechanical polishing composition.

14. The system of claim 13, wherein the semiconductor substrate further comprises a silicon oxide film, wherein the silicon oxide film is selected from the group consisting of Chemical vapor deposition (CVD), Plasma Enhance CVD (PECVD), High Density Deposition CVD(HDP), or spin on silicon oxide film.
15. The system of claim 13, wherein the semiconductor substrate further comprises a silicon nitride film.
16. The system of claim 15, wherein a selectivity of polysilicon removal rate to silicon nitride removal rate is greater than about 50, preferably greater than about 70, and more preferably greater than about 80.