(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 December 2022 (15.12.2022)

WIPO | PCT

(10) International Publication Number
WO 2022/261614 A1

(51) International Patent Classification:
C08F 30/02 (2006.01) *C09K 3/14* (2006.01)
C08G 79/06 (2006.01) *H01L 21/304* (2006.01)
C09G 1/02 (2006.01) *H01L 21/768* (2006.01)

(21) International Application Number:
PCT/US2022/072760

(22) International Filing Date:
03 June 2022 (03.06.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/209,306 10 June 2021 (10.06.2021) US

(71) Applicant: **VERSUM MATERIALS US, LLC** [US/US]; 8555 South River Parkway, Tempe, Arizona 85284 (US).

(72) Inventors: **LARBIG, Gregor**; 8555 South River Parkway, Tempe, Arizona 85284 (US). **DAVIDI, Inbal**; 8555 South River Parkway, Tempe, Arizona 85284 (US). **STENDER, Matthias**; 8555 South River Parkway, Tempe, Arizona 85284 (US). **SHI, Xiaobo**; 8555 South River Parkway, Tempe, Arizona 85284 (US).

(74) Agent: **YANG, Lina**; 7350 Tilghman Street, Suite 104, Allentown, Pennsylvania 18106-9000 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2022/261614 A1

(54) Title: PHOSPHONIUM BASED POLYMERS AND COPOLYMERS AS ADDITIVES FOR CHEMICAL MECHANICAL PLANARIZATION SLURRIES

(57) Abstract: Synthesis of phosphonium based polymers is disclosed. Chemical Mechanical Planarization (CMP) slurries comprise abrasives; activator; oxidizing agent; additive comprising phosphonium based polymers; and water. The use of the synthesized phosphonium based polymers in the CMP slurries reduces dishing and erosion in highly selective tungsten slurries.

TITLE OF THE INVENTION:

PHOSPHONIUM BASED POLYMERS AND COPOLYMERS AS ADDITIVES FOR CHEMICAL MECHANICAL PLANARIZATION SLURRIES

CROSS REFERENCE TO RELATED APPLICATION(S)

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/209,306 filed on June 10, 2021, which is incorporated herein by reference as if fully set forth.

BACKGROUND OF THE INVENTION

[0002] The present disclosure relates to chemical mechanical planarization or polishing ("CMP") slurries (or compositions, or formulations), polishing methods and polishing systems for carrying out chemical mechanical planarization in the production of a semiconductor device. In particular, the present disclosure relates to polishing slurries that are suitably used for polishing patterned semiconductor wafers that include metallic materials containing tungsten.

[0003] Integrated circuits are interconnected through the use of well-known multilevel interconnections. Interconnection structures normally have a first layer of metallization, an interconnection layer, a second level of metallization, and typically third and subsequent levels of metallization. Interlevel dielectric materials such as silicon dioxide and sometimes low-k materials are used to electrically isolate the different levels of metallization in a silicon substrate or well. The electrical connections between different interconnection levels are made through the use of metallized vias and in particular tungsten vias. U.S. Pat. No. 4,789,648 describes a method for preparing multiple metallized layers and metallized vias in insulator films. In a similar manner, metal contacts are used to form electrical connections between interconnection levels and devices formed in a well. The metal vias and contacts are generally filled with tungsten and generally employ an adhesion layer such as titanium nitride (TiN) and/or titanium to adhere a metal layer such as a tungsten metal layer to the dielectric material.

[0004] In one semiconductor manufacturing process, metallized vias or contacts are formed by a blanket tungsten deposition followed by a CMP step. In a typical process, via holes are etched through the interlevel dielectric (ILD) to interconnection lines or to a semiconductor substrate. Next, a thin adhesion layer such as titanium nitride and/or titanium is generally formed over the ILD and is directed into the etched via hole. Then, a tungsten film is blanket deposited over the adhesion layer and into the via. The deposition is continued until the via hole is filled with tungsten. Finally, the excess tungsten is removed by CMP to form metal vias.

[0005] In another semiconductor manufacturing process, tungsten is used as a gate electrode material in the transistor because of its superior electrical characteristics over poly-silicon which has been traditionally used as gate electrode material, as taught by A. Yagishita et al, IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 47, NO. 5, MAY 2000.

[0006] In a typical CMP process, the substrate is placed in direct contact with a rotating polishing pad. A carrier applies pressure against the backside of the substrate. During the polishing process, the pad and table are rotated while a downward force is maintained against the substrate back. An abrasive and chemically reactive solution, commonly referred to as a polishing “slurry”, a polishing “composition” or a polishing “formulation”, is deposited onto the pad during polishing, where rotation and/or movement of the pad relative to the wafer brings said slurry into the space between the polishing pad and the substrate surface. The slurry initiates the polishing process by chemically reacting with the film being polished. The polishing process is facilitated by the rotational movement of the pad relative to the substrate as slurry is provided to the wafer/pad interface. Polishing is continued in this manner until the desired film on the insulator is removed. Removal of tungsten in the CMP is believed to be due to synergy between mechanical abrasion and tungsten oxidation followed by dissolution.

[0007] Despite its relatively simple outward appearance, chemical mechanical planarization (CMP) is a highly complex process as described by Lee Cook in *digital Encyclopedia of Applied Physics*, 2019, DOI:10.1002/3527600434.eap847 10.1002/3527600434.eap847.

[0008] It’s importance as enabling technology for past and future requirements for device scaling and new trends in semiconductor industry is undisputed. A multitude of interactions between wafer, slurry and pad as well as general process parameters determine the CMP outcome. Finally, material removal in CMP is the result of complex

interaction between chemical and mechanical forces as described by Lee, D.; Lee, H.; Jeong, H. Slurry components in metal chemical mechanical planarization (CMP) process: A review. *International Journal of Precision Engineering and Manufacturing* **2016,** *17*, 1751. Large numbers of materials are used in semiconductor device fabrication, all of which require an optimized CMP process. Simultaneous polishing of combinations of completely different materials such as dielectric materials, barrier and metal layers is a real challenge with CMP.

[0009] Highly selective slurries, which have a large difference in removal rate of metal versus rate of dielectric removal, are of great interest for future industry needs. However, there are imperfections associated with the use of these highly selective slurries. Metal layers can easily be over-polished, creating a "dishing" effect. Another unacceptable defect is called "erosion", which describes topographical difference between an area with dielectric and a dense array of metal vias or trenches.

[0010] One of the commonly encountered problems in CMP in particular in metal applications such as tungsten is how to control topological defects such as erosion and dishing.

[0011] Specially designed water-based slurries are considered main drivers in improving CMP performance for future devices. The slurry developments not only affect the removal rate and selectivity between different layers, but also control defects during the polishing process. In general, the slurry composition is a complex combination of abrasives and chemical ingredients with different functions. Polymer additives play a key role in minimizing surface imperfections by interacting with certain materials. For example, positively charged polymers inhibit tungsten removal and can be used to reduce dishing effects in tungsten CMP processes.

[0012] US 5,876,490 describes the use of polish slurry comprising abrasive particles and exhibiting normal stress effect and further comprising polyelectrolyte having ionic moieties of a charge that differs from that associated with said abrasive particles and wherein the concentration of said polyelectrolyte is about 5 to about 50 percent by weight of said abrasive particles and wherein said polyelectrolyte has a molecular weight of about 500 to about 10,000.

[0013] US 2010075501 describes a chemical mechanical polishing aqueous dispersion used to polish a polishing target that includes an interconnect layer that contains tungsten. The chemical mechanical polishing aqueous dispersion includes: (A) a cationic water-soluble polymer; (B) an iron (III) compound; and (C) colloidal silica particles. The

content (M_A) (mass %) of the cationic water soluble polymer (A) and the content (M_B) (mass %) of the iron (III) compound (B) satisfy the relationship "M_A/M_B=0.004 to 0.1". The chemical mechanical polishing aqueous dispersion has a pH of 1 to 3.

[0014] US 2010/0252774 A1 describes a chemical mechanical polishing aqueous dispersion used to polish a polishing target that includes a wiring layer that contains tungsten. The chemical mechanical polishing aqueous dispersion includes: (A) a cationic water-soluble polymer; (B) an iron (III) compound; and (C) colloidal silica having an average particle diameter calculated from a specific surface area determined by the BET method of 10 to 60 nm. The content (M_A) (mass %) of the cationic water soluble polymer (A) and the content (M_C) (mass %) of colloidal silica(C) satisfy the relationship "M_A/M_C=0.0001 to 0.003". the chemical mechanical polishing aqueous dispersion

[0015] US 10,604,678 B1 discloses a process and a composition for polishing tungsten containing select quaternary phosphonium compounds at low concentrations to at least reduce corrosion rate of tungsten. The process and composition include providing a substrate containing tungsten, providing a stable polishing composition, containing, as initial components: water, an oxidizing agent: select quaternary phosphonium compounds at low concentrations to at least reduce corrosion rate: a dicarboxylic acid. a source of iron ions: a colloidal silica abrasive and optionally a pH adjusting agent; providing a chemical mechanical polishing pad, having a polishing surface; creating dynamic contact at an interface between the polishing pad and the substrate; and dispensing the polishing composition onto the polishing surface at or near the interface between the polishing pad and the substrate; wherein some of the tungsten is polished away from the substrate, and corrosion rate of tungsten is reduced.

[0016] US 2009/0081871 discloses a method comprising chemically-mechanically polishing a substrate with an inventive polishing composition comprising a liquid carrier, a cationic polymer, an acid, and abrasive particles that have been treated with an aminosilane compound.

[0017] US 2014/0248823 describes a chemical-mechanical polishing composition containing (a) abrasive particles, (b) a polymer, and (c) water, wherein (i) the polymer possesses an overall charge, (ii) the abrasive particles have a zeta potential Za measured in the absence of the polymer and the abrasive particles have a zeta potential Zb measured in the presence of the polymer, wherein the zeta potential Za is a numerical value that is the same sign as the overall charge of the polymer, and (iii) |zeta

potential Zb| > |zeta potential Za|. The invention also provides a method of polishing a substrate with the polishing composition.

[0018] One of the commonly encountered problems in CMP, particularly in metal applications such as tungsten, is dishing of tungsten lines and erosion of arrays of metal lines. Dishing and erosion are critical CMP parameters that define the planarity of the polished wafers. Dishing of lines typically increases for wider lines. Erosion of arrays typically increases with an increase in pattern density.

[0019] Tungsten CMP slurries must be formulated such that the dishing and erosion can be minimized in order to meet certain design targets critical for a functioning device.

[0020] Finding solutions to control topological defects such as erosion and dishing is key to future CMP requirements. There still has been a need for novel tungsten CMP slurries that can reduce dishing and erosion while maintain desirable removal rate in polishing.

BRIEF SUMMARY OF THE INVENTION

[0021] The present invention satisfies the need by providing intelligent designed tungsten CMP slurries, systems, and methods of using the CMP slurries to minimize the described problem of dishing and erosion in highly selective tungsten slurries while maintain desirable polishing of metal layers, specifically tungsten films.

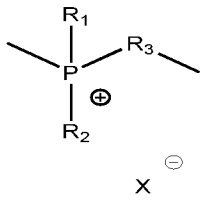
[0022] More specifically, the present invention discloses the synthesis of certain phosphonium based polymers or copolymers; and demonstrates the use of the synthesized phosphonium based polymers or copolymers in the CMP slurries to reduce the described problems.

[0023] Phosphonium based polymers or copolymers are cationic polymer or copolymers having phosphonium - bearing macromolecules contain main-chain, pendant phosphonium groups, or both.

[0024] In addition, several specific aspects of the present invention are outlined below.

Aspect 1: A cationic polymer or copolymer formed by at least one cationic monomer containing at least one phosphonium group, wherein the cationic monomer comprises a structure selected from the group consisting of:

(1)



;

wherein:

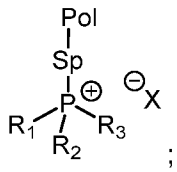
the at least one phosphonium group is in backbone of the cationic polymer or copolymer;

R_1 and R_2 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other;

R_3 is a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic, heteroaromatic, or siloxane moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

the anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F^-, Cl^-, Br^-, and I^-; BF_4^-; PF_6^-; carboxylate such as $RCOO^-$ with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate such as RSO_3^- with R = H, alkyl or aryl; CF_3COO^-; $CF_3SO_3^-$; nitrate; sulfate; carbonate, hydrogen carbonate, and any other appropriate anion;

(2)



;

wherein:

the at least one phosphonium group is in a side chain or side chains of the cationic polymer or copolymer;

Sp denotes at each occurrence a spacer group (Sp) or a single straight or branched bond, a substituted or unsubstituted alkyl chain which chemically links the at least one phosphonium group to the backbone of the cationic polymer or copolymer; wherein Sp can have 1 to 20, preferably 1 to 10 carbon atoms and is optionally mono- or

polysubstituted by F, Cl, Br, I or CN; wherein one or more non-adjacent CH_2 groups each can be independently replaced by -O-, -S-, -NH-, -NR- in a way that no heteroatoms are connected to each other;

Pol denotes backbone of the cationic polymer or copolymer and the backbone type is selected from the group consisting of vinyl, styrene, acrylic or methacrylic, acrylamide or methacrylamide, ethylene glycol, vinyl ether, siloxane, phenol, norbornene type backbone, and combinations thereof;

R_1, R_2, R_3 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

and

anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F-, Cl-, Br-, and I-; BF_4-; PF_6-; carboxylate (RCOO- with R = H, alkyl or aryl); malonate; citrate; fumarate; sulfonate RSO_3^- with R = H, alkyl or aryl; CF_3COO-; CF_3SO_3-; nitrate; sulfate; carbonate; hydrogen carbonate; and any other appropriate anion;

and

(3) combinations of (1) and (2).

Aspect 2: A copolymer formed by at least one cationic monomer according to Aspect 1 and at least one non-ionic monomer which is known in the art include but is not limited to acrylate or methacrylate, acrylamide or methacrylamide, maleimide, vinyl benzene, vinyl-type monomer, ethylene glycol, siloxane, norbornene.

Aspect 3: A cationic polymer or copolymer according to Aspects 1 to 2, wherein the polymerization is a polymerization method selected from the group consisting of free radical polymerization, reversible addition-fragmentation chain-transfer polymerization (RAFT), nitroxide-mediated polymerization (NMP), atomic transfer reaction polymerization (ATRP), ring opening polymerization (ROMP) or polycondensation reaction.

Aspect 4: The copolymer according to Aspects 1 to 3, wherein the copolymer has a block-copolymer character.

Aspect 5: A cationic polymer or copolymer according to Aspects 1 to 4, wherein the cationic polymer or copolymer has functional anions selected from bromide, chloride, nitrate, sulfate, phosphate as counter ions.

Aspect 6: The cationic polymer or copolymer according to Aspect 1, wherein the cationic polymer or copolymer is selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, and poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide.

Aspect 7: A chemical mechanical planarization composition comprising:
an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;
an activator;
an oxidizing agent;
an additive comprising the cationic polymer or copolymer according to Aspects 1 to 6;
water; and optionally
a corrosion inhibitor;
a dishing reducing agent;
a stabilizer;
a pH adjusting agent.

Aspect 8: A system for chemical mechanical planarization, comprising:
a semiconductor substrate comprising at least one surface containing tungsten;
a polishing pad; and
the chemical mechanical planarization composition of Aspect 7;

wherein the at least one surface containing tungsten is in contact with the polishing pad and the chemical mechanical planarization composition.

Aspect 9: A polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing tungsten, comprising the steps of:

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

b) delivering the chemical mechanical planarization composition of Aspect 7;

c) polishing the at least one surface containing tungsten with the chemical mechanical planarization composition.

[0025] The abrasive includes, but is not limited to inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof.

[0026] The inorganic oxide particles include but are not limited to ceria, colloidal silica, high purity colloidal silica, fumed silica, colloidal ceria, alumina, titania, zirconia particles.

[0027] The metal oxide-coated inorganic oxide particles include but are not limited to the ceria-coated inorganic oxide particles, such as, ceria-coated colloidal silica, ceria-coated high purity colloidal silica, ceria-coated alumina, ceria-coated titania, ceria-coated zirconia, or any other ceria-coated inorganic oxide particles.

[0028] The organic polymer particles include, but are not limited to, polystyrene particles, polyurethane particle, polyacrylate particles, or any other organic polymer particles.

[0029] The metal oxide-coated organic polymer particles are selected from the group consisting of ceria-coated organic polymer particles, zirconia-coated organic polymer particles.

[0030] The concentration of abrasive can range from 0.01 wt.% to 30 wt.%, the preferred is from about 0.05 wt.% to about 20 wt.%, the more preferred is from about 0.01 to about 10 wt.%, and the most preferred is from 0.1 wt.% to 2 wt.%. The weight percent is relative to the composition.

[0031] The activator includes, but is not limited to (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the

group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof.

[0032] The activator ranges from 0.00001 wt.% to 5.0 wt.%, 0.0001 wt.% to 2.0 wt.%, 0.0005 wt.% to 1.0 wt.%, or 0.001 wt.% to 0.5 wt.%.

[0033] The oxidizing agent includes, but is not limited to peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-peroxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$.

[0034] The oxidizer concentration can range from about 0.01 wt.% to 30 wt.% while the preferred concentration of oxidizing agents is from about 0.1 wt.% to 20 wt.%, and the more preferred concentration of oxidizing agents is from about 0.5 wt.% to about 10 wt.%. The weight percent is relative to the composition.

[0035] The general amount of additive comprising phosphonium based polymers or copolymers ranges from 0.00001 wt.% to 0.05 wt.%, 0.0001 wt.% to 0.025 wt., 0.0002wt.% to 0.02 wt.%, or 0.0001 wt.% to 0.01 wt.%;

[0036] Suitable pH-adjusting agents to lower the pH of the polishing composition include, but are not limited to, nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids and mixtures thereof. Suitable pH-adjusting agents to raise the pH of the polishing composition include, but are not limited to, potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof.

[0037] The pH of the slurry is between 1 and 14, preferably is between 1 and 7, more preferably is between 1 and 6, and most preferably is between 1.5 and 4.

[0038] The CMP slurries may further comprise surfactant; dispersion agent; chelating agent; film-forming anticorrosion agent; and biocide.

[0039] Other aspects, features and embodiments of the invention will be more fully apparent from the ensuing disclosure and appended claims.

[0040] The embodiments of the invention can be used alone or in combinations with each other.

DETAILED DESCRIPTION OF THE INVENTION

[0041] The present invention satisfies the need by providing intelligent designed tungsten CMP slurries, systems, and methods of using the CMP slurries to reduce the described problem of dishing and erosion in highly selective slurries while maintain desirable polishing of metal layers, specifically tungsten films.

[0042] Among polymers used in CMP slurries, phosphonium-containing macromolecules are surprisingly not described as additives for CMP slurries.

[0043] Phosphonium based polymers or copolymers are phosphonium - bearing macromolecules contain main-chain, pendant phosphorus groups, or both. Phosphorus has a larger atomic radius which can lead to the bond lengths being significantly longer, which changes the steric hindrance of the phosphorus atom. Phosphonium based polymers or copolymers encompass phosphonium-carrying macromolecules derived from various backbone chemistries, including homopolymers, random copolymers and block copolymers.

[0044] It was surprisingly found that the described phosphonium based polymers or copolymers can electrostatically interact with negatively charged metal layer such as tungsten surface and inhibit the removal of the metal during CMP. Specific designed polymers can be used to prevent over-polishing effects and reduce erosion and dishing. As a result, phosphonium-containing polymers are promising candidates for overall topography control and specifically for reducing dishing and erosion.

[0045] The present invention discloses the synthesis of phosphonium based polymers; and demonstrates the use of the synthesized phosphonium based polymers in the CMP slurries to reduce the described problem of dishing and erosion in highly selective tungsten slurries.

[0046] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0047] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention. The use of the term “comprising” in the specification and the claims includes the narrower language of “consisting essentially of” and “consisting of.”

[0048] Embodiments are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

[0049] For ease of reference, “microelectronic device” corresponds to semiconductor substrates, flat panel displays, phase change memory devices, solar panels and other products including solar substrates, photovoltaics, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, or computer chip applications. Solar substrates include, but are not limited to, silicon, amorphous silicon, polycrystalline silicon, monocrystalline silicon, CdTe, copper indium selenide, copper indium sulfide, and gallium arsenide on gallium. The solar substrates may be doped or

undoped. It is to be understood that the term “microelectronic device” is not meant to be limiting in any way and includes any substrate that will eventually become a microelectronic device or microelectronic assembly.

[0050] “Substantially free” is defined herein as less than 0.001 wt. %. “Substantially free” also includes 0.000 wt. %. The term “free of” means 0.000 wt. %.

[0051] As used herein, "about" is intended to correspond to ± 5%, preferably ± 2% of the stated value.

[0052] In all such compositions, wherein specific components of the composition are discussed in reference to weight percentage ranges including a zero lower limit, it will be understood that such components may be present or absent in various specific embodiments of the composition, and that in instances where such components are present, they may be present at concentrations as low as 0.00001 weight percent, based on the total weight of the composition in which such components are employed.

[0053] The CMP slurries in the present invention comprise abrasive, an oxidizing agent (i.e., an oxidizer that is not a free radical producer), an activator or catalyst, an additive comprising an phosphonium based cationic polymer, and water; optionally a corrosion inhibitor, a dishing reducing agent, a stabilizer, and a pH adjusting agent. The pH of the slurry is between 1 and 14, preferably is between 1 and 7, more preferably is between 1 and 6, and most preferably is between 1.5 and 4.

[0054] The CMP slurries may further comprise surfactant; dispersion agent; chelator; film-forming anticorrosion agent; biocide; and a polish enhancement agent.

Abrasive

[0055] The abrasive used in CMP slurries includes, but is not limited to inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, surface modified abrasive particles, and combinations thereof.

[0056] The abrasive used in CMP slurries can be activator-containing particles (i.e., an abrasive having an activator coating); or non-activator-containing particles.

[0057] The inorganic oxide particles include but are not limited to ceria, silica, alumina, titania, germania, spinel, an oxide or nitride of tungsten, zirconia particles, or any of the

above doped with one or more other minerals or elements, and any combination thereof. The oxide abrasive may be produced by any of a variety of techniques, including sol-gel, hydrothermal, hydrolytic, plasma, pyrogenic, aerogel, fuming and precipitation techniques, and any combination thereof.

[0058] Precipitated inorganic oxide particles can be obtained by known processes by reaction of metal salts and acids or other precipitating agents. Pyrogenic metal oxide and/or metalloid oxide particles are obtained by hydrolysis of a suitable, vaporizable starting material in an oxygen/hydrogen flame. An example is pyrogenic silicon dioxide from silicon tetrachloride. The pyrogenic oxides of aluminum oxide, titanium oxide, zirconium oxide, silicon dioxide, cerium oxide, germanium oxide and vanadium oxide and chemical and physical mixtures thereof are suitable.

[0059] The metal oxide-coated inorganic oxide particles include but are not limited to the ceria-coated or alumina-coated inorganic oxide particles, such as, ceria-coated colloidal silica, alumina-coated colloidal silica, ceria-coated high purity colloidal silica, alumina-coated high purity colloidal silica, ceria-coated alumina, ceria-coated titania, alumina-coated titania, ceria-coated zirconia, alumina-coated zirconia, or any other ceria-coated or alumina-coated inorganic oxide particles.

[0060] The metal oxide-coated organic polymer particles are selected from the group consisting of ceria-coated organic polymer particles, zirconia-coated organic polymer.

[0061] The organic polymer particles include, but are not limited to, polystyrene particles, polyurethane particle, polyacrylate particles, or any other organic polymer particles.

[0062] Colloidal silica particles and high purify colloidal silica particles are the preferred abrasive particles. The silica can be any of precipitated silica, fumed silica, silica fumed, pyrogenic silica, silica doped with one or more adjutants, or any other silica based compound.

[0063] Colloidal silica particles and high purify colloidal silica particles being used as abrasives also include the surface chemically modified silica particles through chemical coupling reactions which allow such silica particle surface bearing different chemical functional groups and possess positive or negative charges at different applied pH conditions in CMP slurries. The examples of such surface chemical modified silica particles include, but not limited to, SiO_2-R-

NH_2, -SiO-R-SO_3M; wherein R can be for example, $(CH2)_n$ group with n ranged from 1 to 12, and M can be for example, sodium, potassium, or ammonium.

[0064] In an alternate embodiment the silica can be produced, for example, by a process selected from the group consisting of a sol-gel process, a hydrothermal process, a plasma process, a fuming process, a precipitation process, and any combination thereof.

[0065] The abrasive is generally in the form of an abrasive particle, and typically many abrasive particles, of one material or a combination of different materials. Generally, a suitable abrasive particle is more or less spherical and has an effective diameter of about 10 to 700 nm, about 20 to 500 nm, or about 30 to 300 nanometers (nm), although individual particle size may vary. Abrasive in the form of aggregated or agglomerated particles are preferably processed further to form individual abrasive particles.

[0066] Abrasive particles may be purified using suitable method such as ion exchange to remove metal impurities that may help improve the colloidal stability. Alternatively, high purity abrasive particles are used.

[0067] In general, the above-mentioned abrasives may be used either alone or in combination with one another. It may be advantageous to have two or more abrasive particles with different sizes or different types of abrasives be combined to obtain excellent performance.

[0068] The concentration of abrasive can range from 0.01 wt.% to 30 wt.%, the preferred is from about 0.05 wt.% to about 20 wt.%, the more preferred is from about 0.01 to about 10 wt.%, and the most preferred is from 0.1 wt.% to 2 wt.%. The weight percent is relative to the composition.

Additive

[0069] The CMP slurries of the present invention comprise additives that are phosphonium based polymers or copolymers.

[0070] Phosphonium based polymers are cationic polymers or copolymers having phosphonium - bearing macromolecules contain main-chain, pendant phosphonium groups, or both.

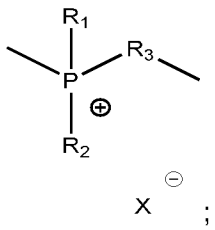
[0071] In principal, it is not important for the mode of action to which polymer backbone the phosphonium group is attached, or which type of polymerization reaction is used. In

addition, copolymers that are either randomly or block-like linked are part of the current solution if they have phosphonium group in the backbone, a side chain or side chains, or in both backbone and side chain (s).

[0072] It is considered that phosphonium based polymers in the CMP slurries can adhere to tungsten surface and form a protective film. Oxidation of tungsten is inhibited, thereby tuning tungsten removal rate, and thus preventing over polishing or, in other words, dishing or erosion.

[0073] A cationic polymer or copolymer formed by at least one cationic monomer containing at least one phosphonium group, wherein the cationic monomer comprises a structure selected from the group consisting of:

(1)



;

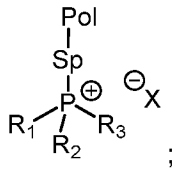
wherein:

the at least one phosphonium group is in the backbone of the cationic polymer or copolymer; R_1 and R_2 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other;

R_3 is a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic, heteroaromatic, or siloxane moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

the anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F^-, Cl^-, Br^-, and I^-; BF_4^-; PF_6^-; carboxylate such as $RCOO^-$ with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate such as RSO_3^- with R = H, alkyl or aryl;CF_3COO^-; $CF_3SO_3^-$; nitrate; sulfate; carbonate; hydrogen carbonate, and any other appropriate anion.

(2)



;

wherein:

the at least one phosphonium group is in a side chain or side chains of the cationic polymer or copolymer;

Sp denotes at each occurrence a spacer group (Sp) or a single straight or branched bond, a substituted or unsubstituted alkyl chain which chemically links the at least one phosphonium group to the backbone of the cationic polymer or copolymer;

Sp can have 1 to 20, preferably 1 to 10 carbon atoms and is optionally mono- or polysubstituted by F, Cl, Br, I or CN; wherein one or more non-adjacent CH_2 groups each can be independently replaced by -O-, -S-, -NH-, -NR- in a way that no heteroatoms are connected to each other;

Pol denotes the backbone of the cationic polymer or copolymer and the backbone type is selected from the group consisting of vinyl, styrene, acrylic or methacrylic, acrylamide, methacrylamide, ethylene glycol, vinyl ether, siloxane, phenol, norbornene type backbone, and combinations thereof;

R_1, R_2, R_3 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

and

anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F-, Cl-, Br-, and I-; BF_4-; PF_6-; carboxylate RCOO- with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate RSO_3^- with R = H, alkyl or aryl; CF_3COO-; CF_3SO_3-; nitrate; sulfate; carbonate; hydrogen carbonate; and

any other appropriate anion;

and

combinations of (1) and (2).

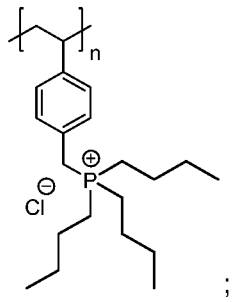
[0074] A cationic copolymer formed by the cationic monomers described in (1) and (2), and at least one non-ionic monomer known in the art including but is not limited to

acrylate or methacrylate, acrylamide or methacrylamide, maleimide, vinyl benzene, vinyl-type monomer, ethylene glycol, siloxane, norbornene, and combinations thereof.

[0075] The cationic copolymer can be a block-copolymer.

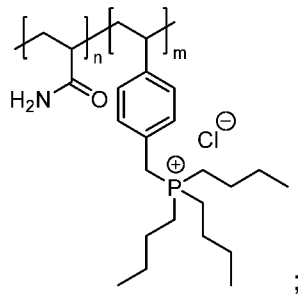
[0076] The cationic polymer or copolymer can have a functional anion selected from the group consisting of bromide, chloride, nitrate, sulfate, phosphate, and combinations thereof as counter ions.

[0077] Examples of the phosphonium based polymers include, but are not limited to (1)poly tributyl(4-vinylbenzyl)phosphonium chloride:



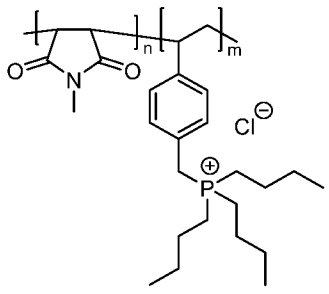
;

(2)poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer),



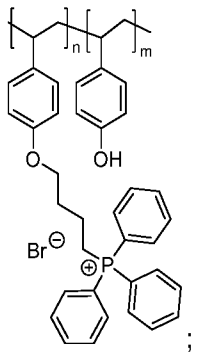
;

(3)poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer),



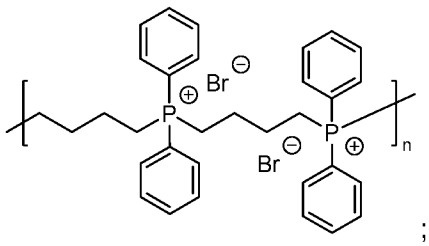
;

(4)poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide,



;

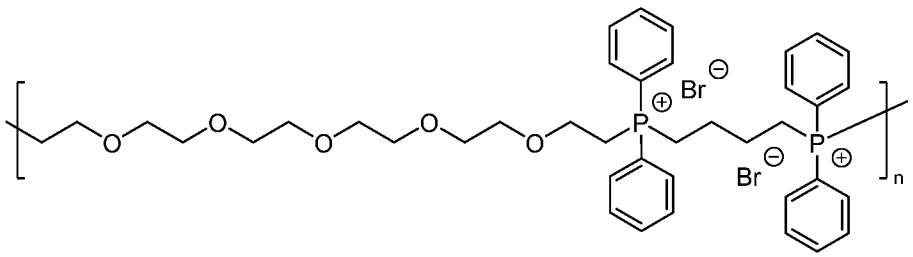
(5)poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide:



;

and

(6) poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide:



.

[0078] Furthermore, the present invention encompasses several controlled radical polymerization techniques, such as free radical polymerization, reversible addition-fragmentation chain-transfer polymerization (RAFT), nitroxide-mediated polymerization (NMP), atomic transfer reaction polymerization (ATRP), ring opening polymerization (ROMP) or polycondensation reaction.

[0079] The additive has a concentration ranging from about 0.00001 wt.% to 0.05 wt.%, 0.0001 wt.% to 0.025 wt., 0.0002wt.% to 0.02 wt.%, or 0.0001 wt.% to 0.01 wt.%;

Oxidizing Agent

[0080] The CMP slurries of the present invention comprise an oxidizing agent or an oxidizer for chemical etching of material.

[0081] The oxidizing agent of the CMP slurry is in a fluid composition which contacts the substrate and assists in the chemical removal of targeted material on the substrate surface. The oxidizing agent component is thus believed to enhance or increase the material removal rate of the composition. Preferably, the amount of oxidizing agent in the composition is sufficient to assist the chemical removal process, while being as low as possible to minimize handling, environmental, or similar or related issues, such as cost.

[0082] Advantageously, in one embodiment of this invention, the oxidizer is a component which will, upon exposure to at least one activator, produce free radicals giving an increased etching rate on at least selected structures. The free radicals described infra will oxidize most metals and will make the surface more susceptible to oxidation from other oxidizers. However, oxidizers are listed separately from the "Compound Producing Free Radicals", to be discussed infra, because some oxidizers do not readily form free radicals when exposed to the activators, and in some embodiments it is advantageous to have one or more oxidizers which provide matched etching or preferential etching rates on a variety of combinations of metals which may be found on a substrate.

[0083] As is known in the art, some oxidizers are better suited for certain components than for other components. In some embodiments of this invention, the selectivity of the CMP system to one metal as opposed to another metal is maximized, as is known in the art. However, in certain embodiments of present invention, the combination of oxidizers is selected to provide substantially similar CMP rates (as opposed to simple etching rates) for a conductor and a barrier combination.

[0084] In one embodiment, the oxidizing agent is an inorganic or organic per-compound.

[0085] A per-compound is generally defined as a compound containing an element in its highest state of oxidation, such as perchloric acid; or a compound containing at least one peroxy group (—O—O—), such as peracetic acid and perchromic acid.

[0086] Suitable per-compounds containing at least one peroxy group include, but are not limited to, peracetic acid or salt thereof, a percarbonate, and an organic peroxide, such as benzoyl peroxide, urea hydrogen peroxide, and/or di-t-butyl peroxide.

[0087] Suitable per-compounds containing at least one peroxy group include peroxides. As used herein, the term "peroxides" encompasses R—O—O—R′, where R

and R′ are each independently H, a C_1 to C_6 straight or branched alkyl, alkanol, carboxylic acid, ketone (for example), or amine, and each of the above can independently be substituted with one or more benzyl group (for example benzoyl peroxide) which may themselves be substituted with OH or C_1-C_5 alkyls, and salts and adducts thereof. This term therefore includes common examples such as hydrogen peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, also encompassed in this term are common complexes of peroxides, for example urea peroxide.

[0088] Suitable per-compounds containing at least one peroxy group include persulfates. As used herein, the term "persulfates" encompasses monopersulfates, di-persulfates, and acids and salts and adducts thereof. Included for example is peroxydisulfates, peroxymonosulfuric acid and/or peroxymonosulfates, Caro's acid, including for example a salt such as potassium peroxymonosulfate, but preferably a non-metallic salt such as ammonium peroxymonosulfate.

[0089] Suitable per-compounds containing at least one peroxy group include perphosphates, defined as above and including peroxydiphosphates.

[0090] Also, ozone is a suitable oxidizing agent either alone or in combination with one or more other suitable oxidizing agents.

[0091] Suitable per-compounds that do not contain a peroxy group include, but are not limited to, periodic acid and/or any periodiate salt (hereafter "periodates"), perchloric acid and/or any perchlorate salt (hereafter "perchlorates") perbromic acid and/or any perbromate salt (hereafter "perbromates"), and perboric acid and/or any perborate salt (hereafter "perbromates").

[0092] Other oxidizing agents are also suitable components of the composition of the present invention. Iodates are useful oxidizers.

[0093] Two and more oxidizers may also be combined to obtain synergistic performance benefits.

[0094] In most embodiments of the present invention, the oxidizer is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium

periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$.

[0095] In some embodiments, the preferred oxidizer is hydrogen peroxide.

[0096] The oxidizer concentration can range from about 0.01 wt.% to 30 wt.% while the preferred concentration of oxidizing agents is from about 0.1 wt.% to 20 wt.%, and the more preferred concentration of oxidizing agents is from about 0.5 wt.% to about 10 wt.%. The weight percent is relative to the composition.

Activator

[0097] An activator or a catalyst, is a material that interacts with an oxidizing agent and facilitates the formation of free radicals by at least one free radical-producing compounds present in the fluid.

[0098] The activator can be a metal-containing compound, in particular a metal selected from the group consisting of the metals known to activate a Fenton's Reaction process in the presence of an oxidizing agent such as, hydrogen peroxide.

[0099] The activator may be a non-metal-containing compound. Iodine is a useful with for example hydrogen peroxide to form free radicals.

[00100] If the activator is a metal ion, or metal-containing compound, it is in a thin layer associated with a surface of a solid which contacts the fluid. If the activator is a non-metal-containing substance, it can be dissolved in the fluid. It is preferred that the activator is present in amount that is sufficient to promote the desired reaction.

[00101] The activator includes, but is not limited to, (1) inorganic oxide particle with transition metal coated onto its surface, where the transition metal is selected from the group consisting of iron, copper, manganese, cobalt, cerium, and combinations thereof; (2)soluble catalyst includes, but is not limited to iron(III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate, a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof.

[00102] The amount of activator in a slurry ranges from about 0.00001 wt.% to 5 wt.%, preferably about 0.0001 wt. % to 2.0 wt. %, more preferably about 0.0005 wt. % to 1.0 wt.%; and most preferably between 0.001 wt. % to 0.5 wt.%. xxx

Water

[00103] The polishing compositions are aqueous based and, thus, comprise water. In the compositions, water functions in various ways such as, for example, to dissolve one or more solid components of the composition, as a carrier of the components, as an aid in the removal of polishing residue, and as a diluent. Preferably, the water employed in the cleaning composition is de-ionized (DI) water.

[00104] It is believed that, for most applications, water will comprise, for example, from about 10 to about 90% by weight or 90 wt. % of water. Other preferred embodiments could comprise from about 30 to about 95 wt. % of water. Yet other preferred embodiments could comprise from about 50 to about 90 wt. % % of water. Still other preferred embodiments could include water in an amount to achieve the desired weight percent of the other ingredients.

Corrosion Inhibitor (Optional)

[00105] Corrosion inhibitors used in the CMP compositions disclosed herein include, but are not limited to, nitrogenous cyclic compounds such as 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, benzothiazoles such as 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate such as 1,3,5-tris(2-hydroxyethyl), and mixtures thereof. Preferred inhibitors are 1,2,4-triazole, 5 amino triazole and 1,3,5-tris(2-hydroxyethyl)isocyanurate.

[00106] The amount of corrosion inhibitors in a slurry ranges from less than 1.0 wt.%, preferably less than 0.5 wt.%, or more preferably less than 0.25 wt.%.

Dishing Reducing Agent (Optional)

[00107] The CMP composition may further comprise a dishing reducing agent or a dishing reducer selected from the group consisting of sarcosinate and related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units, such as polyethylene oxide (PEO); ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds, sulfide, oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; sulfonic acid polymer. Glycine is a preferred dishing reducing agent.

[00108] Where the dishing reducing agent is present, the amount of dishing reducing agent ranges from about 0.001 wt.% to 2.0 wt. %, preferably 0.005 wt.% to 1.5 wt. %, and more preferably 0.01 wt.% to 1.5 wt. % based on weight per weight of the entire CMP composition.

Stabilizers (Optional)

[00109] The composition may also include one or more of various optional additives. Suitable optional additives include stabilization agents. These optional additives are generally employed to facilitate or promote stabilization of the composition against settling, flocculation (including precipitation, aggregation or agglomeration of particles, and the like), and decomposition. Stabilizers can be used to extend the pot-life of the oxidizing agent(s), including compounds that produce free radicals, by isolating the activator material, by quenching free radicals, or by otherwise stabilizing the compounds that form free radicals.

[00110] Some materials are useful to stabilize hydrogen peroxide. One exception to the metal contamination is the presence of selected stabilizing metals such as tin. In some embodiments of this invention, tin can be present in small quantities, typically less than about 25 ppm, for example between about 3 and about 20 ppm. Similarly, zinc is often

used as a stabilizer. In some embodiments of this invention, zinc can be present in small quantities, typically less than about 20 ppm, for example between about 1 and about 20 ppm. In another preferred embodiment the fluid composition contacting the substrate has less than 500 ppm, for example less than 100 ppm, of dissolved metals, except for tin and zinc, having multiple oxidation states. In the most preferred commercial embodiments of this invention, the fluid composition contacting the substrate has less than 9 ppm of dissolved metals having multiple oxidation states, for example less than 2 ppm of dissolved metals having multiple oxidation states, except for tin and zinc. In some preferred embodiments of this invention, the fluid composition contacting the substrate has less than 50 ppm, preferably less than 20 ppm, and more preferably less than 10 ppm of dissolved total metals, except for tin and zinc.

[00111] As metals in solution are generally discouraged, it is preferred that those non-metal-containing oxidizers that are typically present in salt forms, for example persulfates, are in the acid form and/or in the ammonium salt form, such as ammonium persulfate.

[00112] Other stabilizers include free radical quenchers. As discussed, these will impair the utility of the free radicals produced. Therefore, it is preferred that if present they are present in small quantities. Most antioxidants, i.e., vitamin B, vitamin C, citric acid, and the like, are free radical quenchers. Most organic acids are free radical quenchers, but three that are effective and have other beneficial stabilizing properties are phosphonic acid, the binding agent oxalic acid, and the non-radical-scavenging sequestering agent gallic acid.

[00113] In addition, it is believed that carbonate and phosphate will bind onto the activator and hinder access of the fluid. Carbonate is particularly useful as it can be used to stabilize a slurry, but a small amount of acid can quickly remove the stabilizing ions. Stabilization agents useful for absorbed activator can be film forming agents forming films on the silica particle.

[00114] Suitable stabilizing agents include organic acids, such as adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; and, phosphoric acid; substituted or unsubstituted phosphonic acids, i.e., phosphonate compounds; nitriles; and other ligands, such as those that bind the activator material and thus reduce reactions that degrade the oxidizing agent, and any combination of the foregoing agents. As used herein, an acid stabilizing agent refers to both the acid stabilizer and its conjugate base.

That is, the various acid stabilizing agents may also be used in their conjugate form. By way of example, herein, an adipic acid stabilizing agent encompasses adipic acid and/or its conjugate base, a carboxylic acid stabilizing agent encompasses carboxylic acid and/or its conjugate base, carboxylate, and so on for the above mentioned acid stabilizing agents. A suitable stabilizer, used alone or in combination with one or more other stabilizers, decreases the rate at which an oxidizing agent such as hydrogen peroxide decomposes when admixed into the CMP slurry.

[00115] On the other hand, the presence of a stabilization agent in the composition may compromise the efficacy of the activator. The amount should be adjusted to match the required stability with the lowest adverse effect on the effectiveness of the CMP system. In general, any of these optional additives should be present in an amount sufficient to substantially stabilize the composition. The necessary amount varies depending on the particular additive selected and the particular make up of the CMP composition, such as the nature of the surface of the abrasive component. If too little of the additive is used, the additive will have little or no effect on the stability of the composition. On the other hand, if too much of the additive is used, the additive may contribute to the formation of undesirable foam and/or flocculant in the composition.

[00116] Generally, suitable amounts of these stabilizer range from about 0.0001 to 5 wt.% relative to the composition, preferably from about 0.00025 to 2 wt.%, and more preferably from about 0.0005 to about 1 wt.%. The stabilizer may be added directly to the composition or applied to the surface of the abrasive component of the composition.

pH Adjusting Agent (Optional)

[00117] Compositions disclosed herein comprise pH adjusting agents. A pH adjusting agent is typically employed in the compositions disclosed herein 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, as needed.

[00118] Suitable pH-adjusting agents to lower the pH of the polishing composition include, but are not limited to, nitric acid, sulfuric acid, tartaric acid, succinic acid, citric acid, malic acid, malonic acid, various fatty acids, various polycarboxylic acids and mixtures thereof. Suitable pH-adjusting agents to raise the pH of the polishing

composition include, but are not limited to, potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof.

[00119] When employed, the amount of pH-adjusting agent preferably ranges from about 0.01 wt.% to about 5.0 wt.% relative to the total weight of the polishing composition. The preferred range is from about 0.01 wt.% to about 1 wt.% or from about 0.05 wt.% to about 0.15 wt.%.

[00120] The pH of the slurry is between 1 and 14, preferably is between 1 and 7, more preferably is between 1 and 6, and most preferably is between 1.5 and 4.

Surfactant (Optional)

[00121] The compositions disclosed herein optionally comprise a surfactant, which, in part, aids in protecting the wafer surface during and after polishing to reduce defects in the wafer surface. Surfactants may also be used to control the removal rates of some of the films used in polishing such as low-K dielectrics. Suitable surfactants include non-ionic surfactants, anionic surfactants, cationic surfactants, ampholytic surfactants, and mixtures thereof.

[00122] 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.

[00123] 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.

[00124] Anionic surfactants include, but are not limited to salts with suitable hydrophobic tails, such as alkyl carboxylate, alkyl polyacrylic salt, alkyl sulfate, alkyl phosphate, alkyl bicarboxylate, alkyl bisulfate, alkyl biphosphate, such as alkoxy carboxylate, alkoxy sulfate, alkoxy phosphate, alkoxy bicarboxylate, alkoxy bisulfate, alkoxy biphosphate, such as substituted aryl carboxylate, substituted aryl sulfate, substituted aryl phosphate,

substituted aryl bicarboxylate, substituted aryl bisulfate, and substituted aryl biphosphate etc. The counter ions for this type of surfactants include, but are not limited to potassium, ammonium and other positive ions. The molecular weights of these anionic surface wetting agents range from several hundred to several hundred-thousand.

[00125] Cationic surfactants possess the positive net charge on major part of molecular frame. Cationic surfactants are typically halides of molecules comprising hydrophobic chain and cationic charge centers such as amines, quaternary ammonium, benzyalkonium, and alkylpyridinium ions.

[00126] In another aspect, the surfactant can be an ampholytic surfactant, which possess both positive (cationic) and negative (anionic) charges on the main molecular chains and with their relative counter ions. The cationic part is based on primary, secondary, or tertiary amines or quaternary ammonium cations. The anionic part can be more variable and include sulfonates, as in the sultaines CHAPS (3-[(3-Cholamidopropyl)dimethylammonio]-1-propanesulfonate) and cocamidopropyl hydroxysultaine. Betaines such as cocamidopropyl betaine have a carboxylate with the ammonium. Some of the ampholytic surfactants may have a phosphate anion with an amine or ammonium, such as the phospholipids phosphatidylserine, phosphatidylethanolamine, phosphatidylcholine, and sphingomyelins.

[00127] Examples of surfactants also include, but are not limited to, dodecyl sulfate sodium salt, sodium lauryl sulfate, dodecyl sulfate ammonium salt, secondary alkane sulfonates, alcohol ethoxylate, acetylenic surfactant, and any combination thereof. Examples of suitable commercially available surfactants include TRITON™, Tergitol™, DOWFAX™ family of surfactants manufactured by Dow Chemicals and various surfactants in SURFYNOL™, DYNOL™, Zetasperse™, Nonidet™, and Tomadol™ surfactant families, manufactured by Air Products and Chemicals. Suitable surfactants of surfactants may also include polymers comprising ethylene oxide (EO) and propylene oxide (PO) groups. An example of EO-PO polymer is Tetronic™ 90R4 from BASF Chemicals.

[00128] When employed, the amount of surfactant typically ranges from 0.0001 wt.% to about 1.0 wt.% relative to the total weight of the barrier CMP composition. When employed, the preferred range is from about 0.010 wt.% to about 0.1 wt.%.

Chelating Agent (Optional)

[00129] Chelating agents may optionally be employed in the compositions disclosed herein to enhance affinity of chelating ligands for metal cations. Chelating agents may also be used to prevent build-up of metal ions on pads which causes pad staining and instability in removal rates. Suitable chelating agents include, but are not limited to, for example, amine compounds such as ethylene diamine, amino poly-carboxylic acids such as ethylene diamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA); aromatic acids such as benzenesulfonic acid, 4-tolyl sulfonic acid, 2,4-diamino-benzosulfonic acid, and etc.; non-aromatic organic acids, such as itaconic acid, malic acid, malonic acid, tartaric acid, citric acid, oxalic acid, gluconic acid, lactic acid, mandelic acid, or salts thereof; various amino acids and their derivatives such as Glycine, Serine, Proline, Histidine, Isoleucine, Leucine, Lysine, Methionine, Phenylalanine, Threonine, Tryptophan, Valine, Arginine, Asparagine, Aspartic acid, cystein, Glutamic acid, Glutamine, Ornithine, Selenocystein, Tyrosine, Sarcosine, Bicine, Tricine, Aceglutamide, N-Acetylaspartic acid, Acetylcarnitine, Acetylcysteine, N-Acetylglutamic acid, Acetylleucine, Acivicin, S-Adenosyl-L-homocysteine, Agaritine, Alanosine, Aminohippuric acid, L-Arginine ethyl ester, Aspartame, Aspartylglucosamine, Benzylmercapturic acid, Biocytin, Brivanib alaninate, Carbocisteine, N(6)-Carboxymethyllysine, Carglumic acid, Cilastatin, Citiolone, Coprine, Dibromotyrosine, Dihydroxyphenylglycine, Eflornithine, Fenclonine, 4-Fluoro-L-threonine, N-Formylmethionine, Gamma-L-Glutamyl-L-cysteine, 4-(γ-Glutamylamino)butanoic acid, Glutaurine, Glycocyamine, Hadacidin, Hepapressin, Lisinopril, Lymecycline, N-Methyl-D-aspartic acid, N-Methyl-L-glutamic acid, Milacemide, Nitrosoproline, Nocardicin A, Nopaline, Octopine, Ombrabulin, Opine, Orthanilic acid, Oxaceprol, Polylysine, Remacemide, Salicyluric acid, Silk amino acid, Stampidine, Tabtoxin, Tetrazolylglycine, Thiorphan, Thymectacin, Tiopronin, Tryptophan tryptophylquinone, Valaciclovir, Valganciclovir, and phosphonic acid and its derivatives such as, for example, octylphosphonic acid, aminobenzylphosphonic acid, and combinations thereof and salts thereof.

[00130] Chelating agents may be employed where there is a need to chemically bond, for example, copper cations and tantalum cations 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.

[00131] When employed, the amount of chelating agent preferably ranges from about 0.01 wt.% to about 3.0 wt.% relative to the total weight of the composition and, more preferably, from about 0.4 wt.% to about 1.5 wt.%.

Biocide (Optional)

[00132] CMP formulations disclosed herein may also comprise additives to control biological growth such as biocides. Some of the additives to control biological growth are disclosed in U.S. Pat. No. 5,230,833 and U.S. patent application Publication No. 2002/0025762, which is incorporated herein by reference. Biological growth inhibitors include but are not limited to tetramethylammonium chloride, tetraethylammonium chloride, tetrapropylammonium chloride, alkylbenzyldimethylammonium chloride, and alkylbenzyldimethylammonium hydroxide, wherein the alkyl chain ranges from 1 to about 20 carbon atoms, sodium chlorite, sodium hypochlorite, isothiazolinone compounds such as methylisothiazolinone, methylchloroisothiazolinone and benzisothiazolinone. Some of the commercially available preservatives include KATHON™ and NEOLENE™ product families from Dow Chemicals and Preventol™ family from Lanxess.

[00133] The preferred biocides are isothiozilone compounds such as methylisothiazolinone, methylchloroisothiazolinone and benzisothiazolinone.

[00134] The CMP polishing compositions optionally contain a biocide ranging from 0.0001 wt.% to 0.10 wt.%, preferably from 0.0001 wt.% to 0.005 wt.%, and more preferably from 0.0002 wt.% to 0.0025 wt.% to prevent bacterial and fungal growth during storage.

[00135] Compositions disclosed herein may be manufactured in a concentrated form and subsequently diluted at the point of use with DI water. Other components such as, for example, the oxidizer, may be withheld in the concentrate form and added at the point of use to minimize incompatibilities between components in the concentrate form. The compositions disclosed herein may be manufactured in two or more components which can be mixed prior to use.

Working Examples

General Experimental Procedure

[00136] All percentages are weight percentages unless otherwise indicated.

Part I Synthesis Phosphonium-based Polymers

[00137] The present invention encompasses several controlled radical polymerization techniques, such as reversible addition-fragmentation chain-transfer polymerization (RAFT). By using such controlled processes, the specific design of a material with optimized molecular weight and polydispersity is possible, which is a clear distinguishing feature from other described polymers in CMP applications.

[00138] All reagents and solvents were purchased from Sigma-Aldrich (Merck) of highest commercial grade and used as received unless otherwise specified.

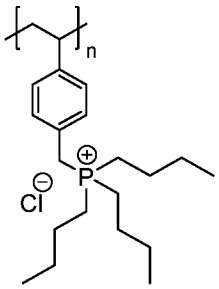
[00139] Characterization Methods

[00140] NMR spectra were recorded on a 500 MHz Bruker Avance II+ spectrometer using deuterated solvents from Sigma-Aldrich (Merck). Chemical shifts were reported as δ values (ppm) and were calibrated according to internal standard $Si(OMe)_4$ (0.00 ppm).

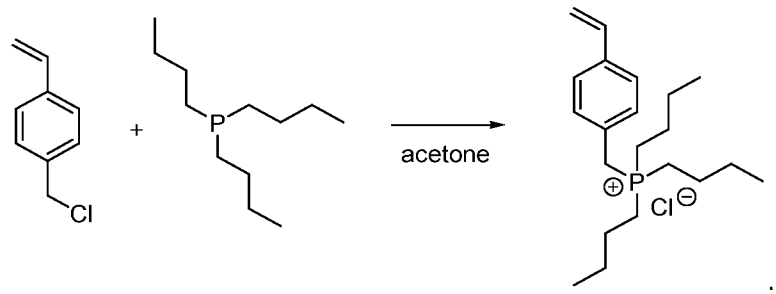
[00141] Polymers were analyzed by size exclusion chromatography (SEC) running in H_2O/MeOH/EtOAc (54/23/23, v/v/v) containing 10 mM sodium acetate at 40 °C (flow rate: 0.5 mL/min). Measurements were carried out on an Agilent 1260 HPLC, equipped with a column set consisting of PSS Novema pre-column and PSS Novema MAX ultraheigh column. The samples were dissolved in the eluent with 0.1% ethylenglycol as internal standard at 50 °C. The average molar mass of polymers was derived from refractive index signals based on poly(2-vinylpyridine) calibration curve.

Example 1

[00142] Synthesis of poly tributyl(4-vinylbenzyl)phosphonium chloride:



[00143] Monomer was synthesized as shown below:

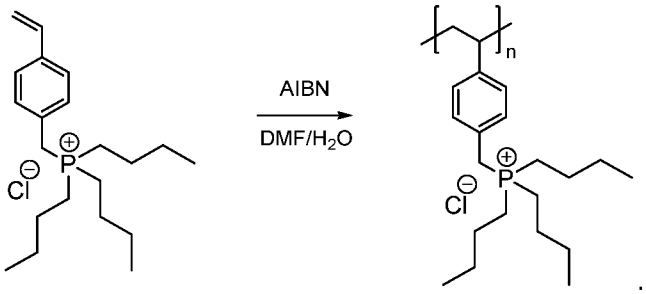


[00144] 4-vinylbenzyl chloride (CAS: 1592-20-7, 10 g, 123 mmol) was dissolved in 233 mL dry acetone. Tributylphosphane (CAS: 998-40-3, 25 g, 123 mmol) was added and the reaction mixture was stirred at reflux for 18 h. The product was precipitated by adding methyl *tert*-butyl ether (MTBE, 1.2 L) to the cooled solution. The solid was filtered, washed twice with 100 mL of MTBE and vacuum-dried to give a white solid (35 g, 80 % yield).

[00145] ^{1}H NMR (500 MHz, D_2O): δ = 7.55 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 8.3, 2.5 Hz, 2H), 6.81 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.89 (dd, *J* = 17.8, 1.0 Hz, 1H), 5.40 – 5.34 (m, 2H), 3.67 (d, *J* = 14.6 Hz, 2H), 2.18 – 2.08 (m, 6H), 1.54 (dq, *J* = 10.1, 7.3 Hz, 6H), 1.45 (hept, *J* = 7.1 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 9H) ppm.

[00146] The polymer was synthesized selected from the processes as shown below.

[00147] Example 1-1:

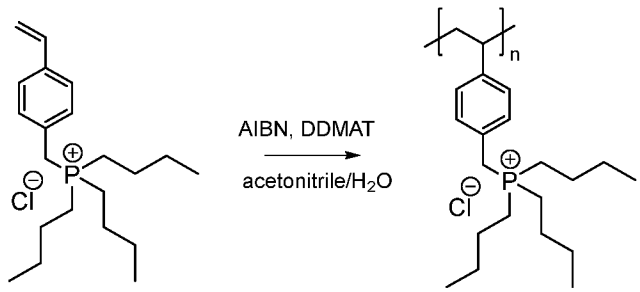


[00148] Tributyl(4-vinylbenzyl)phosphonium chloride (15.7 g, 44.2 mmol) and AIBN (CAS: 78-67-1, 36.4 mg, 0.22 mmol) were dissolved in 84 mL DMF/H2O (1 : 1, v/v), purged with Ar for 30 min and heated at 65 °C for 24 h. The cooled solution was treated with 400 mL THF to precipitate the polymer, which was then washed twice with THF and dried under vacuum at room temperature to give 11.6 of a white solid (74 % yield).

[00149] ^{1}H NMR (500 MHz, Methanol-d_4) δ: 7.30 (broad s), 6.54 (broad s), 4.05 (broad s), 2.32 (broad s), 1.49 (broad s), 0.96 (broad s) ppm.

[00150] SEC: Mn: 90 kDa; Mw: 352 kDa; PDI: 3.9

[00151] Example 1-2:



[00152] A Schlenk flask was charged with tributyl(4-vinylbenzyl)phosphonium chloride (10 g, 28 mmol), AIBN (CAS: 78-67-1, 9.9 mg, 0.06 mmol) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, CAS: 461642-78-4, 0.073 g, 0.2 mmol). The mixture was dissolved in acetonitrile (39 mL), purged with Ar for 30 min and then heated at 65 °C for 16 h. The solution was cooled to room temperature, acetonitrile was removed, and the residue was dissolved in 5 mL dichloromethane. The polymer was finally precipitated by adding 50 mL THF, washed twice with THF and vacuum-dried to give 8.4 g of a yellow solid (84 % yield).

[00153] ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.73 (broad s), 7.03 (broad s), 4.28 (broad s), 2.65 (broad s), 1.96 (broad s), 1.36 (broad s) ppm.

[00154] SEC: Mn: 15.6 kDa; Mw: 23.0 kDa; PDI: 1.5

[00155] Example 1-3:

[00156] Following the same procedure as for example 1-2 using 13 g Tributyl(4-vinylbenzyl)phosphonium chloride (36.6 mmol), AIBN (CAS: 78-67-1, 42 mg, 0.26 mmol) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, CAS: 461642-78-4, 0.294 g, 0.8 mmol). 10.5 g (80 %) of a light yellow polymer was obtained.

[00157] SEC: Mn: 5.1 kDa; Mw: 7.1 kDa; PDI: 1.4

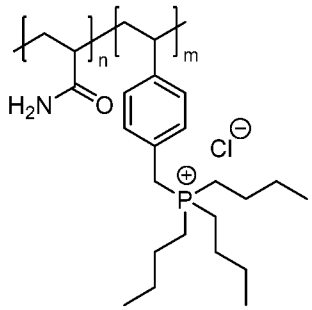
[00158] Example 1-4:

[00159] Following the same procedure as for example 1-2 using 0.036 g (0.1 mmol) DDMAT. 7.9 g (79 %) of a light yellow polymer was obtained.

[00160] SEC: Mn: 20.2 kDa; Mw: 36.1 kDa; PDI: 1.8

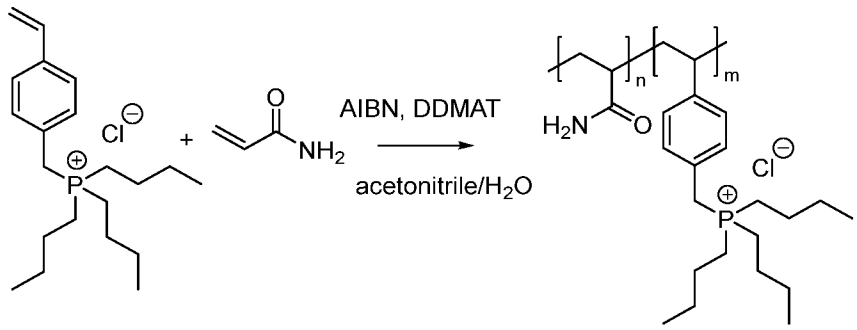
Example 2

Synthesis of poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride



[00161] The polymer was synthesized selected from the processes as shown below.

[00162] Example 2-1:



[00163] A Schlenk flask was charged with tributyl(4-vinylbenzyl)phosphonium chloride (13 g, 36.6 mmol), acrylamide (CAS: 79-06-1, 2.6 g, 36.6 mmol), AIBN (CAS: 78-67-1, 53 mg, 0.322 mmol) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, CAS: 461642-78-4, 0.38 g, 1.04 mmol). The mixture was dissolved in acetonitrile (51 mL), purged with Ar for 30 min and then heated at 65 °C for 18 h. The solution was cooled to room temperature, acetonitrile was removed, and the residue was dissolved in 10 mL dichloromethane. The polymer was finally precipitated by adding 100 mL THF, washed twice with THF and vacuum-dried to give 10.4 g of a yellow solid (67 % yield).

[00164] ^{1}H NMR (500 MHz, Methanol-d_4) δ: 7.25 (broad s), 6.82 (broad s), 3.91 (broad s), 2.26 – 2.14 (m), 1.60 – 1.49 (m), 1.02 – 0.96 (m) ppm.

[00165] SEC: Mn: 5.0 kDa; Mw: 7.8 kDa; PDI: 1.6

[00166] Example 2-2:

[00167] Following the same procedure as in Example 2-1 using 0.114 g (0.31 mmol) DDMAT. 12.6 g (80 %) of a light yellow polymer was obtained.

[00168] SEC: Mn: 10.4 kDa; Mw: 21.3 kDa; PDI: 2.0.

[00169] Example 2-3:

[00170] Following the same procedure as in Example 2-1 using 0.057 g (0.16 mmol) DDMAT. 12.6 g (80 %) of a light yellow polymer was obtained.

[00171] SEC: Mn: 24.2 kDa; Mw: 53.8 kDa; PDI: 2.3

[00172] Example 2-4:

[00173] Following the same procedure as in Example 2-1 using 0.65 g acrylamide (CAS: 79-06-1, 9.2 mmol). 10.7 g (78 %) of a light yellow polymer was obtained.

[00174] SEC: Mn: 5.3 kDa; Mw: 7.2 kDa; PDI: 1.3

[00175] Example 2-5:

[00176] Following the same procedure as in Example 2-1 using 0.65 g acrylamide (CAS: 79-06-1, 9.2 mmol) and 0.114 g (0.31 mmol) DDMAT. 11.5 g (85 %) of a light yellow polymer was obtained.

[00177] SEC: Mn: 11.3 kDa; Mw: 22.6 kDa; PDI: 2.0

[00178] Example 2-6:

[00179] Following the same procedure as in Example 2-1 using 0.65 g acrylamide (CAS: 79-06-1, 9.2 mmol) and 0.057 g (0.16 mmol) DDMAT. 10.4 g (76 %) of a light yellow polymer was obtained.

[00180] SEC: Mn: 14.9 kDa; Mw: 34.7 kDa; PDI: 2.4

[00181] Example 2-7:

[00182] Following the same procedure as in Example 2-1 using 10.4 g acrylamide (CAS: 79-06-1, 146 mmol). 18 g (78 %) of a light yellow polymer was obtained.

[00183] SEC: Mn: 11.4 kDa; Mw: 17.6 kDa; PDI: 1.5

[00184] Example 2-8:

[00185] Following the same procedure as in Example 2-1 using 10.4 g acrylamide (CAS: 79-06-1, 146 mmol) and 0.114 g (0.31 mmol) DDMAT. 16.3 g (70 %) of a light yellow polymer was obtained.

[00186] SEC: Mn: 28.9 kDa; Mw: 46.8 kDa; PDI: 1.6

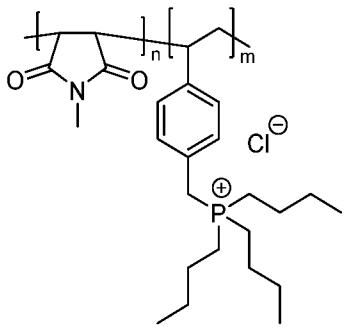
[00187] Example 2-9:

[00188] Following the same procedure as in Example 2-1 using 10.4 g acrylamide (CAS: 79-06-1, 146 mmol) and 0.057 g (0.16 mmol) DDMAT. 17.7 g (75 %) of a light yellow polymer was obtained.

[00189] SEC: Mn: 44.8 kDa; Mw: 92.4 kDa; PDI: 2.1

Example 3

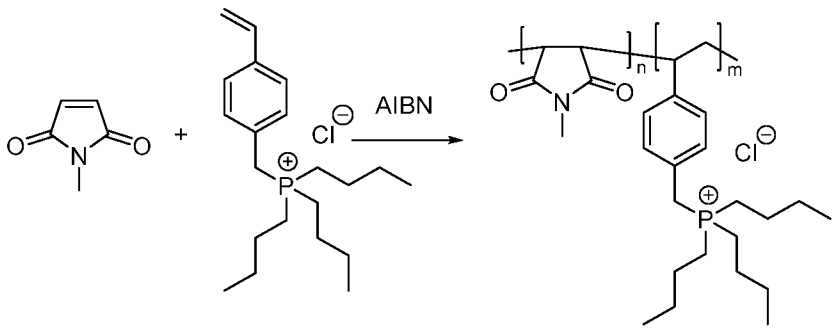
Synthesis of poly tributyl(4-vinyl benzyl phosphonium-co-*N*-methyl maleimide) chloride



[00190] Monomer obtained in Example 1 was used.

[00191] The polymer was synthesized selected from the processes as shown below.

[00192] Example 3-1:



[00193] Tributyl(4-vinylbenzyl)phosphonium chloride (4 g, 11.3 mmol), *N*-methylmaleimide (CAS: 930-88-1, 1.25 g, 11.3 mmol) and AIBN (17.3 mg, 0.105 mmol) were dissolved in 32 mL acetonitrile/H_2O (1 : 1, v/v). The solution was purged with Ar for

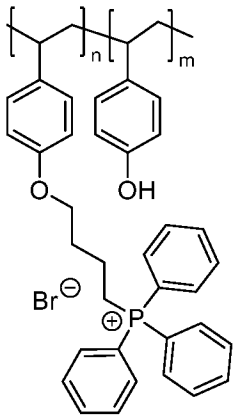
30 min, heated at 65 °C for 24 h and subsequently concentrated *in vacuo*. The crude product was dissolved in dichloromethane (10 mL) and precipitated by adding THF (100 mL) resulting 4.8 g (94 %) polymer as a white solid.

[00194] ^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.29 (broad s), 4.04 (broad s), 2.25 (s), 1.36 (s), 0.87 (s) ppm.

[00195] SEC: Mn: 76; Mw: 259 kDa, PDI: 3.4

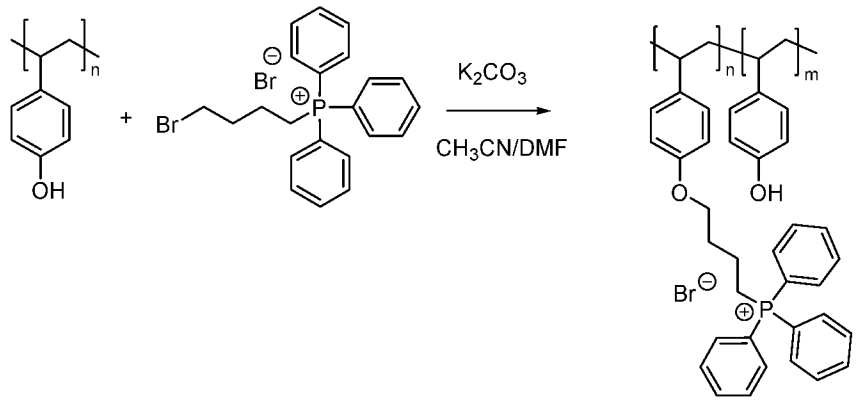
Example 4

Synthesis of poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide



[00196] The polymer was synthesized selected from the processes as shown below.

[00197] Example 4-1:

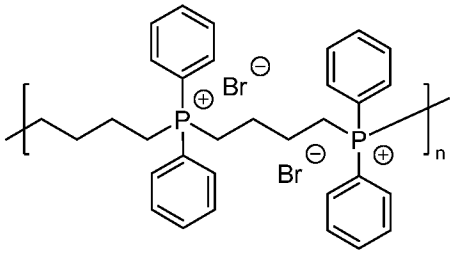


[00198] Poly(4-vinylphenol) (CAS: 24979-70-2, MW: ~11 kDa, 6 g) was dissolved together with potassium carbonate (6.9 g, 50 mmol) in acetonitrile (150 mL). The mixture was heated to reflux for 90 min under Ar atmosphere and then cooled to room temperature and treated with (4-bromobutyl) triphenyl phosphonium bromide (CAS: 7333-63-3, 23.7, 60 mmol) dissolved in 150 mL of DMF. The reaction mixture was stirred at reflux for 48 h, cooled to room temperature and treated with 120 mL of 0.9 M HBr. Solvent was reduced to about a third of the volume, filtered and treated with THF/dichloromethane (4:1, v/v) to precipitate the polymer. The crude polymer was finally freeze dried to give 10.8 g of a white solid.

[00199] SEC: Mn: 20.5 kDa; Mw: 86.4 kDa; PDI: 4.2.

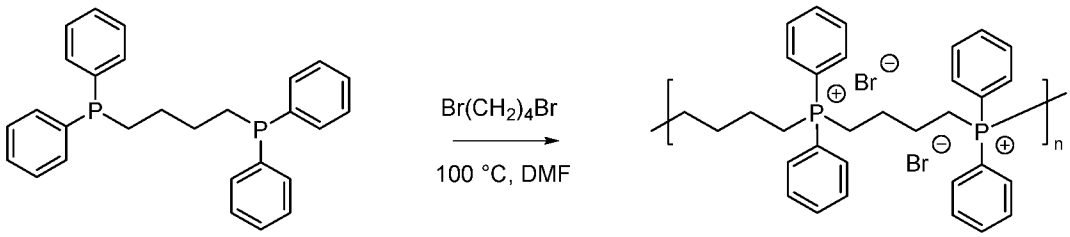
Example 5

Synthesis of poly(4-(butyldiphenylphosphino)butyl)dipenylphosphonium) bromide



[00200] The polymer was synthesized selected from the processes as shown below.

[00201] Example 5-1:



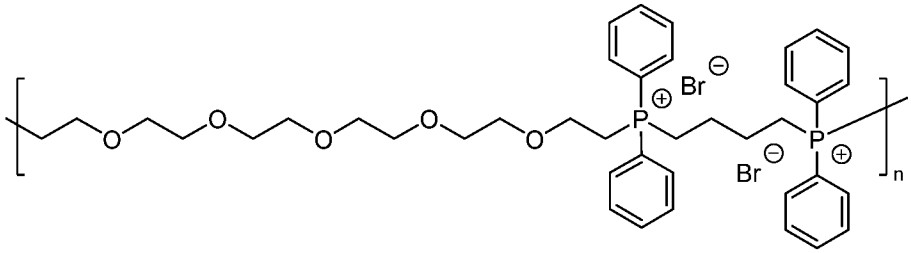
[00202] 1,4-Bis(diphenylphosphino)butane (CAS: 7688-25-7, 5.1 g, 12 mmol) was dissolved together with 1,4-dibromobutane (CAS: 110-52-1, 2.6 g, 12 mmol) in DMF (30 mL). After purging with nitrogen, the resulting mixture was heated 100 °C for 24 h. The resulting polymer solution was concentrated in vacuo and treated with MTBE (400 mL) to

precipitate the polymer. The crude polymer was washed several times with MTBE and dried under vacuum to give 7.6 g of a light brown solid.

[00203] ^{1}H NMR (500 MHz, DMSO-d_6) δ: 8.02 – 7.95 (m), 7.94 – 7.88 (m), 7.80 – 7.64 (m), 3.14 – 2.95 (m), 1.55 – 1.43 (m) ppm.

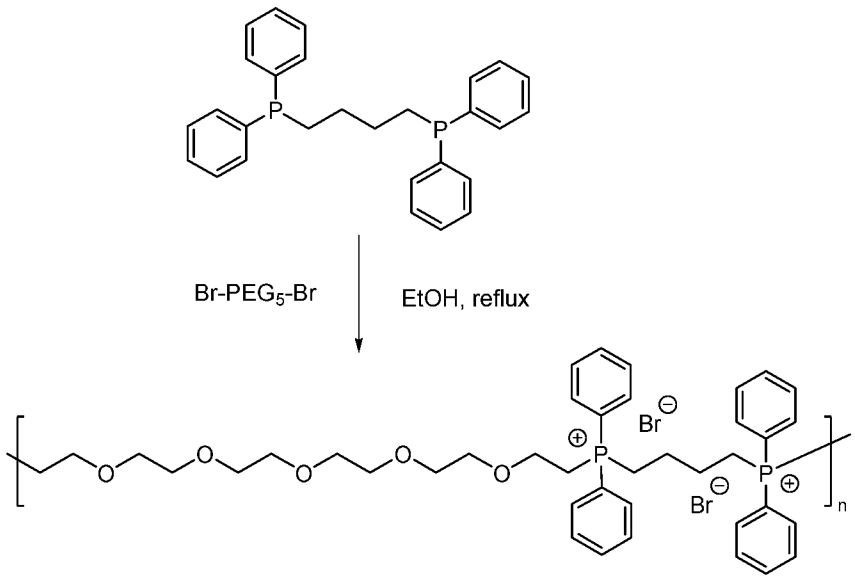
Example 6

Synthesis of poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide



[00204] The polymer was synthesized selected from the processes as shown below.

[00205] Example 6-1:



[00206] 1,4-Bis(diphenylphosphino)butane (CAS: 7688-25-7, 3.6 g, 8 mmol) was dissolved/suspended together with Pr-PEG-Br (BroadPharm, CAS: 67705-77-5, 3.4 g, 8 mmol) in ethanol (25 mL). After purging with nitrogen, the resulting mixture was heated at reflux for 48 h. The solution was cooled to r. t. and concentrated in vacuum. The

resulting white solid was dissolved again in 15 mL DCM and precipitated by adding MTBE (150 mL). The precipitate was treated with water (45 mL), filtered and freeze-dried, resulting in 5.6 g (80 %) of a white solid.

[00207] ^{1}H NMR (500 MHz, D_2O) δ: 7.87 – 7.67 (m), 3.82 – 3.81 (m), 3.72 – 3.66 (m), 3.63 – 3.62 (m), 3.52 – 3.49 (m), 3.36 – 3.22 (m), 3.19 – 2.95 (m), 1.62 – 1.59 (m) ppm.

[00208] SEC: Mn: 3.6 kDa; Mw: 6.4 kDa; PDI: 1.8.

Part II CMP experiments

using synthesized phosphonium-based polymers in Part I

[00209] The polishing composition and associated methods described herein are effective for CMP of a wide variety of substrates, including most of substrates, particularly useful for polishing tungsten substrates.

[00210] In the examples presented below, CMP experiments were run using the procedures and experimental conditions given below.

PARAMETERS:

Å: angstrom(s) – a unit of length

BP: back pressure, in psi units

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)

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

TEOS: silicon oxide films by Chemical Vapor Deposition (CVD) using tetraethyl orthosilicate as the precursor

Wt.%: weight percentage (of a listed component)

Removal Rate (RR) = (film thickness before polishing - film thickness after polishing)/polish time.

Removal Rates and Selectivity

Tungsten Removal Rates: Measured tungsten removal rate at 2.5 psi down pressure of the CMP tool.

TEOS Removal Rates: Measured TEOS removal rate at a given down pressure. The down pressure of the CMP tool was 2.5 psi.

SiN Removal Rates: Measured SiN removal rate at a given down pressure. The down pressure of the CMP tool was 2.5 psi.

[00211] The CMP tool that was used in the examples is a AMAT 200mm Mirra®, manufactured by Applied Materials, Inc. 3050 Bowers Avenue, Santa Clara, California, 95054. IC1010 polishing pad, supplied by Dow Chemicals was used on the platen for the polishing studies.

[00212] 200mm diameter silicon wafers coated with tungsten films, TEOS films, SiN films or tungsten containing SKW patterned structures were obtained from SKW Associate, Inc. 2920 Scott Blvd, Santa Clara, CA 95054. Polish time for blanket films was one minute. Tungsten removal rates were measured using sheet resistance measurement techniques. TEOS removal was measured using optical techniques. Patterned wafers were polished for time based on eddy current technique on the Ebara polisher. Polishing time for patterned wafer was 15 seconds past the end point identified by the eddy current end point technique. Patterned wafers were analyzed with a KLA Tencor P15 Profiler (large feature sizes) or an AFM tool (small feature sizes).

[00213] The polishing was performed using 111 RPM table speed, 113 RPM carrier speed, 200 ml/min slurry flow rate and at 2.5 psi downforce.

[00214] In the polishing process, a substrate (e.g., blanket W or patterned W wafers) was placed face-down on a polishing pad which was fixedly attached to a rotatable platen of a CMP polisher. In this manner, the substrate to be polished and planarized

was placed in direct contact with the polishing pad. A wafer carrier system or polishing head was used to hold the substrate in place and to apply a downward pressure against the backside of the substrate during CMP processing while the platen and the substrate were rotated. The polishing composition (slurry) was applied (usually continuously) on the pad during CMP processing for effective removal of material and planarizing the substrate.

[00215] In the following working examples, a base CMP slurry was made with 0.01 wt.% ferric nitrate (iron (III) nitrate), 0.08 wt.% malonic acid (stabilizer), 2.0 wt.% hydrogen peroxide, 0.1 wt.% glycine and 0.25 wt.% Fuso PL-2C silica particles in water with pH adjusted to 2.3 with nitric acid.

[00216] The removal rates (Å/min) for W, TEOS and SiN; and removal rate selectivity of W:TEOS and W:SiN were shown in Table A.

Table A

	W RR	TEOS RR	W:TEOS selectivity	SiN RR	W:SiN selectivity
Base slurry	2914	44	66	32	91

[00217] Dishing of tungsten was tested on different arrays including, 50 X 50 micron array (tungsten line width/trench separated by dielectric line width/spacer in micron) (50/50 µm), 1 X 1 micron (1/1 µm), 0.5 X 0.5 micron (0.5/0.5 µm), 0.25 X 0.25 micron (0.25/0.25 µm), and 0.18 X 0.18 micron array (0.18/0.18 µm), when the wafer was polished for 15 seconds additional time or over polishing (OP) time after the pattern wafer polish end point was detected by using eddy current measurement. Results were shown in Table B.

Table B W Line Dishing [Å]

	50/50µm	1/1µm	0.5/0.5µm	0.25/0.25µm	0.18/0.18µm
Base slurry	905	232	151	137	121

[00218] Erosion was tested on 7/3 µm, 1/1 µm, 0.5/0.5 µm, 0.25/0.25 µm, 0.18/0.18 µm arrays at 20% over-polish for various formulations. Results were shown in Table C.

Table C Erosion [Å]

	7/3µm	1/1µm	0.5/0.5µm	0.25/0.25µm	0.18/0.18µm
Base slurry	314	111	50	109	112

[00219] In the following working examples, different additives with different amounts were added to the base slurry to make the working examples.

[00220] The working CMP slurries were made with adding phosphonium-based polymers described in Part I into the base CMP slurry. Poly tributyl(4-vinylbenzyl)phosphonium chloride made in Example 1, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride made in Example 2, poly tributyl(4-vinyl benzyl phosphonium-co-*N*-methyl maleimide) chloride made in Example 3, poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide made in Example 4, poly(4-(butyldiphenylphosphino)butyl)dipenylphosphonium) bromide made in Example 5, and poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide made in Example 6, were used in the working CMP slurries respectively.

[00221] Effects of phosphonium-based polymers on tungsten removal rates, erosion and dishing were tested.

[00222] The tungsten removal rate results were Table 1.

[00223] First, various quantities of phosphonium-based polymers (10, 50, 100 ppm) were used to identify a general concentration window for polishing or removing blanket W wafer (tungsten removal rate or W RR), which was then used for tests to identify the effects on erosion and dishing.

Table 1

Polymer made in Example	Concentration	W RR [Å/min]
1-1	10 ppm	2402
1-1	50 ppm	1398
1-1	100 ppm	857
2-1	10 ppm	3759
2-1	50 ppm	2170

2-1	100 ppm	996
2-3	10 ppm	3734
2-3	50 ppm	1716
2-3	100 ppm	1018
2-6	10 ppm	3767
2-6	50 ppm	1827
2-6	100 ppm	915
2-8	10 ppm	3696
2-8	50 ppm	2132
2-8	100 ppm	1604
2-9	10 ppm	4048
2-9	50 ppm	1672
2-9	100 ppm	1438

[00224] As shown in Table 1, working CMP slurries with a small amount of synthesized phosphonium-based polymers (around 10 ppm) provided high tungsten removal rates, with an increase in concentration inhibiting the effect on tungsten removal. A general concentration window of 10 ppm to 50 ppm was adopted.

[00225] Table 2 summarized tungsten, TEOS and SiN removal rate for working CMP slurries comprising synthesized phosphonium-based polymers.

Table 2

Polymer made in Example	W RR [Å/min]	TEOS RR [Å/min]	W:TEOS RR selectivity	SiN RR [Å/min]	W:SiN RR selectivity
1-1 (25 ppm)	3125	29	108	21	149
1-1 (50 ppm)	1517	15	101	26	60
2-1 (12.5 ppm)	2742	39	70	20	137

2-1 (40 ppm)	2196	22	100	18	122
2-3 (25 ppm)	2275	23	99	18	127
2-6 (25 ppm)	2289	28	82	16	143
2-6 (40 ppm)	2219	20	111	18	123
2-8 (25 ppm)	2406	30	80	18	134
2-9 (20 ppm)	2824	24	118	23	123
3-1 (15 ppm)	3089	36	86	21	147
3-1 (30 ppm)	3255	30	109	21	155
4-1 (25 ppm)	2082	53	39	27	77
4-1 (40 ppm)	2100	46	46	39	54
5-1 (10 ppm)	3652	38	93	27	132
5-1 (20 ppm)	2909	37	79	27	108
5-1 (30 ppm)	2017	35	58	29	70
6-1 (15 ppm)	3199	33	97	29	110
6-1 (30 ppm)	3088	29	103	30	106

[00226] As shown in Table 2, working CMP slurries have high W:TEOS RR and W:SiN RR selectivities. Removal rates of TEOS and SiN were extremely low comparing to the removal rate for tungsten.

[00227] Dishing and erosion data for different patterned structures having different line features (Dishing: 50/50 µm, 1/1 µm, 0.5/0.5 µm, 0.25/0.25 µm, 0.18/0.18 µm; Erosion: 7/3 µm, 1/1 µm, 0.5/0.5 µm, 0.25/0.25 µm, 0.18/0.18 µm) at 20% overpolish for various formulations were summarized in Tables 3 and 4, respectively.

Table 3 W Line Dishing [Å]

Polymer made in Example	50/50µm	1/1µm	0.5/0.5µm	0.25/0.25µm	0.18/0.18µm
1-1 (25 ppm)	1152	174	86	76	73
1-1 (50 ppm)	1646	149	73	62	64
2-1 (12.5 ppm)	1207	196	120	110	104
2-1 (40 ppm)	1388	151	58	95	54
2-3 (25 ppm)	1368	161	86	81	75
2-6 (25 ppm)	1413	167	85	70	69
2-6 (40 ppm)	1239	129	57	77	86
2-8 (25 ppm)	1274	168	73	69	72
2-9 (20 ppm)	1265	195	123	97	108
3-1 (15 ppm)	835	227	157	141	105
3-1 (30 ppm)	783	228	-120	-127	-101
4-1 (25 ppm)	1086	253	180	171	104
4-1 (40 ppm)	1199	264	187	154	141
5-1 (10 ppm)	1049	251	143	145	108
5-1 (20 ppm)	921	138	81	81	78
5-1 (30 ppm)	708	170	78	81	70
6-1 (15 ppm)	1102	130	123	104	71
6-1 (30 ppm)	1282	87	102	77	68

Table 4 Erosion [Å]

Polymer made in Example	7/3µm	1/1µm	0.5/0.5µm	0.25/0.25µm	0.18/0.18µm
1-1 (25 ppm)	660	467	283	455	362
1-1 (50 ppm)	1018	934	928	1010	1084
2-1 (12.5 ppm)	723	510	293	574	472
2-1 (40 ppm)	819	754	693	860	788
2-3 (25 ppm)	703	589	512	641	587
2-6 (25 ppm)	811	709	575	715	691
2-6 (40 ppm)	786	622	656	725	652
2-8 (25 ppm)	665	523	473	608	600
2-9 (20 ppm)	707	493	429	474	515
3-1 (15 ppm)	329	83	-43	36	42
3-1 (30 ppm)	258	52	-70	-49	-49
4-1 (25 ppm)	390	240	97	297	176
4-1 (40 ppm)	532	385	133	318	359

5-1 (10 ppm)	490	343	92	155	161
5-1 (20 ppm)	483	390	265	404	359
5-1 (30 ppm)	483	319	145	259	247
6-1 (15 ppm)	646	350	162	345	288
6-1 (30 ppm)	663	569	393	590	556

[00228] There are reported W dishing and erosion data on other W CMP polishing compositions which typically have W line dishing >1500 Å on wide line features and have erosion on high density features such as 70% and 90% density >1000 Å.

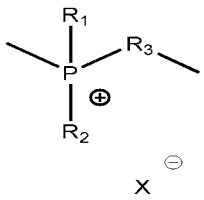
[00229] As is apparent from the results depicted in Table 3 and Table 4 respectively, the use of phosphonium-based polymers significantly reduces erosion and dishing.

[00230] While the principles of the invention have been described above in connection with preferred embodiments, it is to be clearly understood that this description is made only by way of example and not as a limitation of the scope 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.

Claims

1. A cationic polymer or copolymer formed by at least one cationic monomer containing at least one phosphonium group, wherein the cationic monomer comprises a structure selected from the group consisting of:

(1)



wherein:

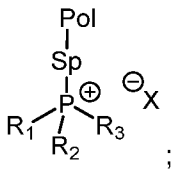
the at least one phosphonium group is in backbone of the cationic polymer or copolymer;

R_1 and R_2 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other;

R_3 is a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic, heteroaromatic, or siloxane moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F^-, Cl^-, Br^-, and I^-; BF_4^-; PF_6^-; carboxylate $RCOO^-$ with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate RSO_3^- with R = H, alkyl or aryl; CF_3COO^-; $CF_3SO_3^-$; nitrate; sulfate; carbonate; and hydrogen carbonate;

(2)



;

wherein:

the at least one phosphonium group is in a side chain or side chains of the cationic polymer or copolymer;

Sp denotes at each occurrence a spacer or a single bond which chemically links the at least one phosphonium group to backbone of the cationic polymer or copolymer; wherein the spacer is a substituted or unsubstituted alkyl chain having 1 to 20, preferably 1 to 10 carbon atoms and is optionally mono- or polysubstituted by F, Cl, Br, I or CN; wherein one or more non-adjacent CH_2 groups each can be independently replaced by -O-, -S-, -NH-, -NR- in a way that no heteroatoms are connected to each other;

Pol denotes backbone of the cationic polymer or copolymer and the backbone type is selected from the group consisting of vinyl, styrene, acrylic or methacrylic, acrylamide, methacrylamide, ethylene glycol, vinyl ether, siloxane, phenol, norbornene type backbone, and combinations thereof;

R_1, R_2, R_3 each is independently a substituted or unsubstituted aliphatic, branched aliphatic or cyclic aliphatic, aromatic or heteroaromatic moieties; wherein CH_2 not in the aromatic or heteroaromatic ring can be replaced by O, S or N in a way that no heteroatoms are connected to each other; and hydrogen can be replaced by F, Cl or CN;

and

anion X^- is selected from the group consisting of a halide anion selected from the group consisting of F-, Cl-, Br-, and I-; BF_4-; PF_6-; carboxylate RCOO- with R = H, alkyl or aryl; malonate; citrate; fumarate; sulfonate RSO_3^- with R = H, alkyl or aryl; CF_3COO-; CF_3SO_3-; nitrate; sulfate; carbonate; and hydrogen carbonate;

and

(3) combinations of (1) and (2).

2. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is formed with at least one non-ionic monomer in addition to the at least one cationic monomer, and the at least one non-ionic monomer is selected from the group consisting of acrylate or methacrylate type monomer, acrylamide or methacrylamide type monomer, maleimide type monomer, vinyl benzene type monomer, vinyl-type monomer, ethylene glycol type monomer, siloxane type monomer, norbornene type monomer, and combinations thereof.

3. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is a cationic copolymer.

4. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is a block-copolymer.

5. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer has functional anions selected from bromide, chloride, nitrate, sulfate, phosphate as counter ions.

6. The cationic polymer or copolymer of Claim 1, wherein the cationic polymer or copolymer is selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, and poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide.

7. The cationic polymer or copolymer of Claim 1, wherein polymerization of the cationic polymer or copolymer is selected from the group consisting of free radical polymerization, reversible addition-fragmentation chain-transfer polymerization (RAFT), nitroxide-mediated polymerization (NMP), atomic transfer reaction polymerization (ATRP), ring opening polymerization (ROMP), polycondensation reaction, and combinations thereof.

8. A chemical mechanical planarization composition comprising:
an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;
an activator;
an oxidizing agent;
an additive comprising the cationic polymer or copolymer of any one of claims 1 to 7;
water; and optionally
a corrosion inhibitor;
a dishing reducing agent;
a stabilizer;

a pH adjusting agent.

9. The chemical mechanical planarization composition of Claim 8, wherein the abrasive ranges from 0.01 wt.% to 30 wt.%, 0.05 wt.% to 20 wt.%, 0.01 wt.% to 10 wt.%, or from 0.1 wt.% to 2 wt.%;
the additive comprising the cationic polymer or copolymer ranges from 0.00001 wt.% to 0.05 wt.%, 0.0001 wt.% to 0.025 wt., 0.0002wt.% to 0.02 wt.%, or 0.0001 wt.% to 0.01 wt.%;
the oxidizing agent ranges from 0.01 wt.% to 30 wt.%, 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%;
the activator ranges from 0.00001 wt.% to 5.0 wt.%, 0.0001 wt.% to 2.0 wt.%, 0.0005 wt.% to 1.0 wt.%, or 0.001 wt.% to 0.5 wt.%;
the corrosion inhibitor ranges from less than 1.0 wt.%, less than 0.5 wt.%, or less than 0.25 wt.%;
the dishing reducing agent ranges from 0.001 wt.% to 2.0 wt. %, 0.005 wt.% to 1.5 wt. %, or 0.01 wt.% to 1.0 wt. %; and
the stabilizer ranges from 0.0001 to 5 wt.%, 0.00025 to 2 wt.%, or 0.0005 to 1 wt.%.

10. The chemical mechanical planarization composition of Claim 8, wherein the abrasive is silica particles.

11. The chemical mechanical planarization composition of Claim 8, wherein the oxidizing agent is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

12. The chemical mechanical planarization composition of Claim 8, wherein the activator is selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and

ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof .

13. The chemical mechanical planarization composition of Claim 8, wherein the corrosion inhibitor is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate such as 1,3,5-Tris(2-hydroxyethyl), and combinations thereof.

14. The chemical mechanical planarization composition of Claim 8, wherein the pH adjusting agent is 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 mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH; wherein pH of the composition is between 1 and 14, 1 and 7, 1 and 6, or 1.5 and 4

15. The chemical mechanical planarization composition of Claim 8, wherein the dishing reducing agent is selected from the group consisting of sarcosinate and related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units, such as polyethylene oxide (PEO); ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds; sulfide; oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; and sulfonic acid polymer; and combinations thereof.

16. The chemical mechanical planarization composition of Claim 8, wherein the stabilizer is selected from the group consisting of adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; phosphoric acid; substituted or unsubstituted phosphonic acids; nitriles; and combinations thereof.

17. The chemical mechanical planarization composition of Claim 8, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate, malonic acid, hydrogen peroxide, a cationic polymer or copolymer selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide, and combinations thereof; and water; the pH of the composition is between 1.5 and 4.

18. A polishing method for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing tungsten, comprising the steps of:

a) providing a polishing pad;

b) providing a chemical mechanical planarization composition comprising:

an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;

an activator;

an oxidizing agent;

an additive comprising the cationic polymer or copolymer of any one of claims 1 to 7;

water; and optionally

a corrosion inhibitor;

a dishing reducing agent;

a stabilizer;

a pH adjusting agent; and

c) polishing the at least one surface containing tungsten with the chemical mechanical planarization composition.

19. The polishing method of Claim 18, wherein the chemical mechanical planarization composition has
the abrasive ranging from 0.01 wt.% to 30 wt.%, 0.05 wt.% to 20 wt.%, 0.01 wt.% to 10 wt.%, or from 0.1 wt.% to 2 wt.%;
the additive ranges from 0.00001 wt.% to 0.05 wt.%, 0.0001 wt.% to 0.025 wt., 0.0002wt.% to 0.02 wt.%, or 0.0001 wt.% to 0.01 wt.%;
the oxidizing agent ranges from 0.01 wt.% to 30 wt.%, 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%;
the activator ranges from 0.00001 wt.% to 5.0 wt.%, 0.0001 wt.% to 2.0 wt.%, 0.0005 wt.% to 1.0 wt.%, or 0.001 wt.% to 0.5 wt.%;
the corrosion inhibitor ranges from less than 1.0 wt.%, less than 0.5 wt.%, or less than 0.25 wt.%;
the dishing reducing agent ranges from 0.001 wt.% to 2.0 wt. %, 0.005 wt.% to 1.5 wt. %, or 0.01 wt.% to 1.0 wt. %; and
the stabilizer ranges from 0.0001 to 5 wt.%, 0.00025 to 2 wt.%, or 0.0005 to 1 wt.%.

20. The polishing method of Claim 18, wherein the chemical mechanical planarization composition has silica particles as the abrasive.

21. The polishing method of Claim 18, wherein the oxidizing agent in the chemical mechanical planarization composition is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

22. The polishing method of Claim 18, wherein the activator in the chemical mechanical planarization composition is selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof;

(2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof.

23. The polishing method of Claim 18, wherein the corrosion inhibitor in the chemical mechanical planarization composition is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate such as 1,3,5-Tris(2-hydroxyethyl), and combinations thereof.

24. The polishing method of Claim 18, wherein the pH adjusting agent in the chemical mechanical planarization composition is 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 mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH; wherein pH of the composition is between 1 and 14, 1 and 7, 1 and 6, or 1.5 and 4.

25. The polishing method of Claim 18, wherein the dishing reducing agent in the chemical mechanical planarization composition is selected from the group consisting of sarcosinate and related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units, such as polyethylene oxide (PEO); ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds; sulfide; oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or

a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; and sulfonic acid polymer; and combinations thereof.

26. The polishing method of Claim 18, wherein the stabilizer in the chemical mechanical planarization composition is selected from the group consisting of adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; phosphoric acid; substituted or unsubstituted phosphonic acids; nitriles; and combinations thereof.

27. The polishing method of Claim 18, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; a cationic polymer or copolymer selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide, and combinations thereof; and water; the pH of the composition is between 1.5 and 4.

28. The polishing method of Claim 20, wherein the at least one surface containing tungsten comprises a dishing topography of less than 2000 or less than 1000 Angstroms and an erosion topography of less than 2000 or less than 1000 Angstroms.

29. A system for chemical mechanical planarization of a semiconductor substrate comprising at least one surface containing tungsten, comprising:
a) a polishing pad; and
b) a chemical mechanical planarization composition comprising:
an abrasive selected from the group consisting of inorganic oxide particles, metal oxide-coated inorganic oxide particles, organic polymer particles, metal oxide-coated organic polymer particles, and combinations thereof;
an activator;
an oxidizing agent;

an additive comprising the cationic polymer or copolymer of any one of claims 1 to 7;
water; and optionally
a corrosion inhibitor;
a dishing reducing agent;
a stabilizer;
a pH adjusting agent; and
wherein the at least one surface containing tungsten is in contact with the polishing pad and the chemical mechanical planarization composition polishing the at least one surface containing tungsten with the chemical mechanical planarization composition.

30. The system of claim 29, wherein the chemical mechanical planarization composition has
the abrasive ranging from 0.01 wt.% to 30 wt.%, 0.05 wt.% to 20 wt.%, 0.01 wt.% to 10 wt.%, or from 0.1 wt.% to 2 wt.%;
the additive ranges from 0.00001 wt.% to 0.05 wt.%, 0.0001 wt.% to 0.025 wt., 0.0002wt.% to 0.02 wt.%, or 0.0001 wt.% to 0.01 wt.%;
the oxidizing agent ranges from 0.01 wt.% to 30 wt.%, 0.1 wt.% to 20 wt.%, or 0.5 wt.% to 10 wt.%;
the activator ranges from 0.00001 wt.% to 5.0 wt.%, 0.0001 wt.% to 2.0 wt.%, 0.0005 wt.% to 1.0 wt.%, or 0.001 wt.% to 0.5 wt.%;
the corrosion inhibitor ranges from less than 1.0 wt.%, less than 0.5 wt.%, or less than 0.25 wt.%;
the dishing reducing agent ranges from 0.001 wt.% to 2.0 wt. %, 0.005 wt.% to 1.5 wt. %, or 0.01 wt.% to 1.0 wt. %; and
the stabilizer ranges from 0.0001 to 5 wt.%, 0.00025 to 2 wt.%, or 0.0005 to 1 wt.%.

31. The system of claim 29, wherein the chemical mechanical planarization composition has silica particles as the abrasive.

32. The system of claim 29, wherein the oxidizing agent in the chemical mechanical planarization composition is selected from the group consisting of peroxy compound selected from the group consisting of hydrogen peroxide, urea peroxide, peroxyformic acid, peracetic acid, propaneperoxoic acid, substituted or unsubstituted

butaneperoxoic acid, hydroperoxy-acetaldehyde, potassium periodate, ammonium peroxymonosulfate; and non-per-oxy compound selected from the group consisting of ferric nitrite, $KClO_4$, $KBrO_4$, $KMnO_4$; and combinations thereof.

33. The system of claim 29, wherein the activator in the chemical mechanical planarization composition is selected from the group consisting of (1) inorganic oxide particle with transition metal coated onto its surface; and the transition metal is selected from the group consisting of Fe, Cu, Mn, Co, Ce, and combinations thereof; (2)soluble catalyst selected from the group consisting of iron (III) nitrate, ammonium iron (III) oxalate trihydrate, iron(III) citrate tribasic monohydrate, iron(III) acetylacetonate and ethylenediamine tetraacetic acid, iron (III) sodium salt hydrate;(3) a metal compound having multiple oxidation states selected from the group consisting of Ag, Co, Cr, Cu, Fe, Mo, Mn, Nb, Ni, Os, Pd, Ru, Sn, Ti, V; and combinations thereof.

34. The system of claim 29, wherein the corrosion inhibitor in the chemical mechanical planarization composition is selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, 1,2,3-benzotriazole, 5-methylbenzotriazole, benzotriazole, 1-hydroxybenzotriazole, 4-hydroxybenzotriazole, 3-amino-1,2,4-triazole, 4-amino-4H-1,2,4-triazole, 5 amino triazole, benzimidazole, 2,1,3-benzothiadiazole, triazinethiol, triazinedithiol, and triazinetrithiol, pyrazoles, imidazoles, isocyanurate such as 1,3,5-Tris(2-hydroxyethyl), and combinations thereof.

35. The system of claim 29, wherein the pH adjusting agent in the chemical mechanical planarization composition is 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 mixtures thereof to lower the pH; and (b) potassium hydroxide, sodium hydroxide, ammonia, tetraethylammonium hydroxide, ethylenediamine, piperazine, polyethyleneimine, modified polyethyleneimine, and mixtures thereof to raise the pH; wherein pH of the composition is between 1 and 14, 1 and 7, 1 and 6, or 1.5 and 4.

36. The system of claim 29, wherein the dishing reducing agent in the chemical mechanical planarization composition is selected from the group consisting of

sarcosinate and related carboxylic compounds; hydrocarbon substituted sarcosinate; amino acids; organic polymers and copolymers having molecules containing ethylene oxide repeating units, such as polyethylene oxide (PEO); ethoxylated surfactants; nitrogen containing heterocycles without nitrogen-hydrogen bonds; sulfide; oxazolidine or mixture of functional groups in one compound; nitrogen containing compounds having three or more carbon atoms that form alkylammonium ions; amino alkyls having three or more carbon atoms; polymeric corrosion inhibitor comprising a repeating group of at least one nitrogen-containing heterocyclic ring or a tertiary or quaternary nitrogen atom; polycationic amine compound; cyclodextrin compound; polyethyleneimine compound; glycolic acid; chitosan; sugar alcohols; polysaccharides; alginate compound; and sulfonic acid polymer; and combinations thereof.

37. The system of claim 29, wherein the stabilizer in the chemical mechanical planarization composition is selected from the group consisting of adipic acid, phthalic acid, citric acid, malonic acid, orthophthalic acid; phosphoric acid; substituted or unsubstituted phosphonic acids; nitriles; and combinations thereof.

38. The system of claim 29, wherein the chemical mechanical planarization composition comprises silica particles; iron (III) nitrate; malonic acid; hydrogen peroxide; a cationic polymer or copolymer selected from the group consisting of poly tributyl(4-vinylbenzyl)phosphonium chloride, poly tributyl(4-vinylbenzyl)phosphonium-co-acrylamide chloride (Copolymer), poly tributyl(4-vinylbenzyl)phosphonium-co-*N*-methylmaleimide chloride (Copolymer), poly(4-vinylphenol-co-triphenyl(4-(4-vinylphenoxy)butyl) phosphonium) bromide, poly(4-(butyldiphenylphosphino) butyl)dipenylphosphonium) bromide, poly(PEG5-diphenylphosphino)butyl)dipenylphosphonium) bromide, and combinations thereof; and water; the pH of the composition is between 1.5 and 4.

39. The system of claim 29, wherein the at least one surface containing tungsten comprises a dishing topography of less than 2000 or less than 1000 Angstroms and an erosion topography of less than 2000 or less than 1000 Angstroms.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2022/072760

A. CLASSIFICATION OF SUBJECT MATTER

C08F 30/02(2006.01)i; **C08G 79/06**(2006.01)i; **C09G 1/02**(2006.01)i; **C09K 3/14**(2006.01)i; **H01L 21/304**(2006.01)i; **H01L 21/768**(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F 30/02(2006.01); C09G 1/02(2006.01); C09K 3/00(2006.01); C09K 3/14(2006.01); H01L 21/304(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal), STN(Registry, Caplus), Google & keywords: cationic polymer, chemical-mechanical planarization(CMP), abrasive, activator, oxidizer, water, corrosion inhibitor, dishing reducing agent, stabilizer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 5439617 A (AKHAVAN-TAFTI, H.) 08 August 1995 (1995-08-08)	
X	columns 11, 14	1,3,5,6
Y		8-39
A		2,4,7
	JANGU, C. et al., "Phosphonium cation-containing polymers: From ionic liquids to polyelectrolytes", Polymer, 2014, Vol. 55, No. 16, pp. 3298-3304	
X	pages 3300, 3301; figures 4, 7, 12	1-5,7
	KANAZAWA, A. et al., "Polymeric phosphonium salts as a novel class of cationic biocides. II. Effects of counter anion and molecular weight on antibacterial activity of polymeric phosphonium salts", Journal of polymer science part A: polymer chemistry, 1993, Vol. 31, No. 6, pp. 1441-1447	
X	pages 1442, 1443	1-3,5-7

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 September 2022	**20 September 2022**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office **189 Cheongsa-ro, Seo-gu, Daejeon** **35208, Republic of Korea**	**HEO, Joo Hyung**
Facsimile No. **+82-42-481-8578**	Telephone No. **+82-42-481-5373**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2021-011196 A1 (CABOT MICROELECTRONICS CORPORATION) 21 January 2021 (2021-01-21) paragraphs [0003], [0005], [0058]-[0061], [0065]-[0068], [0072]; claims 1, 13-20, 28 Y: 8-39	8-39
Y	WO 2006-052433 A2 (CABOT MICROELECTRONICS CORPORATION) 18 May 2006 (2006-05-18) paragraph [0015]; claims 1-6, 14-24, 35, 36	8-39
X	HEMP, S. T. et al., "Phosphonium ionenes from well-defined step-growth polymerization: Thermal and melt rheological properties", Polymer chemistry, 2013, Vol. 4, No. 12, pp. 3582-3590. abstract; scheme 1	1,6,7

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2022/072760

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
US 5439617 A	08 August 1995	EP 0561033 A1	22 September 1993
		EP 0561033 B1	15 March 2000
		JP 05-287267 A	02 November 1993
		JP 09-136923 A	27 May 1997
		JP 2648423 B2	27 August 1997
		JP 3471530 B2	02 December 2003
		US 5393469 A	28 February 1995
		US 5431845 A	11 July 1995
		US 5474725 A	12 December 1995
		US 5582775 A	10 December 1996
WO 2021-011196 A1	21 January 2021	CN 114127211 A	01 March 2022
		EP 3999605 A1	25 May 2022
		KR 10-2022-0034854 A	18 March 2022
		TW 202111076 A	16 March 2021
		US 2021-0017421 A1	21 January 2021
WO 2006-052433 A2	18 May 2006	CN 101065458 A	31 October 2007
		CN 101065458 B	05 September 2012
		CN 102046743 A	04 May 2011
		CN 102046743 B	31 October 2012
		EP 1831321 A2	12 September 2007
		EP 1831321 B1	24 June 2015
		IL 182797 A	31 August 2011
		JP 2008-519466 A	05 June 2008
		JP 2009-518855 A	07 May 2009
		JP 5102040 B2	19 December 2012
		JP 5188980 B2	24 April 2013
		KR 10-1117401 B1	29 February 2012
		KR 10-1309324 B1	16 September 2013
		KR 10-2007-0085738 A	27 August 2007
		KR 10-2008-0078818 A	28 August 2008
		MY 149519 A	13 September 2013
		MY 160422 A	15 March 2017
		SG 157354 A1	29 December 2009
		TW 200630472 A	01 September 2006
		TW 200732460 A	01 September 2007
		TW I323274 B	11 April 2010
		TW I347356 B	21 August 2011
		US 2006-0099814 A1	11 May 2006
		US 2006-0108326 A1	25 May 2006
		US 2009-0137124 A1	28 May 2009
		US 2009-0215271 A1	27 August 2009
		US 7504044 B2	17 March 2009
		US 7531105 B2	12 May 2009
		US 7846842 B2	07 December 2010
		US 8138091 B2	20 March 2012
		WO 2006-052433 A3	31 August 2006
		WO 2007-067294 A2	14 June 2007
		WO 2007-067294 A3	28 July 2011