

BARRIER CHEMICAL MECHANICAL PLANARIZATION COMPOSITION AND METHOD OF USE THEREOF

The present invention relates to barrier chemical mechanical planarization ("CMP")

5 polishing compositions (or slurries, polishing composition and polishing slurry are used interchangeably) used in the production of a semiconductor device, and polishing methods for carrying out chemical mechanical planarization. In particular, it relates to barrier polishing compositions that are suitably used for polishing patterned semiconductor wafers that are composed of multi-type films, such as barrier, low k or
10 ultra low k, dielectric, and metal lines, vias or trenches.

Usually, a barrier layer covers the patterned dielectric layer and a metal layer covers the barrier layer. The metal layer has at least sufficient thickness to fill the patterned trenches with metal to form circuit interconnects.

A barrier typically is a metal, metal alloy or intermetallic compound, such as tantalum or
15 tantalum nitride. The barrier forms a layer that prevents migration or diffusion between layers within a wafer. For example, barriers prevent the diffusion of interconnect metal such as copper or silver into an adjacent dielectric. Barrier materials must be resistant to corrosion by most acids, and thereby, resist dissolution in a fluid polishing composition for CMP. Furthermore, these barrier materials may exhibit a toughness that resists
20 removal by abrasion abrasive particles in a CMP slurry and from fixed abrasive pads.

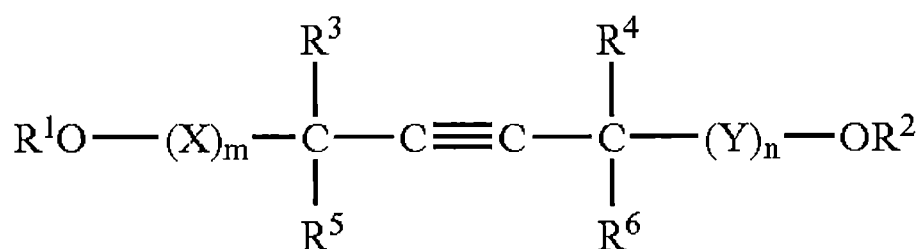
In relation to CMP, the current state of this technology involves the use of a multi-step, such as a two-step, process to achieve local and global planarization.

During step 1 of a CMP process, a metal layer such as the overburden copper is removed, while leaving a smooth planar surface on the wafer with metal-filled lines, vias
25 and trenches that provide circuit interconnects planar to the polished surface. First step polishing steps tend to remove excess interconnect metals, such as copper. Then step 2 of the CMP process, frequently referred to as a barrier CMP process, follows to remove the barrier layer and excess metal layers and other films on the surface of the patterned wafers to achieve both local and global planarization surface on the dielectric layer.

30 US patent application publication US2007/0082456A discloses a polishing composition which allows high-speed polishing while etching and erosion are prevented and the flatness of metal film is maintained. The polishing composition comprises (A) a

compound having three or more azole moieties, (B) an oxidizing agent, and (C) one or more species selected from among an amino acid, an organic acid, and an inorganic acid.

- 5 US patent application publication US2007/0181534 teaches a barrier polishing liquid which includes (a) a nonionic surfactant represented by the formula below, (b) at least one type of organic acid selected from the group consisting of an aromatic sulfonic acid, an aromatic carboxylic acid, and a derivative thereof, (c) colloidal silica, and (d) benzotriazole or a derivative thereof.



- 10 In the formula, R^1 to R^6 independently denote a hydrogen atom or an alkyl group having 1 to 10 carbons, X and Y independently denote an ethyleneoxy group or a propyleneoxy group, and m and n independently denote an integer of 0 to 20. There is also provided a chemical mechanical polishing method that includes supplying the barrier polishing liquid to a polishing pad on a polishing platen at a rate per unit area of a semiconductor
15 substrate per unit time of 0.035 to 0.25 mL/(min cm^2), and polishing by making the polishing pad and a surface to be polished move relative to each other while they are in a contacted state.

- US patent application publication US2008/0149884 A1 describes a composition and associated method for the chemical mechanical planarization (CMP) of metal substrates
20 on semiconductor wafers. The composition contains a nonionic fluorocarbon surfactant and a per-type oxidizer (e.g. hydrogen peroxide). The composition and associated method are effective in controlling removal rates of low-k films during copper CMP and provide for tuneability in removal rates of low-k films in relation to removal rates of copper, tantalum, and oxide films.

- 25 US patent application publication US2013/0168348 A1 discloses an aqueous polishing composition comprising (A) at least one type of abrasive particles which are positively charged when dispersed in an aqueous medium free from component (B) and having a

pH in the range of from 3 to 9 as evidenced by the electrophoretic mobility; (B) at least one water-soluble polymer selected from the group consisting of linear and branched alkylene oxide homopolymers and copolymers; and (C) at least one anionic phosphate dispersing agent; and a process for polishing substrate materials for electrical,

5 mechanical and optical devices making use of the aqueous polishing composition.

US patent application publication US2009/0004863 A1 discloses a polishing liquid for polishing a ruthenium-containing barrier layer, the polishing liquid being used in chemical mechanical polishing for a semi-conductor device having a ruthenium-containing barrier layer and conductive metal wiring lines on a surface thereof, the polishing liquid

10 comprising an oxidizing agent; and a polishing particulate having hardness of 5 or higher on the Mohs scale and having a composition in which a main component is other than silicon dioxide (SiO₂). The present invention also provides a polishing method for chemical mechanical polishing of a semi-conductor device, the method contacting the polishing liquid with the surface of a substrate to be polished, and polishing the surface
15 to be polished such that contacting pressure from a polishing pad to the surface to be polished is from 0.69 kPa to 20.68 kPa.

US2013/0171824 A1 discloses a CMP process for substrates containing silicon oxide dielectric films and polysilicon and/or silicon nitride films comprising the steps of (1) contacting the substrate with an aqueous composition containing (A) abrasive particles
20 which are positively charged when dispersed in an aqueous medium having a pH in the range of from 3 to 9; (B) a water-soluble or water-dispersible linear or branched alkylene oxide homopolymer or copolymer; and (C) a water-soluble or water-dispersible polymer selected from (c1) aliphatic and cycloaliphatic poly(N-vinylamide) homopolymers and copolymers, (c2) homopolymers and copolymers of acrylamide monomers of the general
25 formulas I and II: $H_2C=C(-R)-C(=O)-N(-R^1)(-R^2)$ (I), $H_2C=C(-R)-C(=O)-R^3$ (II), wherein the variables have the following meaning R hydrogen atom, fluorine atom, chlorine atom, nitrile group, or organic residue; R¹ and R² hydrogen atom or organic residue; R³ saturated N-heterocyclic ring; (c3) cationic polymeric flocculants; and (c4) mixtures thereof; (2) polishing the substrate until the silicon oxide dielectric film is
30 removed and the polysilicon and/or silicon nitride film is or are exposed.

Typically, abrasives are used in most barrier CMP compositions (or slurries). The abrasives with variable particle size and shapes provide mechanical friction forces

between polishing pad and wafer surface under applied pressure. When abrasives are used, especially with high concentration, abrasive damage (scratching) can occur. Barrier slurry compositions need to meet several stringent requirements including high barrier removal rates, very low post-polish topography, no corrosion defects and very low scratches or residue defects. Therefore, there are significant needs for barrier CMP compositions, CMP process(es) or methods when these requirements become more and more stringent as the semiconductor industry continues to move towards smaller and smaller feature sizes.

BRIEF SUMMARY OF THE INVENTION

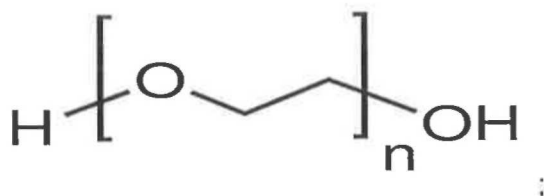
Described herein are barrier CMP polishing compositions and methods for the CMP processing.

In one embodiment, described herein is a polishing method for chemical mechanical planarization a surface of a semiconductor substrate having at least one feature thereon comprising conductive metal lines, vias or trenches, a metal-containing barrier layer and a dielectric layer; 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:

abrasive;

organic polymer containing ethylene oxide repeating units having the general molecular structure of



wherein n refers to the total numbers of the repeating unit ranging from 6,818 to 181,817; and the organic polymer having molecular weights ranging from 300,000 (or 100,000) to 8,000,000;

oxidizing agent;

corrosion inhibitor; and
chelator;

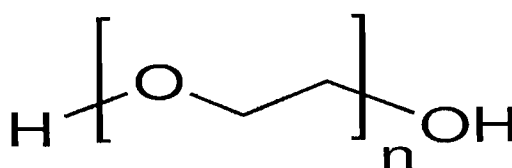
and

C) polishing the substrate with the polishing composition.

- 5 In a further embodiment, described herein is a barrier chemical mechanical planarization polishing composition comprising:

abrasive;

organic polymer containing ethylene oxide repeating units having the general molecular structure of



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wherein n refers to the total numbers of the repeating unit ranging from 6,818 to 181,817; and the organic polymer having molecular weights ranging from 300,000 (or 100,000) to
15 8,000,000;

oxidizing agent;

corrosion inhibitor; and

chelator.

The term "molecular weight" includes viscosity average molecular weight.

- 20 The remainder of the composition is preferably water, more preferably deionized water.

The organic polymer containing ethylene oxide repeating units has molecular weights ranging preferably from 300,000 to 4,000,000; and most preferably from 400,000 to 1,000,000; and has concentration ranging from 5 ppm to 5,000 ppm; preferably from 25 ppm to 2,000 ppm; and most preferred concentration range is from about 50 ppm to
25 about 1,000 ppm.

The abrasive is preferably selected from the group consisting of colloidal silica, alumina, ceria, germania, silica, titania, zirconia, alumina doped colloidal silica in lattices, organic polymer particles, composite particles of inorganic and organic particles, surface

modified inorganic/organic particles, and combinations thereof; and is preferably present in an amount ranging from about 0.1% to about 15wt %; more preferably from about 1 wt% to about 3 wt %.

5 The oxidizing agent is preferably selected from the group consisting of hydrogen peroxide, periodic acid, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, ammonia, amine compounds, and combinations thereof; and is preferably present in an amount ranging from about 0.05 wt% to about 10 wt%; preferably from about 0.5 wt% to about 2 wt%.

10 The corrosion inhibitor is preferably selected from the group consisting of benzotriazole or benzotriazole derivatives, 3-amino-1, 2, 4-triazole, 3, 5-diamine-1, 2, 4-triazole, and combinations thereof; and is preferably present in an amount ranging from about 0.001 wt% to about 1.0 wt%; preferably from about 0.01 wt% to about 0.1 wt%;

15 The chelator is preferably selected from the group consisting of benzosulfonic acid, 4-tolyl sulfonic acid, 2,4-diamino-benzosulfonic acid and mandelic acid and also non-aromatic organic acids, such as itaconic acid, malic acid, malonic acid, tartaric acid, citric acid, oxalic acid, gluconic acid, lactic acid, and combinations thereof; and is preferably present in an amount ranging from about 0.01 wt% to about 3.0 wt%; preferably about from 0.4 wt% to about 1.5wt%.

20 The polishing composition optionally further comprises a pH adjuster preferably selected from the group consisting of (a) nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids and combinations thereof to lower pH of the polishing composition; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide,
25 ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and combinations thereof to raise pH of the polishing composition; the pH adjuster is preferably present in an amount ranging from about 0.0001 wt% to about 2 wt%; and the polishing composition preferably has a pH from about 2 to about 12, preferably about 9 to about 11.5.

30 The conductive metal can be copper. The metal-containing barrier layer can be a tantalum-containing barrier layer, such as tantalum or tantalum nitride or tantalum tungsten silicon carbide; a titanium containing barrier layer, such as titanium or titanium nitride; a cobalt or self-forming manganese oxide layer; noble metals such as ruthenium;

The dielectric layer can be TEOS; a porous or a non-porous low-k film comprising silicon, carbon, oxygen and hydrogen; a porous low k material with a capping layer of a non-porous material.

Further aspects of the invention include:

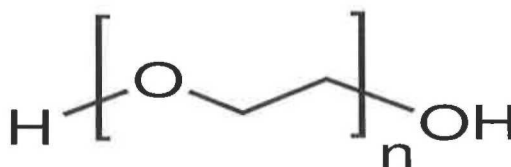
- 5 #1. A polishing method for chemical mechanical planarization of a semiconductor substrate having at least one surface having conductive metal lines, vias or trenches, a metal-containing barrier layer and a dielectric layer or low-k on thereof, comprising the steps of:

c) contacting the at least one surface with a polishing pad;

- 10 d) delivering a polishing composition to the at least one surface, the polishing composition comprising:

abrasive;

organic polymer containing ethylene oxide repeating units having the general molecular structure of



15 wherein n refers to the total numbers of the repeating unit ranging from 6,818 to 181,817; the organic polymer containing ethylene oxide repeating units having molecular weights ranging from 300,000 to 8,000,000 and concentration ranging from about 5 ppm to about 5,000 ppm;

oxidizing agent;

corrosion inhibitor; and

chelator;

25 and

C) polishing the substrate with the polishing composition.

#2. The method of #1 wherein the organic polymer containing ethylene oxide repeating units having molecular weights ranging from 400,000 to 1,000,000; and concentration ranging from about 25 ppm to about 2,000 ppm.

- 5 #3. The method of #1 wherein the abrasive is selected from the group consisting of colloidal silica, alumina, ceria, germania, silica, titania, zirconia, alumina dopes colloidal silica in lattices, organic polymer particles, composite particles comprising organic and inorganic particles, surface modified organic or inorganic particles, and combinations thereof; and in an amount ranging from about 0.1% to about 15 wt %.
- 10 #4. The method of #1 wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, periodic acid, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, ammonia, amine compounds, and combinations thereof; and in an amount ranging from about 0.01 wt% to about 10 wt%.
- 15 #5. The method of #1 wherein the corrosion inhibitor is selected from the group consisting of benzotriazole or benzotriazole derivatives, 3-amino-1, 2, 4-triazole, 3, 5-diamine-1, 2, 4-triazole, and combinations thereof; and in an amount ranging from about 0.001 wt% to about 1.0 wt%.
- 20 #6. The method of #1 wherein the chelator is selected from the group consisting of benzosulfonic acid, 4-tolyl sulfonic acid, 2,4-diamino-benzosulfonic acid, itaconic acid, malic acid, malonic acid, tartaric acid, citric acid, oxalic acid, gluconic acid, lactic acid, mandelic acid, and combinations thereof; and in an amount ranging from about 0.01 wt% to about 3.0 wt%.
- 25 #7. The method of #1 wherein the polishing composition further comprising a pH adjustor selected from the group consisting of (a) nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, fatty acid, polycarboxylic acid and combinations thereof to lower pH of the polishing composition; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and combinations thereof to raise pH of the polishing composition; and in an amount ranging from about 0.0001 wt% to 2 wt%; and the polishing composition has a pH from about 2 to about 12.
- 30 #8. The method of #1 wherein the polishing composition further comprising a surfactant selected from the group consisting of nonionic, anionic, cationic or amphoteric surfactants, and combinations thereof; and in an amount ranging from about 0.0001 wt% to about 1.0 wt %

#9. The method of #1 wherein the conductive metal is copper; the metal-containing barrier layer is a tantalum-containing barrier layer; the dielectric layer is selected from the group consisting of TEOS, and low-k material.

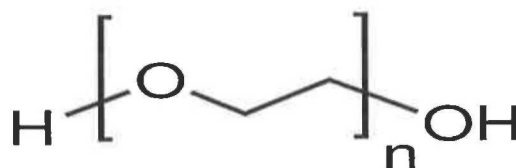
#10. The method of #9 wherein the abrasive is colloidal silica in an amount ranging from about 1 wt% to about 3 wt %; the oxidizing agent is hydrogen peroxide in an amount ranging from about 0.5 wt% to about 2 wt%; the corrosion inhibitor is benzotriazole or benzotriazole derivatives in an amount ranging from about 0.01 wt% to about 0.1 wt%; the chelator is benzosulfonic acid in an amount ranging from about 0.4 wt% to about 1.5wt%; the organic polymer containing ethylene oxide repeating units having molecular weights ranging from 300,000 to 1,000,000, and concentration ranging from about 50 ppm to about 1,000 ppm; the surfactant is tricosaeethylene glycol dodecyl ether in an amount ranging from about 0.010% to about 0.1%; and the composition has a pH from about 9 to about 11.5.

#11. The method of #10 wherein the polishing composition providing a TaN to TEOS selectivity about 1.5 to about 0.84.

#12. A polishing composition comprising:

abrasive;

organic polymer containing ethylene oxide repeating units having the general molecular structure of



wherein n refers to the total numbers of the repeating unit ranging from 6,818 to 181,817; and the organic polymer having molecular weights ranging from 300,000 to 8,000,000 and concentration ranging from about 5 ppm to about 5,000 ppm;

oxidizing agent;

corrosion inhibitor; and

chelator;

wherein the polishing composition is a barrier chemical mechanical planarization polishing composition.

#13. The composition of #12 wherein the organic polymer containing ethylene oxide repeating units having molecular weights ranging from 400,000 to 1,000,000; and concentration ranging from about 25 ppm to about 2,000 ppm.

#14. The composition of #12 wherein the abrasive is selected from the group consisting of colloidal silica, alumina, ceria, germania, silica, titania, zirconia, alumina dopes colloidal silica in lattices, organic polymer particles, composite particles comprising organic and inorganic particles, surface modified organic or inorganic particles, and combinations thereof; and in an amount ranging from about 0.1 wt% to about 15wt %.

#15. The composition of #12 wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, periodic acid, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, ammonia, amine compounds, and combinations thereof; and in an amount ranging from about 0.01 wt% to about 10 wt%.

#16. The composition of #12 wherein the corrosion inhibitor is selected from the group consisting of benzotriazole or benzotriazole derivatives, 3-amino-1, 2, 4-triazole, 3, 5-diamine-1, 2, 4-triazole, and combinations thereof; and in an amount ranging from about 0.001 wt% to about 1.0 wt%.

#17. The composition of #12 wherein the chelator is selected from the group consisting of benzosulfonic acid, 4-tolyl sulfonic acid, 2,4-diamino-benzosulfonic acid, itaconic acid, malic acid, malonic acid, tartaric acid, citric acid, oxalic acid, gluconic acid, lactic acid, mandelic acid, and combinations thereof; and in an amount ranging from about 0.01 wt% to about 3.0 wt%.

#18. The composition of #12 wherein the polishing composition further comprising a pH adjustor selected from the group consisting of (a) nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids and combinations thereof to lower pH of the polishing composition; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and combinations thereof to raise pH of the polishing composition; and in an amount

ranging from about 0.0001 wt% to about 2 wt%; and the polishing composition has a pH from about 2 to about 12.

5 #19. The composition of #12 wherein the polishing composition further comprising a surfactant selected from the group consisting of nonionic, anionic, cationic or amphoteric surfactants, and combinations thereof; and in an amount ranging from about 0.0001 wt% to about 1.0 wt % The preferred range is from about 0.010% to about 0.1%.

10 #20. The composition of #12 wherein the abrasive is colloidal silica in an amount ranging from about 1 wt% to about 3 wt %; the oxidizing agent is hydrogen peroxide in an amount ranging from about 0.5 wt% to about 2 wt%; the corrosion inhibitor is benzotriazole or benzotriazole derivatives in an amount ranging from about 0.01 wt% to about 0.1 wt%; the chelator is benzosulfonic acid in an amount ranging from about 0.4 wt% to about 1.5wt%; and the organic polymer containing ethylene oxide repeating units having molecular weights ranging from 400,000 to 1,000,000, and concentration ranging from about 50 ppm to about 1,000 ppm; the surfactant is tricosaeethylene glycol dodecyl
15 ether in an amount ranging from about 0.010% to about 0.1%; and the composition has a pH from about 9 to about 11.5.

Features described in connection with one aspect of the invention can be used with any other aspect of the invention.

20 BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

Figure 1 shows the removal rates of TaN, Cu and TEOS when PEO was used as the chemical additive.

Figure 2 shows the defect counts on Cu substrates when PEO was used as the chemical additive.

25 Figure 3 shows the removal rates of TaN, Cu and TEOS when PEO was used as the chemical additive and low concentration silica was used as the abrasive.

Figure 4 shows the defect counts on Cu substrates when PEO was used as the chemical additive and low concentration silica was used as the abrasive.

DETAILED DESCRIPTION OF THE INVENTION

Generally, after removal of overburden copper in step 1, polished wafer surfaces have non-uniform local and global planarity due to differences in the step heights at various locations of the wafer surfaces. Low density features tend to have higher copper step heights whereas high density features tend to have low step heights. Due to differences in the step heights after step 1, step 2 CMP slurries with selective barrier layer relative to copper removal rates and copper to oxide removal rates are highly desirable. The ratio of the removal rate of tantalum to the removal rate of copper is called the "selectivity" for removal of tantalum in relation to copper during CMP processing of substrates comprised of copper, tantalum and dielectric material.

The barrier chemical mechanical polishing composition is preferably effective for use in the second stage of chemical mechanical polishing of the patterned wafers and preferably provides at least one of the following: affords a desirable removal rate of various types of film, affords a desirable low level of within a wafer non-uniformity ("WIW NU%"), results in low residue level(s) being present on the polished wafer(s) subsequent to CMP processing, and affords desirable selectivity among various films.

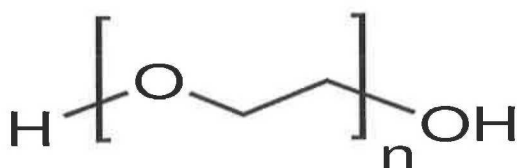
A specific featured distortion that is unsuitable for semiconductor manufacturing is damage to copper vias or metal lines caused by the further corrosion of chemical components interacting with copper vias or metal lines in a chemical mechanical polishing process. Therefore, it is very important to use corrosion inhibitor in barrier CMP slurry to reduce and control further corrosion of copper vias or trenches during chemical mechanical polishing processes, and also to reduce the defects.

In step 2 CMP processes, the chemical reactions involved in using barrier CMP composition include: oxidation reactions induced by the oxidizing agent used in the barrier CMP slurry, for example, H_2O_2 . The surfaces of metal, such as copper, lines, vias or trenches, and barrier material, such as Ta, are oxidized into the respective metal oxide films. Typically, metal copper is oxidized into a mixture of cuprous and cupric oxides, and Ta is oxidized to Ta_2O_5 (the preferred oxide form for Ta). Chelators, ligands or other suitable chemical additives which can be chemically bonded to the copper cations and tantalum cations may be used in barrier CMP slurry to accelerate the dissolution of copper oxide and tantalum oxide to yield the desirable removal rates of copper lines, vias, or trenches and barrier layer, or barrier films.

Described and disclosed herein are barrier CMP slurry formulations, and methods for polishing. It is believed that these formulations can boost the barrier film removal rates, lower the abrasive concentration, and reduce defects during CMP processing. The barrier CMP slurry formulations are used for chemical mechanical planarization of a surface of a semiconductor substrate having at least one feature thereon comprising conductive metal lines, vias or trenches, a metal-containing barrier layer and a dielectric layer. In a preferred embodiment the barrier CMP slurry formulations contain high purity colloidal silica particles as abrasives; corrosion inhibitor to provide corrosion inhibition on metal lines, vias, or trenches; a suitable chemical additive to enhance the removal rate of barrier layer/film; a surface wetting agent or surfactant that wets the surface and reduces surface tension on wafer surfaces, and a pH adjusting agent that is used to adjust pH of the barrier polishing composition to the optimized pH condition. Also, hydrogen peroxide is selected and used as a preferred oxidizing agent for the disclosed barrier CMP polishing compositions.

- 15 Optionally, an aromatic organic acid may be used in the disclosed barrier polishing composition herein to tune some film removal rates. The aromatic organic acid can be described as a ligand that can interact with some films on the surfaces of the wafers.

The suitable chemical additives are organic polymer molecules containing ethylene oxide repeating units, such as polyethylene oxide (PEO), having the general molecular structure of



- wherein n refers to the total numbers of the repeating unit ranging from 6,818 to 181,817; and/or the molecular weights ranging from 100,000 to 8,000,000. An example of a suitable PEO is Sigma-Aldrich Product No. 372773 (MV CA. 400,000), CAS Number 25322-68-3.

The ethylene oxide repeating units of polyethylene oxide (PEO) are believed to be able to form coordination bonds with oxidized metal cations in barrier film. Those more soft complexes in barrier films are believed to lead to enhanced barrier film removal rates.

Suitable abrasives for this invention include, but are not limited to, high purity colloidal silica, alumina, ceria, germania, silica, titania, zirconia, alumina doped colloidal silica in lattices, and mixtures thereof. For example, high purity colloidal silica is preferably used as abrasive in the disclosed barrier CMP slurry. The high purity colloidal silica can be made from sodium silicate, or can be made from TEOS or TMOS.

The amount of abrasive preferably ranges from about 0.1% to about 15% relative to the total weight of the barrier CMP composition. The preferred range is from about 1% to about 5%. A surfactant is optionally used in the barrier CMP slurry as surface wetting agent; suitable surfactant compounds that may be added to the barrier CMP slurry as surface wetting agent include any of the numerous nonionic, anionic, cationic or amphoteric surfactants known to those skilled in the arts. One example of nonionic surfactant is tricosaeethylene glycol dodecyl ether.

The amount of surfactant preferably ranges from about 0.0001% to about 1.0 wt % relative to the total weight of the barrier CMP composition. The preferred range is from about 0.01% to about 0.1%.

Chelators, or chelating ligands, are used in the barrier CMP slurry to enhance affinity of chelating ligands for metal cations. Suitable chelators, or chelating ligands include organic aromatic acids.

A pH-adjusting agent is optionally used in the barrier CMP slurry to raise or lower the pH of the polishing composition. The pH-adjusting agent may be used to improve the stability of the polishing composition, to tune the ionic strength of the polishing composition, and to improve the safety in handling and use. The amount of pH-adjusting agent ranges from about 0.0001 wt % to about 5 wt % relative to the total weight of the barrier CMP composition. The preferred range is about 0.01 wt % to about 1 wt %.

The barrier polishing composition further comprises a corrosion inhibitor.

The polishing composition includes an oxidizing agent, or oxidizer. The oxidizing agent can be any suitable oxidizing agent. Suitable oxidizing agents include, but are not limited to, one or more peroxy-compounds, which comprise at least one peroxy group (-O-O-). Suitable peroxy-compounds include, for example, peroxides, persulfates (e.g., monopersulfates and dipersulfates), percarbonates, and acids thereof, and salts thereof, and mixtures thereof. Other suitable oxidizing agents include, for example, oxidized halides (e.g., iodates, periodates, and acids thereof, and mixtures thereof, and the like), perboric acid, perborates, percarbonates, peroxyacids (e.g., peracetic acid, perbenzoic

acid, salts thereof, mixtures thereof, and the like), permanganates, cerium compounds, ferricyanides (e.g., potassium ferricyanide), mixtures thereof, and the like.

Preferred oxidizing agents include, for example, hydrogen peroxide and urea-hydrogen peroxide.

- 5 The amount of aromatic organic acids preferably ranges from about 0.1 to about 3.0 wt % relative to the total weight of the barrier CMP composition. The preferred range is about 0.25% to about 1.5%.

In some embodiments, the described barrier polishing compositions for barrier CMP processing, comprise a corrosion inhibitor such as BTA or BTA derivatives, triazole or
10 triazole derivatives; more specifically, such as 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole or others; a chelating ligand such as benzenesulfonic acid; a surface wetting agent such as tricosaeethylene glycol dodecyl ether; an organic polymer such as polyethylene oxide polymer as chemical additive; an abrasive; a pH-adjusting agent and
15 an oxidizing agent. Such compositions have been successfully used in the present invention as barrier CMP polishing slurries for the advanced node applications, and provided the desirable removal rates in polishing multi-type films and the desirable selectivity.

The polishing compositions and methods described herein will be illustrated in more detail with reference to the following examples, but it should be understood that the
20 invention is not deemed to be limited thereto.

Working Examples

Polishing Pad Polishing pad, Fujibo H7000HN, was used during CMP, supplied by Narubeni America Corporation.

- 25 PETEOS Plasma enhanced deposition of tetraethoxysilane, dielectric oxide layer.

TEOS Tetraethyl orthosilicate

PARAMETERS:

Å: angstrom(s) – a unit of length

BP: back pressure, in psi units

- 30 CMP: chemical mechanical planarization = chemical mechanical polishing

CS: carrier speed

DF: Down force: pressure applied during CMP, units psi

min: minute(s)

ml: milliliter(s)

5 mV: millivolt(s)

psi: pounds per square inch

PS: platen rotational speed of polishing tool, in rpm (revolution(s) per minute)

SF: polishing composition flow, ml/min

Removal Rates and Selectivity

10 Cu RR 2.0 psi Measured copper removal rate at 2.0 psi (13.8 kPa) down pressure of the CMP tool

TaN RR 2.0 psi Measured tantalum removal rate at 2.0 psi (13.8 kPa) down pressure of the CMP tool

15 TEOS RR 2.0 psi Measured TEOS removal rate at 2.0 psi (13.8 kPa) down pressure of the CMP tool

BD1 RR 2.0 psi Measured BD1 removal rate at 2.0 psi (13.8 kPa) down pressure of the CMP tool

Selectivity of Cu/BD/TaN/TEOS = Cu RR/BD RR/TaN RR/TEOS RR at same down force (psi)

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General Experimental Procedure

All percentages are weight percentages unless otherwise indicated. In the examples presented below, CMP experiments were run using the procedures and experimental conditions given below.

25 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®), TEOS and tantalum nitride wafers. These blanket wafers were purchased from Silicon Valley Microelectronics, 1150 Campbell Ave, CA, 95126, and Advantiv Corporation.

The film thickness specifications are summarized below:

Copper: 10,000 Å electroplated copper/1,000 Å copper seed/250 Å Ta on silicon

Tantalum Nitride: 3000 Å/5,000 Å on silicon

BD: BD1 10,000 Å

TEOS: 15,000 Å

Example 1

A reference or control barrier CMP polishing composition contained about 3 wt % high purity colloidal silica, 1.0 wt% hydrogen peroxide, about 0.01 wt % BTA as corrosion inhibitor, about 0.0075 wt % of a surfactant (tricosaeethylene glycol dodecyl ether), and a chelator or chelating ligand (benzosulfonic acid, 0.4447 wt %). The remainder was deionized water. The pH of the composition was about 11.0 before adding hydrogen peroxide and 10.5 after the addition of hydrogen peroxide.

Polyethylene oxide (PEO) polymer (purchased from Sigma-Aldrich) as the chemical additive was added to the reference polishing composition. The CMP barrier slurry with 1X PEO had a concentration of 100 ppm; and molecular weight of 1000,000. The CMP barrier slurry with 10X PEO contained 10 times as much PEO as in 1X PEO barrier slurry. All three barrier CMP polishing compositions had same type and concentration of colloidal silica particles as abrasives.

Removal rates were measured using the CMP tool. The results from three barrier CMP polishing compositions: the reference polishing composition, the 1X PEO and 10X PEO polishing compositions are shown in Table 1.

Table 1 presented the removal rates of TaN, Cu and TEOS from all three barrier CMP polishing compositions. The reference barrier polishing composition gave TaN film removal rate at 614Å/min., for the barrier polishing compositions that contain 1X, and 10X concentration PEO polymer as the chemical additive, the removal rates of TaN film

were increased by about 10.4%, and about 30.3% respectively. TaN film removal rates were boosted by using polyethylene oxide polymer as the chemical additive.

The effects of polyethylene oxide as the chemical additive in barrier CMP polishing compositions on the removal rates of TaN, Cu, and TEOS are also depicted in Figure 1.

- 5 As the results show in Figure 1, the removal rates of copper films and TEOS were not greatly affected by adding polyethylene oxide polymer as the chemical additive. The largest effects of polyethylene oxide polymer as the chemical additive in barrier polishing composition were on TaN barrier film removal rate changes.

Table 1. Effects of PEO additives in Barrier Slurries on The Removal Rates of TaN and Cu Films and TEOS

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Formulations (3 wt % Silica)	TaN Removal Rate (A/min.)	TaN Removal Rate% Change	Cu Removal Rate (A/min.)	TEOS Removal Rate (A/min.)
Control barrier slurry, no PEO	614	---	311	689
Barrier slurry with 1X PEO	678	+10.4%	299	647
Barrier slurry with 10X PEO	800	+30.3%	344	690

The removal rates of copper film and TEOS were not greatly affected by adding PEO polymer as the chemical additive. Since the removal rate of TaN film was boosted, this gives the important result that adding PEO polymer as the chemical additive could afford

15 desirable selectivity among various films.

The effects of polyethylene oxide polymer as the chemical additive in barrier CMP polishing compositions on defect counts were also observed. The results were listed in Table 2.

Table 2. Effects of PEO additives in Barrier Slurries on Defect Counts on Cu Wafers

20

Formulations (3 wt % Silica)	Defect Count on Cu (0.125micron)	Defect% Change (0.125micron)	Defect Count on Cu (0.20micron)
Control slurry without PEO	205	---	84

Slurry with 1X PEO	94	-54.1%	72
Slurry with 10XPEO	149	-27.3%	73

As the results shown in Table 2, the defect counts on copper wafer surface were reduced by using polyethylene oxide polymer as the chemical additive in the disclosed barrier polishing compositions at both defect inspection resolutions. With the defect inspection resolution setting at 0.125micron, the defect count was reduced by about 54.1% for 1X concentrated PEO as the chemical additive, and by about 27.3% for 10X concentrated PEO as the chemical additive. With the defect inspection resolution setting at 0.20micron, the defect counts were reduced by about 13% to about 14% respectively for 1X, and 10X concentrated PEO used as the chemical additives in the barrier CMP polishing compositions.

The effects of polyethylene oxide as the chemical additive in barrier CMP polishing compositions on the defect counts on Cu substrate surface were also depicted in Figure 2. As the results shown in Figure 2, using polyethylene oxide polymer as the chemical additive in the disclosed herein barrier CMP polishing compositions indeed led to the reduction of defect counts on Cu substrate surface after barrier CMP process.

Example 2

The polishing tests in Example 1 had shown that the removal rate of TaN film was boosted by adding polyethylene oxide polymer as the chemical additive at 1X, and 10X concentrations. To further reduce the defects, believed to be mainly from the abrasive, barrier polishing compositions could contain lower concentrations of the abrasives but still provide the same range of removal rate for the TaN film. In this Example, the tests were carried out using the barrier CMP polishing compositions containing 2 wt % abrasive (high purity colloidal silica) and polyethylene oxide polymer as the chemical additive at 1X, and 10X concentrations, respectively. 2 wt % and 3 wt% abrasive concentrations were used as the reference barrier CMP polishing compositions. The colloidal silica particles used in all tested barrier CMP polishing compositions possessed the same shape, size, and particle size distributions.

As the results shown in Table 3, for the barrier polishing composition having 1X concentration of polyethylene oxide polymer as the chemical additive and 2 wt% colloidal silica abrasive, the removal rate of TaN film was 513A/min., which was about 8% higher

than the removal rate from the 2 wt % colloidal silica abrasive reference, but about 23% lower than the removal rate obtained from the reference barrier slurry with 3 wt% colloidal silica abrasive. For the barrier polishing composition with 10X concentration of polyethylene oxide polymer as the chemical additive and 2 wt% colloidal silica abrasive, the removal rates of TaN film was 650A/min, which was about 36% higher than the removal rate from the 2 wt % colloidal silica abrasive reference, and was almost the same as the TaN removal rate obtained for the reference barrier slurry with 3 wt% colloidal silica concentration (at 666A/min).

Table 3. Effects of PEO as the chemical additive on the Removal Rates of TaN, Cu and TEOS with Low Abrasive Concentration

Formulations	TaN Removal Rate (A/min.)	Cu Removal Rate (A/min.)	TEOS Removal Rate (A/min.)
Control barrier slurry 2 wt% silica and no PEO	477	444	450
Barrier slurry with 2 wt% silica and 1X PEO	513	215	407
Barrier slurry with 2wt% Silica and 10X PEO	650	247	468
Control barrier slurry 3 wt% silica and no PEO	666	316	687

The reduced removal rates (compared to both references) of copper film and TEOS from the polishing compositions having 1X and 10X concentration of polyethylene oxide polymer could expand the desirable selectivity among various films.

The effects of polyethylene oxide polymer as the chemical additive in barrier CMP polishing compositions on defect counts were also observed. The results were listed in Table 4.

As the results shown in Table 4, with 1X concentration polyethylene oxide as the chemical additive and 2 wt % colloidal silica as the abrasive, the defect count was reduced from 315 for the referenced standard barrier slurry with 3 wt % colloidal silica to 114 representing about 63.8% reduction in defect count on copper substrate. With 10X concentration polyethylene oxide as the chemical additive and 2 wt % colloidal silica as the abrasive, the defect count on copper substrate was reduced from 314 for the referenced standard barrier slurry with 3 wt % colloidal silica to 151, representing 52.1% reduction in defect count on copper substrate.

When compared with the reference barrier slurry formulation with 2 wt % colloidal silica as abrasive, with the addition of 1X concentration of PEO as chemical additive, the defect on Cu wafer was reduced by about 26%, and almost no change was observed when 10X concentrated PEO used as the chemical additive.

Table 4. Effects of PEO as the chemical additive and Lower Abrasive Concentration in Barrier Slurries on the Defect Counts on Cu and TEOS Substrates

Formulations	Defect Count on Cu (0.125micron)	Defect% Change (3 wt %; 2 wt % silica)	Defect Count on TEOS (0.13micron)
Control barrier slurry no PEO and 3 wt % silica	315	---	114
Control barrier slurry no PEO and 2 wt % silica	154	---	209
Barrier slurry with 1X PEO and 2 wt % silica	114	-63.8%;-26%	24
Barrier slurry with 10X PEO and 2 wt % Silica	151	-52.1%; same	61

As also shown in Table 4, the defect counts on TEOS wafers were greatly reduced with the use of PEO as chemical additives for barrier slurry formulations. The defects on TEOS were reduced from 209 for the reference formulation with 2 wt % colloidal silica to

24 with 1X PEO and 61 with 10X PEO as the chemical additive in the formulations. These defect reductions on TEOS wafers were 89% for 1X PEO and 71% for 10X PEO as the chemical additive in the polishing compositions. The effects of polyethylene oxide as the chemical additive in the barrier polishing compositions with lower colloidal silica
5 abrasive concentration on the polishing removal rates and defect counts are also depicted in Figure 3 and Figure 4 respectively.

This Example indicates that using the combined effects of adding polyethylene oxide polymer as the chemical additive to boost TaN film removal rates and to reduce defects, barrier polishing compositions having lower abrasive concentration compared to the
10 standard reference barrier polishing composition still provided comparable removal rates for TaN film while further reducing the defect counts on copper and TEOS substrate surfaces.

Example 3

15 The polishing removal rates and defect counts were measured using different polymer molecular weights of polyethylene oxide polymer as the chemical additive in barrier CMP polishing compositions. Polyethylene oxide polymers with molecular weights of 100,000; 300,000; 400,000; 600,000; and 1,000,000 were tested. The wt % range of PEO is from 100 ppm to 1,000 ppm.

20 Two different molecular weight distributions of polyethylene oxide polymer with same concentration at about 0.01 wt % to about 0.1 wt% were used in the barrier CMP polishing compositions having 2 wt % or 3 wt % colloidal silica abrasive to compare the polishing performances. The results are listed in Table 5.

As the results show in Table 5, when polyethylene oxide having molecular weight of
25 600,000 was used, TaN removal rate was increased from 577A/min. to 703A/min., representing about 21.8% increase on TaN removal rate. When polyethylene oxide having molecular weight of 1,000,000 was used, TaN removal rate was increased from 577A/min. to 737A/min., representing about 27.7% increase on TaN removal rate. Therefore, polyethylene oxide as the chemical additive in barrier CMP polishing
30 composition boosted barrier film removal rates.

Table 5. Effects of PEO with different MW on the removal rates

Formulations (2 wt % silica)	TaN RR (A/min.)	Cu RR (A/min.)	TEOS RR (A/min.)	BD1 RR (A/min.)
Control barrier slurry no PEO	577	309	691	924
Barrier slurry with PEO MW 600,000	703	473	558	439
Barrier slurry with PEO MW 1,000,000	737	467	532	379

It is also worth pointing out that the use of polyethylene oxide as the chemical additive in barrier slurries led to the suppression of removal rates on low-k film, BD1 (Black Diamond® 1). This is also useful for some advanced node applications which demand the suppression of low-k or ultra low-k film removal rates.

The results for the effects on defect counts on of polyethylene oxide with different molecular weight distributions but the same concentration on copper and TEOS substrates are listed in Table 6.

Table 6. Effects of PEO with different MW on Defect Count on Cu and TEOS

Formulations (2 wt % silica)	Defect Count on Cu (0.125micron)	Defect% Change (0.125micron)	Defect Count on TEOS (0.13micron)
Control barrier slurry without PEO	213	---	50
Barrier slurry with PEO MW 600,000	101	-52.6%	22
Barrier slurry with PEO MW 1,000,000	101	-52.6%	18

As the results show in Table 6, when polyethylene oxide additives either with molecular weight at 600,000 or 1,000,000 were used in barrier CMP polishing compositions, defect counts on copper and TEOS substrates were both reduced.

More specifically, for both molecular weights of polyethylene oxide being used as the chemical additive in barrier CMP polishing compositions, the defect count on copper substrate was reduced by about 52.6%. The defect counts on TEOS substrate were reduced from 50 to 22 for polyethylene oxide with 600,000 molecular weight, and to 18 for polyethylene oxide with 1,000,000 molecular weight, respectively.

In a different data set, other molecular weights and concentrations of PEO were also tested for the TaN film removal rates. The results are summarized in Table 7. All the barrier CMP polishing compositions contained the same type and concentration of colloidal silica as abrasives and all abrasive were at 2 wt% concentration for the formulations with or without PEO.

Table 7. Effects of PEO with different MW on the removal rates

Formulations (2 wt % silica)	TaN RR(A/min.)	Cu RR(A/min.)	TEOS RR (A/min.)
Control barrier slurry no PEO	477	444	450
Barrier slurry with 1X PEO MW 100,000	474	364	427
Barrier slurry with 10X PEO MW 100,000	483	375	380
Barrier slurry with 1X PEO MW 300,000	486	408	403
Barrier slurry with 10X PEO MW 300,000	567	403	385
Barrier slurry with 5X PEO MW 400,000	588	431	408
Barrier slurry with 1X PEO MW 1,000,000	524	447	391
Barrier slurry with 10X PEO MW 1,000,000	625	374	424

As the results show in Table 7, when lower molecular weight 100,000 of PEO was used as the chemical additive, at 1X concentration, the TaN removal rate was similar to the removal rate from the reference. Thus, the lower molecular weight of PEO less or equal 100,000 did not boost TaN film removal rates.

- 5 When 1X and 10X concentrated PEO with molecular weight 300,000 were used as the chemical additive, increases in the TaN removal rates were clearly observed. The rates increased from 477A/min. to 486 and 567A/min., representing about 2% and about 19% TaN removal rate boosting, respectively.

10 The reduced removal rates (compared to the reference) of copper film and TEOS from the polishing compositions having polyethylene oxide polymer with different molecular weights could expand the desirable selectivity among various films.

The polishing removal rate data, as shown in the aforementioned Tables indicate that the tantalum nitride removal rate was boosted due to the use of polyethylene oxide polymer as the chemical additive. This result made it possible to use lower abrasive
15 concentrations in the invented barrier CMP polishing compositions to achieve excellent defect reduction performances but still provide similar removal rates while polishing barrier films, and to provide desirable selectivity among various films.

Using polyethylene oxide polymer with different molecular weight distributions as key chemical additives in the invented barrier CMP polishing compositions increased
20 removal rates while polishing barrier film, such as TaN. Using polyethylene oxide polymer with different molecular weight distributions as key chemical additives in the invented barrier CMP polishing compositions reduced defect counts on wafer surfaces. The lower abrasive concentration was adopted in the invented barrier polishing compositions due to the boosted barrier film removal rates by using polyethylene oxide
25 polymer as the chemical additive. Thus, further reduction on defect counts was achieved due to the adoption of using lower abrasive concentration in barrier polishing compositions and still provided the desirable removal rates on removing barrier films; and provided the desirable selectivity while polishing multi-types of films in barrier CMP process.

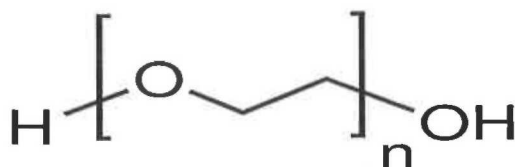
30 The foregoing examples and description of the embodiments should be taken as illustrating, rather than as limiting the present invention as defined by the claims. As will be readily appreciated, numerous variations and combinations of the features set forth above can be utilized without departing from the present invention as set forth in the

claims. Such variations are intended to be included within the scope of the following claims.

CLAIMS

1. A polishing composition comprising:
abrasive;

5 organic polymer containing ethylene oxide repeating units having the general molecular structure of



10 wherein n refers to the total number of the repeating unit; the organic polymer having a molecular weight in the range of 100,000 to 8,000,000, and a concentration in the range of 5 ppm to 5,000 ppm;

oxidizing agent;

corrosion inhibitor; and

chelator;

15 wherein the polishing composition is a barrier chemical mechanical planarization polishing composition.

2. The polishing composition of Claim 1 wherein the organic polymer has a molecular weight in the range of 400,000 to 1,500,000; and/or the organic polymer has a concentration in the range of 25 ppm to 2,000 ppm.

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3. The polishing composition of Claim 1 or Claim 2 wherein the abrasive is selected from the group consisting of colloidal silica, alumina, ceria, germania, silica, titania, zirconia, alumina doped colloidal silica in lattices, organic polymer particles, composite particles comprising organic and inorganic particles, surface modified organic or inorganic particles, and combinations thereof; and/or the abrasive is present in an amount in the range of 0.1% to 15 wt %.

25

4. The polishing composition of Claim 3 wherein the abrasive is present in an amount in the range of 1% to 2.5 wt %.

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5. The polishing composition of any one of the preceding claims wherein the oxidizing agent is selected from the group consisting of peroxy-compounds, oxidized halides, permanganates, cerium compounds, ferricyanides, and combinations thereof, and/or the oxidizing agent is present in an amount in the range of 0.01 wt% to 10 wt%.
6. The polishing composition of any one of the preceding claims wherein the oxidizing agent is selected from the group consisting of hydrogen peroxide, urea-hydrogen peroxide, periodic acid, potassium iodate, potassium permanganate, ammonium persulfate, ammonium molybdate, ferric nitrate, nitric acid, potassium nitrate, and combinations thereof; and/or the oxidizing agent is present in an amount in the range of 0.01 wt% to 10 wt%.
7. The polishing composition of any one of the preceding claims wherein the corrosion inhibitor is selected from the group consisting of benzotriazole or benzotriazole derivatives, 3-amino-1,2,4-triazole, 3,5-diamine-1,2,4-triazole, and combinations thereof; and/or the corrosion inhibitor is present in an amount in the range of 0.001 wt% to 1.0 wt%.
8. The polishing composition of any one of the preceding claims wherein the chelator is selected from the group consisting of benzosulfonic acid, 4-tolyl sulfonic acid, 2,4-diamino-benzosulfonic acid, itaconic acid, malic acid, malonic acid, tartaric acid, citric acid, oxalic acid, gluconic acid, lactic acid, mandelic acid, and combinations thereof; and/or the chelator is present in an amount in the range of 0.01 wt% to 3.0 wt%.
9. The polishing composition of any one of the preceding claims wherein the polishing composition further comprises a pH adjuster optionally selected from the group consisting of (a) nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, fatty acid, polycarboxylic acid and combinations thereof to lower pH of the polishing composition; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and combinations thereof to raise pH of the polishing composition; wherein the pH adjuster is preferably present in an

amount in the range of 0.0001 wt% to 5 wt%; and wherein the polishing composition preferably has a pH from about 2 to about 12.

- 5 10. The polishing composition of any one of the preceding claims wherein the polishing composition further comprises a surfactant optionally selected from the group consisting of nonionic, anionic, cationic or amphoteric surfactants, and combinations thereof; and wherein the surfactant is preferably present in an amount in the range of 0.0001 wt% to 1.0 wt %.
- 10 11. The polishing composition of any one of the preceding claims wherein the abrasive is colloidal silica in an amount in the range of 1 wt% to 3 wt %; the oxidizing agent is hydrogen peroxide in an amount in the range of 0.5 wt% to 2 wt%; the corrosion inhibitor is benzotriazole or a benzotriazole derivative in an amount in the range of 0.01 wt% to 0.1 wt%; the chelator is benzosulfonic acid in an amount in the range of 15 0.4 wt% to 1.5wt%; the organic polymer containing ethylene oxide repeating units has a molecular weight in the range of 300,000 to 1,000,000 and a concentration in the range of 50 ppm to 1,000 ppm; the surfactant is tricosaeethylene glycol dodecyl ether in an amount in the range of 0.001 wt% to 0.1 wt%; and the composition has a pH in the range of 9 to 11.5.
- 20 12. A polishing method for chemical mechanical planarization of a semiconductor substrate having at least one surface having conductive metal lines, vias and/or trenches, a metal-containing barrier layer and a dielectric or low-k layer thereon, comprising the steps of:
- 25 a) contacting the at least one surface with a polishing pad;
- b) delivering a polishing composition as claimed in any one of the preceding claims to the at least one surface; and
- c) polishing the substrate with the polishing composition.
- 30 13. The method of Claim 12 wherein the conductive metal is copper; the metal-containing barrier layer is a tantalum-containing barrier layer; and/or the dielectric layer is selected from the group consisting of TEOS and low-k material.

14. The method of Claim 13 wherein the polishing composition provides a TaN to TEOS selectivity in the range of 0.84 to 1.5.

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