

Thus, some CMP applications require very low removal rates for SiN and/or SiC, since they might be used as a stop layer in a certain film stack.

5 **[0007]** There are works been done in the art to achieve very low SiN rates for shallow trench isolation (STI) applications. Babu et al. (Journal of The Electrochemical Society, 156, 12, H936-H943, 2009) or Carter et al. (US7071105; Electrochemical and Solid-State Letters, 8, 8, G218-G221, 2005) reported on additives to increase the selectivity of silicon oxide to silicon nitride.

10 **[0008]** Mainly, the addition of certain organic acids was used in the CMP slurries, as for example picolinic acid. However, all these prior art examples use ceria particles as abrasive which features a completely different removal mechanism than silica particles as abrasive so that additives which work with ceria like picolinic acid do not work at all with silica particles.

15 **[0009]** Furthermore, STI slurries are usually used at a pH range of 4-7 which is not suitable for advanced barrier applications due to potential corrosion issues on metal films.

[0010] Additionally, ceria slurries cannot be used in combination with hydrogen peroxide or other suitable oxidizer which are generally required to achieve sufficient metal or barrier film removal rates.

20 **[0011]** Therefore, there are significant needs for CMP slurries, methods, and systems that can perform CMP for very low removal rate on the stop layer (such as silicon containing layers) while providing other meeting other requirements such as removal rates for other layers, low dishing and low defects.

SUMMARY

25 **[0012]** Described herein are CMP polishing compositions, methods and systems that satisfy the need. Present invention discloses the use of an additive in CMP slurries, for suppressing removal rates of a silicon containing films during CMP process; wherein the additive is a water soluble aluminium compound.

30 **[0013]** In one embodiment, described herein is a CMP polishing composition comprising:

0.01 wt % to 20 wt% of an abrasive selected from the group consisting of high purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia, alumina dopes colloidal silica in lattices, and mixtures thereof;

- 0.01 % to about 10 wt % of a water soluble aluminium compound ;
optionally,
0.0001 wt % to about 5 wt % of a pH adjusting agent;
0.0001 wt% to 10 wt % of a surfactant selected from the group consisting of a).
5 non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic surface
wetting agents; d). ampholytic surface wetting agents; and mixtures thereof;
0.0005wt % to about 0.5wt % of a corrosion inhibitor;
0.01 wt % to 10 wt % of an oxidizing agent selected from the group consisting of
peroxy-compound comprising at least one peroxy group (O-O), oxidized halide, perboric
10 acid, perborate, percarbonate, peroxyacid, permanganate, chromate, cerium compound,
ferricyanide, and mixtures thereof; and
0.1 wt % to 5 wt % of an organic acid;
and
water;
15 wherein the polishing composition has a pH above 7; preferably from about 8 to
12; more preferably from about 10 to 12.

[0014] In a further embodiment, described herein is a polishing method for chemical
mechanical planarization of a semiconductor device comprising at least one surface
20 having a first material and a second material comprising at least one silicon containing
material; comprising the steps of:

- a) contacting the at least one surface with a polishing pad;
b) delivering a polishing composition to the at least one surface, the polishing
composition comprising:
25 0.01 wt % to 20 wt% of an abrasive selected from the group consisting of high
purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia,
alumina dopes colloidal silica in lattices, and mixtures thereof;
0.01 % to about 10 wt % of a water soluble aluminium compound;
optionally,
30 0.0001 wt % to about 5 wt % of a pH adjusting agent;
0.0001 wt% to 10 wt % of a surfactant selected from the group consisting of a).
non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic
surface wetting agents; d). ampholytic surface wetting agents; and mixtures
thereof;

0.0005wt % to about 0.5wt % of a corrosion inhibitor;
 0.01 wt % to 10 wt % of an oxidizing agent selected from the group consisting of
 peroxy-compound comprising at least one peroxy group (O-O), oxidized halide,
 perboric acid, perborate, percarbonate, peroxyacid, permanganate, chromate,
 5 cerium compound, ferricyanide, and mixtures thereof; and
 0.1 wt % to 5 wt % of an organic acid;
 and
 water;
 wherein the polishing composition has a pH above 7; preferably from about 8 to
 10 12; more preferably from about 10 to 12;
 c) polishing the at least one surface with the polishing composition to remove the
 first material and to stop-on the second material.

[0015] In yet another embodiment, described herein is a system for chemical
 mechanical planarization, comprising:

15 a patterned substrate comprising at least one surface having a first material and
 a second material comprising at least one silicon containing material;
 a polishing pad; and
 a polishing composition to the at least one surface, the polishing composition
 comprising:
 20 0.01 wt % to 20 wt% of an abrasive selected from the group consisting of high
 purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia,
 alumina dopes colloidal silica in lattices, and mixtures thereof;
 0.01 % to about 10 wt % of a water soluble aluminium compound;
 optionally,
 25 0.0001 wt % to about 5 wt % of a pH adjusting agent;
 0.0001 wt% to 10 wt % of a surfactant selected from the group consisting of a).
 non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic
 surface wetting agents; d). ampholytic surface wetting agents; and mixtures
 thereof;
 30 0.0005wt % to about 0.5wt % of a corrosion inhibitor;
 0.01 wt % to 10 wt % of an oxidizing agent selected from the group consisting of
 peroxy-compound comprising at least one peroxy group (O-O), oxidized halide,
 perboric acid, perborate, percarbonate, peroxyacid, permanganate, chromate,
 cerium compound, ferricyanide, and mixtures thereof; and

0.1 wt % to 5 wt % of an organic acid;

and

water;

wherein the polishing composition has a pH above 7; preferably from about 8 to

5 12; more preferably from about 10 to 12; and

the at least one surface is in contact with the polishing pad and the polishing composition.

[0016] The water soluble aluminium compound additive includes, but is not limited to, sodium aluminate, potassium aluminate, aluminium acetate, aluminium chloride,
10 aluminium sulfate, aluminium hydroxide, and combinations thereof. It is desired that the aluminium compound should be soluble in slurry formulation at the concentrations added. Aluminate salts are preferable forms of aluminium compounds. Aluminate salt can be generated in situ in the CMP slurry formulation by using compounds of aluminium such as aluminium hydroxide, $\text{Al}(\text{OH})_3$ or aluminium salts such as aluminium acetate,
15 aluminium chloride, aluminium sulfate, etc. with a suitable hydroxide base such as potassium hydroxide, KOH, or sodium hydroxide, NaOH.

[0017] The water soluble aluminium compound may be present in the concentration ranging from 0.01 % to about 10 wt %, or more preferably between 0.05% to about 5 wt% or more preferably between 0.1 wt% and 1 wt%.

20 **[0018]** The pH-adjusting agent in the polishing composition is selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, chloroacetic acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, sulfonic acid, phosphoric acid, fatty acid, polycarboxylic acid, hydrogen chloride, and mixtures thereof; or is selected from the group consisting of potassium hydroxide, sodium hydroxide, ammonia, quaternary
25 organic ammonium hydroxide (e.g. tetramethylammonium hydroxide), ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof.

[0019] The corrosion inhibitor in the polishing composition is a chemical additive containing nitrogen atoms in the molecules, preferably selected from the group consisting of benzotriazole (BTA) and its derivatives, triazole and its derivatives (e.g. 3-
30 amino-1,2,4-triazole and 3,5-diamino-1,2,4-triazole); imidazole and its derivatives, pyrazole and its derivatives, benzimidazole and its derivatives, and combinations thereof. The organic acid can be any suitable organic acid includes but is not limited to an aromatic organic acid (e.g. benzenesulfonic acid, toluenesulfonic acid), and amino acid or salt thereof.

[0032] Figure 7 shows the removal rates of different films in barrier layer using barrier CMP polishing slurries containing an aluminate salt (aluminium acetate) with no oxidizing agent.

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DETAILED DESCRIPTION

[0033] Many CMP applications involve simultaneous polishing of two or more layers, wherein the one or more layers is polished at high rates relative to another layer (stopping layer) which needs to be polished at a much lower rate. Many applications use a stopping layer comprising silicon or a compound of silicon including but not limited to
10 silicon oxide, silicon nitride, silicon oxy-nitride, silicon carbide or silicon oxy-carbide, polysilicon, amorphous silicon or any other combination comprising silicon, oxygen, oxygen, carbon, nitrogen, hydrogen. This can be very difficult to achieve since high removal rates for other films in the stack may be only achievable with a high abrasive loading inevitably leading to a higher removal rate for the stopping film. This is particularly problematic if
15 silica particles are used as abrasives and a higher pH (>7) is necessary for performance reasons. Silicon containing films such as SiN or SiO₂ undergo hydrolysis in alkaline pH range resulting in higher removal rates of the films. Therefore, there is a need for additives that allow stopping on SiN and/or SiC without sacrificing any other removal rates or selectivities.

20 **[0034]** The first material includes but is not limited to metal films selected from the group consisting of Cu, W, Co, Al and combinations thereof; barrier or liner films selected from the group consisting of Ta, TaN, Ti, TiN, Ru and combinations thereof; dielectric films including low-k material; and combinations thereof; and the at least one silicon containing material includes but is not limited to silicon nitride, silicon oxide, silicon
25 carbide, and combinations thereof.

[0035] Formulations of this invention are especially useful for polishing semiconductor wafers containing different levels of materials. The wafer contains at least a surface comprising a first material and at least one silicon containing material.

30 **[0036]** Formulations of this invention are especially useful for reducing the removal rates of silicon containing films such as silicon oxide (SiO₂), silicon nitride (SiN), silicon carbide (SiC), silicon oxy-carbide (SiOC)

[0037] Compositions of this invention provides at least one of the following: (1) low removal rates of a stop layer; (2) maintaining a high removal rates of various types of other film/layer; (3) desirable selectivity among various films; (4) a desirable low level of within a wafer non-uniformity ("WIW NU%"); and (5) low residue level(s) being present on the polished wafer(s) subsequent to CMP processing.

[0038] Present invention discloses the use of an additive in CMP slurries, for suppressing removal rates of a silicon containing films during CMP process; wherein the additive is a water soluble aluminium compound.

[0039] CMP compositions of present invention comprise abrasive particles, water soluble aluminium compound, and water. Optionally compositions may also comprise other functional additives including but not limited to complexing or chelating agents, pH modifiers, removal rate selectivity modifiers, corrosion inhibitors, oxidizers, surfactants, dispersants, catalysts, and biocides or preservatives.

[0040] The water soluble aluminium compound additive includes, but is not limited to, sodium aluminate, potassium aluminate, aluminium acetate, aluminium chloride, aluminium sulfate, aluminium hydroxide, and combinations thereof. Preferable for of aluminium containing compound is aluminates. Alternatively, the aluminate salt can be generated in situ in the CMP slurry formulation by using a compounds of aluminium such as aluminium hydroxide, $\text{Al}(\text{OH})_3$ or aluminium salts such as aluminium acetate, aluminium chloride, aluminium sulfate, etc. with a suitable hydroxide base such as potassium hydroxide, KOH, or sodium hydroxide, NaOH. In alkaline pH, the salts may undergo hydrolysis and form aluminate anions ($[\text{Al}(\text{OH})_4]^-$). Aluminate anions may undergo polymerization to form dimeric or polymeric aluminium complexes.

[0041] Without being limited by theory, it is believed that Si containing films hydrolyze and form silanol species (Si-OH) at the surface in during CMP which is generally regarded as essential step for achieving high removal rates for CMP. Aluminate species subsequently forms an insoluble complex with it similar to Al-silicate. The insoluble complex acts as an inhibitor against further hydrolysis of the films, thereby suppressing the removal rates of the Si containing films.

[0042] The amount of a water soluble aluminium compound ranges from about 0.01 wt % to about 10 wt % relative to the total weight of the CMP composition. The preferred range is from about 0.05 wt % to about 3 wt %, and more preferred range is from about 0.1 wt % to about 1 wt %.

[0043] The suitable abrasives for this invention include, but are not limited to, high purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia, alumina dopes colloidal silica in lattices, ceria coated silica particles and mixtures thereof.

5 **[0044]** The preferred particulate material is colloidal silica. The colloidal silica can be made from sodium silicate, or can be made from TEOS (tetraethylorthosilicate) or TMOS (tetramethylorthosilicate). Still preferred is high purity colloidal silica with very low levels of trace metal impurities (alkali metals <300 ppb and heavy metals < 100ppb). Examples of high purity colloidal silica that can be used are Fuso™ PL-3, PL2, PL3H and PL3L high purity colloidal silica particles obtained from Fuso Chemical Company, Japan.

10 **[0045]** A mixture of colloidal silica particles of different particle sizes and types may also yield improved performance

[0046] The abrasive is present in an amount from 0.01 wt % to 20 wt%, preferably, from 0.05 wt % to 10 wt%, more preferably, from about 0.1wt % to about 5 wt %.

15 **[0047]** The polishing composition has a pH above 7; preferably from about 8 to 12; more preferably from about 10 to 12.

[0048] Formulations of this invention are especially effective at pH 7 or higher where solubility of the water soluble aluminium compound is higher. Alkaline pH is also suitable for CMP compositions that require protection of metals such as copper and cobalt. Higher pH is also desired for improved colloidal stability for the particles used in the CMP
20 slurry.

[0049] The polishing composition may optionally include an oxidizing agent.

[0050] The oxidizing agent can be any suitable oxidizing agent.

[0051] Suitable oxidizing agents includes, but is not limited to, one or more peroxy-compounds, which comprise at least one peroxy group (O-O). Suitable peroxy-
25 compounds include, for example, but are not limited to, peroxides, persulfates (e.g., monopersulfates and dipersulfates), percarbonates, and acids thereof, and salts thereof, and mixtures thereof.

[0052] Other suitable oxidizing agents include, for example, oxidized halides (e.g., chlorates, bromates, iodates, perchlorates, perbromates, periodates, and acids thereof,
30 and mixtures thereof, and the like), perboric acid, perborates, percarbonates, peroxyacids (e.g., peracetic acid, perbenzoic acid, m-chloroperbenzoic acid, salts

thereof, mixtures thereof, and the like), permanganates, chromates, cerium compounds, ferricyanides (e.g., potassium ferricyanide), mixtures thereof, and the like. Some specific oxidizers that are useful in the composition and method described herein include, but are not limited to, hydrogen peroxide, periodic acid, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and mixtures thereof.

[0053] Preferred oxidizing agent is peroxide including, for example, hydrogen peroxide and urea-hydrogen peroxide.

[0054] The amount of oxidizing agent ranges from about 0.01 wt % to 10 wt % relative to the total weight of the CMP composition. The preferred range is from about 0.1 wt % to 4 wt %, and more preferred range is from about 0.5 wt % to 2 wt %.

[0055] Removal rates of Si containing films such as SiN, SiC, TEOS during CMP formulations can be suppressed with the water soluble aluminium compound even in the absence of oxidizing agent. However certain applications such as metal and barrier CMP would need oxidizer addition.

[0056] CMP slurry formulations may also optionally include surfactants or surface wetting agents. Surfactants may be used to for a variety of purposes such as reducing defects on the wafers, tuning of removal rates and reduction in post-polish topography. The suitable surfactant includes, but is not limited to, a). non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic surface wetting agents; d). ampholytic surface wetting agents; and mixtures thereof.

[0057] In one aspect, the surfactant can be a nonionic surfactant. Non-ionic surfactants may be chosen from a range of chemical types including but not limited to long chain alcohols, ethoxylated alcohols, ethoxylated acetylenic diol surfactants, polyethylene glycol alkyl ethers, propylene glycol alkyl ethers, glucoside alkyl ethers, polyethylene glycol octylphenyl ethers, polyethylene glycol alkylphenyl ethers, glycerol alkyl esters, polyoxyethylene glycol sorbiton alkyl esters, sorbiton alkyl esters, cocamide monoethanol amine, cocamide diethanol amine dodecyl dimethylamine oxide, block copolymers of polyethylene glycol and polypropylene glycol, polyethoxylated tallow amines, fluorosurfactants. The molecular weight of surfactants may range from several hundreds to over 1 million. The viscosities of these materials also possess a very broad distribution.

[0068] The CMP composition may further comprise a corrosion inhibitor.

[0069] The suitable corrosion inhibitor includes, but is not limited to, chemical additives contain nitrogen atoms in the molecules. Examples of corrosion inhibitors include but not limited to benzotriazole (BTA) and benzotriazole derivatives, triazole and their relative derivatives; imidazole, pyrazole and its derivatives, benzimidazole and its derivatives, and combinations thereof.

[0070] The amount of corrosion inhibitor ranges from about 0.0005wt % to about 0.5wt % relative to the total weight of the CMP composition. The preferred range is from about 0.0025% to about 0.15wt %, and more preferred range is from about 0.01wt % to about 0.1wt %,

[0071] CMP composition may further comprise organic acid. The organic acid can be any suitable organic acid includes but is not limited to an aromatic organic acid, and amino acid or salt thereof. The aromatic organic acid can be described as a ligand that can have some interactions with some films on the surfaces of the wafers.

[0072] The aromatic organic acid includes, but is not limited to benzenesulfonic acid or toluenesulfonic acid or any other organic acid or amino acid.

[0073] The amount of organic acid ranges from about 0.1 wt % to about 5 wt % relative to the total weight of the CMP composition. The preferred range is from about 0.2 wt % to about 2 wt %, and more preferred range is from about 0.25 wt % to about 1 wt %.

[0074] CMP slurry may include a chelating or complexing agent. Complexing agent may serve different purposes such as increasing removal rates during CMP, reduce pad staining, increasing solutbility of the water soluble aluminium compound, increasing the pH range where the aluminium compounds are soluble.

[0075] The suitable chelating agent includes, but is not limited to organic acids and their salts; polymeric acids and their salts; water soluble copolymers and their salts; copolymers and their salts containing at least two different types of acid groups selected from carboxylic acid groups; sulfonic acid groups; phosphoric acids; and pyridine acids in the same molecule of a copolymer; polyvinyl acids and their salts, inorganic potassium silicate and ammonium silicate; polyethylene oxide; polypropylene oxide; pyridine, pyridine derivatives, bipyridine, bipyridine derivatives, and combinations thereof.

[0076] The organic acids include but are not limited to amino acids; carboxylic acids; phosphoric acids; sulfonic acids; polyvinyl acids; and pyridine acids; bipyridine acids.

[00112] The CMP tool that was used in the examples is a Mirra®, manufactured by Applied Materials, 3050 Bowers Avenue, Santa Clara, California, 95054. A Fujibo H7000HN pad, supplied by Narubeni America Corporation, was used on the platen for the blanket wafer polishing studies. Pads were broken-in by polishing twenty-five dummy oxide (deposited by plasma enhanced CVD from a TEOS precursor, PETEOS) wafers. In order to qualify the tool settings and the pad break-in, two PETEOS monitors were polished with Syton® OX-K colloidal silica, supplied by Air Products Chemical Incorporation, at baseline conditions. Polishing experiments were conducted using electroplating deposited copper, low-k dielectric layer materials (Black Diamond®), tantalum nitride, PVD cobalt and silicon nitride wafers. These blanket wafers were purchased from Silicon Valley Microelectronics, 1150 Campbell Ave, CA, 95126, and Advantiv Corporation.

[00113] In the examples, the chemicals, such as aluminate salt, or the chemicals used to generate the aluminate salt, such as aluminium hydroxide or $\text{Al}(\text{OH})_3$, potassium hydroxide or KOH, sodium hydroxide or NaOH, were purchased from Sigma-Aldrich Corporation.

Working Examples

[00114] In the following working examples, the CMP polishing slurries comprised a corrosion inhibitor such as benzotriazole (BTA) and benzotriazole derivatives, triazole or triazole derivatives, such as 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, a chemical additive as ligand such as benzenesulfonic acid as the surface wetting agent/surfactant, an aluminate salt, an abrasive, a pH-adjusting agent, and optionally an oxidizing agent and an aromatic organic acid.

Table I

Control Composition	Wt %
Potassium hydroxide(KOH)	0.7021
Benzotriazole	0.0105
Benzenesulfonic acid	0.4540
Fuso PL3	3.1035
Dynol 607	0.0078
Water	95.7221

[00115] The barrier CMP slurries were used for polishing various types of films of relevance for barrier applications. The pH of the CMP polishing slurries were around 10-11.

5 [00116] A barrier CMP composition (shown in Table I) was used as a control or reference composition.

[00117] The working barrier CMP polishing slurries were obtained by adding different amount of aluminate salt to the control composition. Alternatively, the aluminate salt can be generated in situ by mixing a stoichiometric amount of aluminium hydroxide, $\text{Al}(\text{OH})_3$ with potassium hydroxide, KOH, or sodium hydroxide, NaOH.

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Example 1

[00118] 0.10 wt%, 0.15 wt% and 0.25 wt% of sodium aluminate (NaAlO_2) were added to the control composition (as shown in Table I) to obtain the barrier CMP polishing slurries as shown in Table II. The CMP slurries were then used to polish SiN substrate. The SiN removal rate results were shown in Table II and Figure 1.

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[00119] Figure 2 gave the SiN removal rate as the function of the concentrations of sodium aluminate in the slurries.

Table II

CMP polishing Composition	SiN RR ($\text{\AA}/\text{min}$)
Control	147
Control + 0.10 wt% Sodium Aluminate	95
Control + 0.15 wt% Sodium Aluminate	84
Control + 0.25 wt% Sodium Aluminate	0

[00120] The results showed that with the addition of 0.10 wt% of sodium aluminate (NaAlO_2) the SiN removal rate was reduced by 35% versus the control composition without any aluminate salt additive. The addition of 0.15wt% of sodium aluminate brought down the SiN removal rate by 43% versus the control composition. While with the addition of 0.25 wt% of sodium aluminate, the SiN removal rate dropped to 0.

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[00121] The data also indicated that the SiN removal rate could be tuned as desired.

25

Example 4

[00128] 0.10 wt%, 0.20 wt%, 0.25 wt% and 0.3 wt % of potassium aluminate (KAlO_2) were added to the control composition (as shown in Table I) to obtain the barrier CMP polishing slurries.

- 5 [00129] The potassium aluminate (KAlO_2) was generated in situ by mixing a stoichiometric amount of aluminium hydroxide, $\text{Al}(\text{OH})_3$ with potassium hydroxide, KOH .

[00130] The CMP slurries were used to polish a number of films of relevance for barrier application such as cobalt, copper, low-K (BD1), silicon oxide (SiO_2) (TEOS), and silicon nitride(SiN).

- 10 [00131] The results of removal rates were shown in Table V and Figures 5 and 6.

Table V

	SiN RR($\text{\AA}/\text{min}$)	TEOS RR($\text{\AA}/\text{min}$)	BD1 RR($\text{\AA}/\text{min}$)	Co RR($\text{\AA}/\text{min}$)	Cu RR($\text{\AA}/\text{min}$)
Control (Ctrl)	337	779	1061	301	231
Ctrl + 0.1wt% Potassium Aluminate	232	485	1116	280	268
Ctrl + 0.2wt% Potassium Aluminate	109	142	981	300	258
Ctrl + 0.25wt% Potassium Aluminate	0	0	851	279	212
Ctrl + 0.3wt% Potassium Aluminate	0	0	724	214	219

- [00132] The results showed that with the addition of potassium aluminate (KAlO_2) both SiN removal rate and TEOS removal rate were reduced versus the control composition without any aluminate salt additive. The addition of 0.25wt% of potassium aluminate brought down the SiN removal rate and TEOS removal rate to 0.
- 15

[00133] The data also indicated that the SiN removal rate and TEOS removal rate could be tuned as desired.

- [00134] As the results for using sodium aluminate, the removal rates of other films such as cobalt, copper, or a low-K film like Black Diamond 1TM (BD1) were least affected.
- 20

Example 5

[00135] 0.2078 wt% of Aluminium Acetate(AlAc) was added to the control composition (as shown in Table I) to obtain the barrier CMP polishing composition.

[00136] The CMP composition was used to polish a number of films of relevance for barrier application such as cobalt, copper, low-K (BD1), silicon oxide (SiO₂) (TEOS), and silicon nitride(SiN).

[00137] The results of removal rates were shown in Table VI and Figure 7.

5

Table VI

	SiN RR(Å/min)	TEOS RR(Å/min)	BD1 RR(Å/min)	Co RR(Å/min)	Cu RR(Å/min)
Control (Ctrl)	325	789	1002	225	209
Ctrl + 0.2078wt% AlAc	224	477	1079	236	246

[00138] The results showed that with the addition of 0.2078 wt% aluminium acetate, the SiN removal rate was reduced by 31% versus the control composition; and TEOS removal rate was reduced by 40% versus the control composition. While, the composition had no effect on the removal rates of other films.

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[00139] It has been demonstrated that the addition of an aluminate salt to a colloidal silica composition resulted in a reduction of removal rates for silicon containing films (such SiN and TEOS) while no or minimum effect on other films such as cobalt, copper, or a low-K film like a low-K film like Black Diamond 1TM (BD1).

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[00140] The ensuing detailed description provides preferred exemplary embodiments only, and is not intended to limit the scope, applicability, or configuration of the invention. Rather, the ensuing detailed description of the preferred exemplary embodiments will provide those skilled in the art with an enabling description for implementing the preferred exemplary embodiments of the invention. Various changes may be made in the function and arrangement of elements without departing from the spirit and scope of the invention, as set forth in the appended claims.

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CLAIMS

1. A polishing composition comprising:
0.01 wt % to 20 wt% of an abrasive selected from the group consisting of high
purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia,
alumina dopes colloidal silica in lattices, and mixtures thereof;
0.01 % to 10 wt % of a water soluble aluminium compound;
and
water;
wherein the polishing composition has a pH above 7.
2. The polishing composition of Claim 1, wherein
the water soluble aluminium compound is selected from the group consisting of
sodium aluminate, potassium aluminate, aluminium acetate, aluminium chloride,
aluminium sulfate, aluminium hydroxide, and combinations thereof.
3. The polishing composition of Claim 1
further comprises at least one of:
0.0001 wt % to 5 wt % of a pH adjusting agent;
0.0001 wt% to 10 wt % of a surfactant selected from the group consisting of a).
non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic
surface wetting agents; d). ampholytic surface wetting agents; and mixtures
thereof;
0.0005wt % to 0.5wt % of a corrosion inhibitor;
0.01 wt % to 10 wt % of an oxidizing agent selected from the group consisting of
peroxy-compound comprising at least one peroxy group (O-O), oxidized halide,
perboric acid, perborate, percarbonate, peroxyacid, permanganate, chromate,
cerium compound, ferricyanide, and mixtures thereof; and
0.1 wt % to 5 wt % of an organic acid.
4. The polishing composition of Claim 3, wherein
the corrosion inhibitor is a chemical additive containing nitrogen atoms in the
molecules selected from the group consisting of benzotriazole (BTA) and its
derivatives, triazole and its derivatives; imidazole and its derivatives, pyrazole
and its derivatives, benzimidazole and its derivatives, and combinations thereof;

the pH-adjusting agent is selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, chloroacetic acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, sulfonic acid, phosphoric acid, fatty acid, polycarboxylic acid, hydrogen chloride, and mixtures thereof; or is selected from the group
5 consisting of potassium hydroxide, sodium hydroxide, ammonia, quaternary organic ammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof;
and
the organic acid is selected from the group consisting of aromatic organic acid,
10 amino acid or salt thereof, and combinations thereof.

5. The polishing composition of Claim 3, wherein
the non-ionic surface wetting agent is selected from the group consisting of
ethoxylated alcohol, ethoxylated acetylenic diol surfactant, polyethylene glycol
15 alkyl ether, propylene glycol alkyl ether, glucoside alkyl ether, polyethylene glycol octylphenyl ether, polyethylene glycol alkylphenyl ether, glycerol alkyl ester, polyoxyethylene glycol sorbiton alkyl ester, sorbiton alkyl ester, cocamide monoethanol amine, cocamide diethanol amine, dodecyl dimethylamine oxide, block copolymers of polyethylene glycol and polypropylene glycol,
20 polyethoxylated tallow amines, fluorosurfactant, and combinations thereof;
the anionic surface wetting agent is selected from the group consisting of alkyl carboxylate, alkyl polyacrylic salt, alkyl sulfate, alkyl phosphate, alkyl bicarboxylate, alkyl bisulfate, alkyl biphosphate, alkoxy carboxylate, alkoxy sulfate, alkoxy phosphate, alkoxy bicarboxylate, alkoxy bisulfate, alkoxy
25 biphosphate, substituted aryl carboxylate, substituted aryl sulfate, substituted aryl phosphate, substituted aryl bicarboxylate, substituted aryl bisulfate, substituted aryl biphosphate, and combinations thereof;
the cationic surface wetting agent is a halide of molecules comprising
hydrophobic chain and cationic charge center selected from the group consisting
30 of amine, quaternary ammonium, benzyalkonium and alkylpyridinium ion;
and
the ampholytic surface wetting agent possess both positive (cationic) and negative (anionic) charges on the main molecular chains and with their relative counter ions.

- 5 6. The polishing composition of Claim 3 comprises high purity colloidal silica particles; water soluble aluminium compound selected from the group consisting of sodium aluminate, potassium aluminate, aluminium acetate, aluminium hydroxide, and combinations thereof; and the polishing composition has a pH of 8 to 12.
- 10 7. The polishing composition of Claim 6 further comprising corrosion inhibitor selected from the group consisting of benzotriazole (BTA) and its derivatives, triazole and its derivatives, and combinations thereof; potassium hydroxide; benzenesulfonic acid; optionally a peroxy-compound comprising at least one peroxy group; and the polishing composition has a pH of 10 to 12.
- 15 8. A polishing method for chemical mechanical planarization of a semiconductor device comprising at least one surface having a first material and a second material, comprising the steps of:
- a) contacting the at least one surface with a polishing pad;
- b) delivering a polishing composition to the at least one surface, the polishing composition comprising:
- 20 0.01 wt % to 20 wt% of an abrasive selected from the group consisting of high purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia, alumina dopes colloidal silica in lattices, and mixtures thereof;
- 0.01 % to 10 wt % of a water soluble aluminium compound;
- and
- 25 water;
- wherein the polishing composition has a pH above 7;
- c) polishing the at least one surface with the polishing composition to remove the first material and to stop-on the second material;
- wherein
- 30 the first material is selected from the group consisting of a metal, a barrier or liner material, a dielectric material, and combinations thereof; and the second material comprises at least one silicon containing material.
9. The method of Claim 8, wherein

the water soluble aluminium compound in the polishing composition is selected from the group consisting of sodium aluminate, potassium aluminate, aluminium acetate, aluminium chloride, aluminium sulfate, aluminium hydroxide, and combinations thereof.

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10. The method of Claim 8, wherein

the polishing composition further comprises at least one of:

0.0001 wt % to 5 wt % of a pH adjusting agent;

0.0001 wt% to 10 wt % of a surfactant selected from the group consisting of a).

10 non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic surface wetting agents; d). ampholytic surface wetting agents; and mixtures thereof;

0.0005wt % to 0.5wt % of a corrosion inhibitor;

15 0.01 wt % to 10 wt % of an oxidizing agent selected from the group consisting of peroxy-compound comprising at least one peroxy group (O-O), oxidized halide, perboric acid, perborate, percarbonate, peroxyacid, permanganate, chromate, cerium compound, ferricyanide, and mixtures thereof; and

0.1 wt % to 5 wt % of an organic acid.

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11. The method of Claim 10, wherein

the corrosion inhibitor in the polishing composition is a chemical additive

containing nitrogen atoms in the molecules selected from the group consisting of benzotriazole (BTA) and its derivatives, triazole and its relative derivatives;

imidazole and its derivatives, pyrazole and its derivatives, benzimidazole and its
25 derivatives, and combinations thereof;

the pH-adjusting agent is selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, chloroacetic acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, sulfonic acid, phosphoric acid, fatty acid, polycarboxylic acid, hydrogen chloride, and mixtures thereof; or is selected from the group

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consisting of potassium hydroxide, sodium hydroxide, ammonia, quaternary organic ammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof;

and

the organic acid is selected from the group consisting of aromatic organic acid, amino acid or salt thereof, and combinations thereof.

12. The method of Claim 10, wherein

5 the non-ionic surface wetting agent is selected from the group consisting of ethoxylated alcohol, ethoxylated acetylenic diol surfactant, polyethylene glycol alkyl ether, propylene glycol alkyl ether, glucoside alkyl ether, polyethylene glycol octylphenyl ether, polyethylene glycol alkylphenyl ether, glycerol alkyl ester, polyoxyethylene glycol sorbiton alkyl ester, sorbiton alkyl ester, cocamide
10 monoethanol amine, cocamide diethanol amine, dodecyl dimethylamine oxide, block copolymers of polyethylene glycol and polypropylene glycol, polyethoxylated tallow amines, fluorosurfactant, and combinations thereof; the anionic surface wetting agent is selected from the group consisting of alkyl carboxylate, alkyl polyacrylic salt, alkyl sulfate, alkyl phosphate, alkyl
15 bicarboxylate, alkyl bisulfate, alkyl biphosphate, alkoxy carboxylate, alkoxy sulfate, alkoxy phosphate, alkoxy bicarboxylate, alkoxy bisulfate, alkoxy biphosphate, substituted aryl carboxylate, substituted aryl sulfate, substituted aryl phosphate, substituted aryl bicarboxylate, substituted aryl bisulfate, substituted aryl biphosphate, and combinations thereof;
20 the cationic surface wetting agent is a halide of molecules comprising hydrophobic chain and cationic charge center selected from the group consisting of amine, quaternary ammonium, benzyalkonium and alkylpyridinium ion; and
the ampholytic surface wetting agent possess both positive (cationic) and
25 negative (anionic) charges on the main molecular chains and with their relative counter ions.

13. The method of Claim 10, wherein

the polishing composition comprises high purity colloidal silica particles; water
30 soluble aluminium compound selected from the group consisting of sodium aluminate, potassium aluminate, aluminium acetate, aluminium chloride, aluminium sulfate, aluminium hydroxide, and combinations thereof; and the polishing composition has a pH of 8 to 12; and the first material is selected from the group consisting of metal film selected from the group consisting of Cu, W,
35 Co, Al and combinations

thereof; barrier or liner film selected from the group consisting of Ta, TaN, Ti, TiN, Ru and combinations thereof; low-k material dielectric film; and combinations thereof; and the at least one silicon containing material is selected from the group consisting of silicon nitride, silicon oxide, silicon carbide, and combinations thereof.

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14. The method of Claim 13, wherein the polishing composition further comprising corrosion inhibitor selected from the group consisting of benzotriazole (BTA) and its derivatives, triazole and its derivatives, and combinations thereof; potassium hydroxide; benzenesulfonic acid; optionally a peroxy-compound comprising at least one peroxy group; and the polishing composition has a pH of 10 to 12.

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15. A system for chemical mechanical planarization, comprising:
a patterned substrate comprising at least one surface having a first material selected from the group consisting of a metal, a barrier or liner material, a dielectric material and combinations thereof; and a second material comprising at least one silicon containing material;
a polishing pad; and
a polishing composition to the at least one surface, the polishing composition comprising:
0.01 wt % to 20 wt% of an abrasive selected from the group consisting of high purity colloidal silica particles, alumina, ceria, germania, silica, titania, zirconia, alumina dopes colloidal silica in lattices, and mixtures thereof;
0.01 % to 10 wt % of a water soluble aluminium compound;
and
water;
wherein the polishing composition has a pH above 7;
and
the at least one surface is in contact with the polishing pad and the polishing composition.

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16. The system of Claim 15, wherein
the water soluble aluminium compound in the polishing composition is selected from the group consisting of sodium aluminate, potassium aluminate, aluminium

acetate, aluminium chloride, aluminium sulfate, aluminium hydroxide, and combinations thereof.

17. The system of Claim 15, wherein

5 the polishing composition further comprises at least one of:

0.0001 wt % to 5 wt % of a pH adjusting agent;

0.0001 wt% to 10 wt % of a surfactant selected from the group consisting of a). non-ionic surface wetting agents; b). anionic surface wetting agents; c). cationic surface wetting agents; d). ampholytic surface wetting agents; and mixtures

10 thereof;

0.0005wt % to 0.5wt % of a corrosion inhibitor;

0.01 wt % to 10 wt % of an oxidizing agent selected from the group consisting of peroxy-compound comprising at least one peroxy group (O–O), oxidized halide, perboric acid, perborate, percarbonate, peroxyacid, permanganate, chromate,

15 cerium compound, ferricyanide, and mixtures thereof; and

0.1 wt % to 5 wt % of an organic acid.

18. The system of Claim 17, wherein

the corrosion inhibitor in the polishing composition is a chemical additive

20 containing nitrogen atoms in the molecules selected from the group consisting of benzotriazole (BTA) and its derivatives, triazole and its derivatives; imidazole and its derivatives, pyrazole and its derivatives, benzimidazole and its derivatives, and combinations thereof;

the pH-adjusting agent is selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, chloroacetic acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, sulfonic acid, phosphoric acid, fatty acid, polycarboxylic acid, hydrogen chloride, and mixtures thereof; or is selected from the group

25 consisting of potassium hydroxide, sodium hydroxide, ammonia, quaternary organic ammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof;

30 and

the organic acid is selected from the group consisting of aromatic organic acid, amino acid or salt thereof, and combinations thereof.

19. The system of Claim 17, wherein

the non-ionic surface wetting agent is selected from the group consisting of ethoxylated alcohol, ethoxylated acetylenic diol surfactant, polyethylene glycol alkyl ether, propylene glycol alkyl ether, glucoside alkyl ether, polyethylene glycol octylphenyl ether, polyethylene glycol alkylphenyl ether, glycerol alkyl ester, polyoxyethylene glycol sorbiton alkyl ester, sorbiton alkyl ester, cocamide monoethanol amine, cocamide diethanol amine, dodecyl dimethylamine oxide, block copolymers of polyethylene glycol and polypropylene glycol, polyethoxylated tallow amines, fluorosurfactant, and combinations thereof;

the anionic surface wetting agent is selected from the group consisting of alkyl carboxylate, alkyl polyacrylic salt, alkyl sulfate, alkyl phosphate, alkyl bicarboxylate, alkyl bisulfate, alkyl biphosphate, alkoxy carboxylate, alkoxy sulfate, alkoxy phosphate, alkoxy bicarboxylate, alkoxy bisulfate, alkoxy biphosphate, substituted aryl carboxylate, substituted aryl sulfate, substituted aryl phosphate, substituted aryl bicarboxylate, substituted aryl bisulfate, substituted aryl biphosphate, and combinations thereof;

the cationic surface wetting agent is a halide of molecules comprising hydrophobic chain and cationic charge center selected from the group consisting of amine, quaternary ammonium, benzyalkonium and alkylpyridinium ion;

and

the ampholytic surface wetting agent possess both positive (cationic) and negative (anionic) charges on the main molecular chains and with their relative counter ions.

20. The system of Claim 17, wherein

the polishing composition comprises high purity colloidal silica particles; water soluble aluminium compound selected from the group consisting of sodium aluminate, potassium aluminate, aluminium acetate, aluminium chloride, aluminium sulfate, aluminium hydroxide, and combinations thereof; and the polishing composition has a pH of 8 to 12;

the metal film is selected from the group consisting of Cu, W, Co, Al and combinations thereof; the barrier or liner film is selected from the group consisting of Ta, TaN, Ti, TiN, Ru and combinations thereof; and the dielectric film is a low-k material; and