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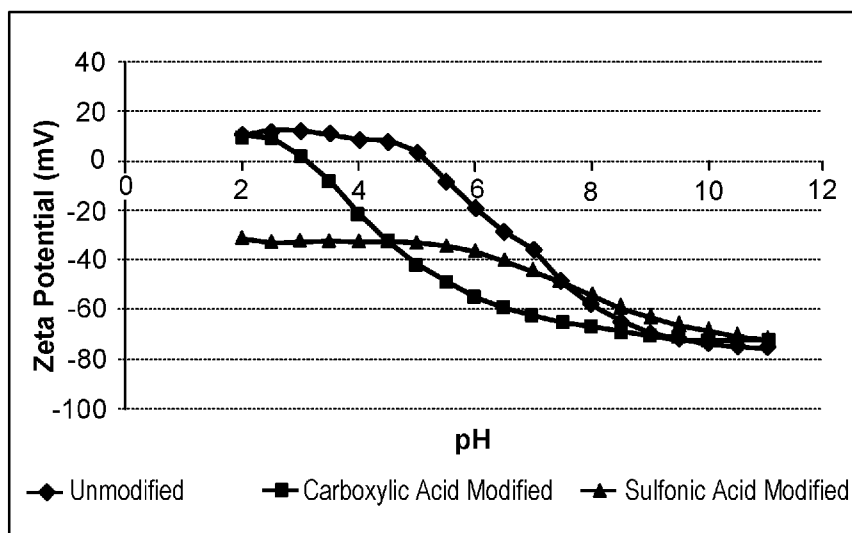


FIG. 1

(57) Abstract: A polishing composition includes an anionic abrasive, a pH adjuster a low-k removal rate inhibitor, a ruthenium removal rate enhancer, and water. A method of polishing a substrate includes the steps of: applying the polishing composition described herein to a surface of a substrate, wherein the surface comprises ruthenium or a hard mask material; and bringing a pad into contact with the surface of the substrate and moving the pad in relation to the substrate.



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POLISHING COMPOSITIONS AND METHODS OF USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims priority to U.S. Provisional Application Serial No. 63/272,719, filed on October 28, 2021, the contents of which are hereby incorporated by
5 reference in their entirety.

BACKGROUND

The semiconductor industry is continually driven to improve chip performance by further miniaturization of devices by process, materials, and integration innovations. Earlier materials innovations included the introduction of copper, replacing aluminum as the conductive material
10 in the interconnect structure, and the use of tantalum (Ta)/tantalum nitride (TaN) as diffusion barrier to separate the Cu conductive material from the non-conductive/insulator dielectric material. Copper (Cu) was chosen as the interconnect material because of its low resistivity and superior resistance against electro-migration.

15 However, as the features of newer generation chips shrink, the multilayer Cu/barrier/dielectric stacks have to be thinner and more conformal to maintain effective interconnect resistivity in Back End of Line (BEOL). The thinner Cu and the Ta/TaN barrier film schemes present problems with resistivity and flexibility in deposition. For example, with
20 smaller dimensions and advanced manufacturing nodes, resistivity is proceeding to be exponentially worse and improvements in transistor circuit speed (at Front End of Line (FEOL)) are being cut in half by the delay coming from the conductive Cu/Barrier wiring (BEOL). Ruthenium (Ru) has emerged as a leading candidate for use as a liner material, a barrier layer, as well as a conductive layer. Ruthenium has superior anti-Cu diffusion to dielectric layers, but also can facilitate direct copper electro-filling in small dimension trenches without using a
25 copper seed layer. Furthermore, ruthenium is also being investigated as a material for VIAs to replace conventional tungsten (W) metal.

SUMMARY

This summary is provided to introduce a selection of concepts that are further described below in the detailed description. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used as an aid in limiting the scope of the claimed subject matter.

As defined herein, unless otherwise noted, all percentages expressed should be understood to be percentages by weight to the total weight of a polishing composition.

In one aspect, this disclosure features a polishing composition that includes a polishing composition that includes (1) an anionic silica abrasive, wherein the anionic silica abrasive includes terminal groups of formula (I): $-\text{O}_m\text{-Si}-(\text{CH}_2)_n\text{-CH}_3$ (I), in which m is an integer from 1 to 3; n is an integer from 0 to 10; and the $-(\text{CH}_2)_n\text{-CH}_3$ group is substituted by at least one carboxylic acid group; (2) a pH adjuster; (3) a low-k removal rate inhibitor; (4) a ruthenium removal rate enhancer; and (5) water. The polishing composition has a pH of about 7 to about 14.

In another aspect, this disclosure features a method of polishing a substrate, including the steps of: applying the polishing composition described herein to a surface of a substrate, wherein the surface comprises ruthenium or a hard mask material; and bringing a pad into contact with the surface of the substrate and moving the pad in relation to the substrate.

Other aspects and advantages of the claimed subject matter will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot showing the change in Zeta Potential as the pH is changed for aqueous dispersions containing three different types of silica abrasives.

FIG. 2 is a plot showing the change in the mean particle size (MPS) over time for aqueous dispersions containing unmodified silica, cationic modified silica, sulfonic acid modified silica, and carboxylic acid modified silica.

DETAILED DESCRIPTION

5 Embodiments disclosed herein relate generally to compositions and methods of using said compositions to polish substrates that include at least a ruthenium portion and/or a hard mask portion (e.g., tungsten, carbide, nitride ceramic (e.g., TiN), and doped derivatives thereof) and can, more specifically, include at least ruthenium, hard mask, and copper portions. The compositions disclosed herein can effectively remove ruthenium, copper and/or hard mask
10 materials while minimizing copper corrosion (e.g., minimizing surface roughness). For example, the compositions disclosed herein can be particularly useful for polishing advanced node films that include copper, a ruthenium liner, a hard mask material (e.g., titanium and doped derivatives thereof, tungsten and doped derivatives thereof (e.g., WB₄), carbides (e.g., BC, B₄C, TiC, SiC, and WC), boron-containing materials (e.g., B₂O, BC₂N, and AlMgB₁₄), and nitride ceramic
15 materials (e.g., SiN, TiN, BN), barrier materials (e.g., Ta, TaN), and dielectric materials (e.g., TEOS, low-k, ultra low-k, etc.). In some embodiments, the compositions disclosed herein can remove copper at a relatively high removal rate while minimizing copper corrosion (e.g., minimizing surface roughness).

20 Many currently available CMP slurries were specifically designed to remove materials more common in older chip designs, such as the aforementioned copper and tungsten. However, in back-end-of-line (BEOL) applications in the semiconductor industry, ruthenium is finding use as a liner material because it has favorable electrical conductivity, deposition properties, and is resistant to Cu diffusion. Unlike some other materials, such as cobalt and copper, ruthenium is
25 relatively chemically stable and thus does not deteriorate and can be hard to remove during polishing. Further, ruthenium is often used in conjunction with copper being the conductive layer. As mentioned above, copper is a relatively soft material and thus easy to remove. Copper is essential to the function of many semiconductor devices, so if a CMP slurry is used that too easily strips away or damages copper layers or inlays, it can adversely affect the performance of

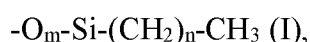
the finished device. Older CMP slurries may not be able to effectively remove ruthenium without also causing deleterious and unacceptable defects in copper, since copper is more susceptible to chemical corrosion. As a result, less advanced slurries may present unacceptable corrosion, wafer topography, and/or removal rate selectivity with respect to one or more components of the multicomponent substrate to be polished. Furthermore, more complex integration schemes may use a hard mask as an etch mask in conjunction with the Ru liner and Cu conductive layer and this presents yet another material that the polishing slurry needs to be capable of effectively removing.

10 With the increasing use and shrinking size of multicomponent integration schemes in semiconductor fabrication, there is a market need for CMP slurries that can effectively polish a substrate that includes ruthenium, copper, and a hard mask material with minimal copper corrosion but favorable removal rates and selectivity for all other components.

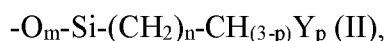
15 In one or more embodiments, the polishing composition described herein includes an anionic silica abrasive, a pH adjuster, a low-k removal rate inhibitor, a ruthenium removal rate enhancer, and water. In one or more embodiments, the polishing composition can optionally include a barrier film removal rate enhancer, an azole-containing corrosion inhibitor, a chelating agent and/or an oxidizing agent. In one or more embodiments, a polishing composition
20 described herein can include from about 0.1% to about 50% by weight abrasive, from about 0.0001% to about 30% by weight pH adjuster, from about 0.0005% to about 5% by weight low-k removal rate inhibitor, from about 0.0001% to about 5% by weight ruthenium removal rate enhancer, and the remaining percent by weight (e.g., from about 20% to about 99% by weight) of solvent (e.g., deionized water). In one or more embodiments, the polishing composition can
25 further include from about 0.002% to about 4% by weight barrier film rate removal enhancer, from about 0.0001% to about 1% by weight azole-containing corrosion inhibitor, from about 0.001% to about 1% by weight chelating agent, and/or from about 0.001% to about 5% by weight oxidizing agent.

In one or more embodiments, the present disclosure provides a concentrated polishing composition that can be diluted with water prior to use by up to a factor of two, or up to a factor of four, or up to a factor of six, or up to a factor of eight, or up to a factor of ten. In other embodiments, the present disclosure provides a point-of-use (POU) polishing composition for use on ruthenium containing substrates, comprising the above-described polishing composition, water, and optionally an oxidizing agent.

In one or more embodiments, the polishing composition described herein can include at least one (e.g., two or three) anionic silica abrasive. In one or more embodiments, the at least one anionic silica abrasive can include one or more (e.g., two or three) terminal groups of formula (I):



in which m is an integer from 1 to 3; n is an integer from 0 to 10; and the $-(\text{CH}_2)_n\text{-CH}_3$ group is substituted by at least one (e.g., two, three, or four) carboxylic acid group. In some embodiments, the substitution by the carboxylic group(s) can be at a middle carbon and/or at the terminal carbon of the $-(\text{CH}_2)_n\text{-CH}_3$ group. In some embodiments, the terminal group can be of formula (II):



in which m is an integer from 1 to 3; n is an integer from 0 to 10; p is an integer from 1 to 3; and Y is a carboxylic acid group

In some embodiments, the at least one anionic silica abrasive is high-purity, and can have less than about 100 ppm of alcohol, less than about 100 ppm of ammonia, and less than about 100 parts per billion (ppb) of an alkali cation such as sodium cation. Without wishing to be bound by theory, it is believed that the anionic silica abrasive containing a carboxylic acid group can significantly reduce defects formed on a semiconductor substrate polished by a polishing composition.

In one or more embodiments, the abrasive described herein can have a mean particle size of from at least about 1 nm (e.g., at least about 5 nm, at least about 10 nm, at least about 20 nm,

at least about 40 nm, at least about 50 nm, at least about 60 nm, at least about 80 nm, or at least about 100 nm) to at most about 1000 nm (e.g., at most about 800 nm, at most about 600 nm, at most about 500 nm, at most about 400 nm, at most about 200 nm, or at most about 150 nm). As used herein, the mean particle size (MPS) is determined by dynamic light scattering techniques.

5 In one or more embodiments, the abrasive can be particles of a single chemical species (e.g., silica particles) and the polishing composition may not include abrasives that are composites of two or more materials (e.g., silica particles embedded in a ceramic matrix).

In one or more embodiments, the at least one anionic silica abrasive is in an amount of
10 from at least about 0.1% (e.g., at least about 0.5%, at least about 1%, at least about 2%, at least about 4%, at least about 5%, at least about 10%, at least about 12%, at least about 15%, or at least about 20%) by weight to at most about 50% (e.g., at most about 45%, at most about 40%, at most about 35%, at most about 30%, at most about 25%, at most about 20%, at most about 15%, at most about 12%, at most about 10%, or at most about 5%) by weight of the polishing
15 composition described herein.

In one or more embodiments, the polishing composition described herein can include at least one (e.g., two or three) pH adjuster or pH adjusting agent. In some embodiments, the at least one pH adjuster is selected from the group consisting of formic acid, acetic acid, malonic
20 acid, citric acid, propionic acid, malic acid, adipic acid, succinic acid, lactic acid, oxalic acid, peracetic acid, potassium acetate, phenoxyacetic acid, benzoic acid, nitric acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphonic acid, hydrochloric acid, periodic acid, lithium hydroxide, potassium hydroxide, sodium hydroxide, cesium hydroxide, ammonium hydroxide, triethanolamine, diethanolamine, monoethanolamine, methylethanolamine,
25 methyldiethanolamine, tetrabutylammonium hydroxide, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetramethylammonium hydroxide, ethyltrimethylammonium hydroxide, diethyldimethylammonium hydroxide, dimethyldipropylammonium hydroxide, benzyltrimethylammonium hydroxide, tris(2-hydroxyethyl)methylammonium hydroxide, choline hydroxide, and mixtures thereof. In one or more embodiments, the pH adjuster is a
30 monocarboxylic acid, a dicarboxylic acid, or a tricarboxylic acid.

In one or more embodiments, the at least one pH adjuster is in an amount of from at least about 0.0001% (e.g., at least about 0.0005%, at least about 0.001%, at least about 0.005%, at least about 0.01%, at least about 0.05%, at least about 0.1%, at least about 0.5%, at least about 1%, at least about 2%, at least about 4%, at least about 5%, at least about 6%, or at least about 8%) by weight to at most about 30% (e.g., at most about 25%, at most about 20%, at most about 15%, at most about 10%, at most about 9%, at most about 8%, at most about 7%, at most about 6%, at most about 5%, at most about 4%, at most about 3%, at most about 2%, at most about 1%, at most about 0.5%, at most about 0.2%, or at most about 0.1%) by weight of the polishing composition described herein.

In one or more embodiments, the pH value of the polishing composition can range from at least about 7 (e.g., at least about 7.5, at least about 8, at least about 8.5, at least about 9, at least about 9.5, at least about 10, at least about 10.5, at least about 11, at least about 11.5, or at least about 12) to at most about 14 (e.g., at most about 13.5, at most about 13, at most about 12.5, at most about 12, at most about 11.5, at most about 11, at least about 10.5, at most about 10, at most about 9.5, or at most about 9). Without wishing to be bound by theory, it is believed that a polishing composition having a pH lower than 7 would significantly increase copper removal rate and corrosion, and a polishing composition having a pH higher than 14 would affect the stability of the suspended abrasive and would significantly increase the roughness and decrease the overall quality of a film polished by such a composition.

In one or more embodiments, the polishing composition described herein can include at least one (e.g., two or three) low-k removal rate inhibitor. In some embodiments, the at least one low-k removal rate inhibitor is a nonionic surfactant. In one or more embodiments, the nonionic surfactant is selected from the group consisting of alcohol alkoxylates, alkylphenol alkoxylates, tristyrylphenol alkoxylates, sorbitan ester alkoxylates, polyalkoxylates, polyalkylene oxide block copolymers, alkoxylated diamines, and mixtures thereof. In one or more embodiments, the nonionic surfactant does not include an alkylphenol alkoxylate. In one or more embodiments, the nonionic surfactant is a polymer having a number average molecular weight of at least about 500

g/mol, or at least about 1,000 g/mol, or at least about 2,500 g/mol, or at least about 5,000 g/mol, or at least about 7,500 g/mol, or at least about 10,000 g/mol. In one or more embodiments, the nonionic surfactant is a polymer having a number average molecular weight of at most about 1,000,000 g/mol, or at most about 750,000 g/mol, or at most about 500,000 g/mol, or at most about 250,000 g/mol, or at most about 100,000 g/mol. In one or more embodiments, the alkoxy groups of the alkoxyated nonionic surfactants are ethoxy, propoxy, or a combination of ethoxy and propoxy groups. Without wishing to be bound by theory, it is surprising that a nonionic surfactant (such as those described above) can be used as a low-k removal rate inhibitor in the polishing composition described herein to reduce or minimize the removal rate of a low-k film (e.g., a carbon doped silicon oxide film) in a semiconductor substrate.

In one or more embodiments, the low-k removal rate inhibitor is in an amount of from at least about 0.0005% (e.g., at least about 0.001%, at least about 0.005%, at least about 0.01%, at least about 0.05%, at least about 0.1%, at least about 0.5%, at least about 1%, at least about 1.5%, at least about 2%, or at least about 3%) by weight to at most about 5% (e.g., at most about 4.5%, at most about 4%, at most about 3.5%, at most about 3%, at most about 2.5%, at most about 2%, at most about 1.5%, at most about 1%, at most about 0.5%, or at most about 0.1%) by weight of the polishing composition described herein.

In one or more embodiments, the polishing composition described herein can include at least one (e.g., two or three) ruthenium removal rate enhancer. In some embodiments, the at least one ruthenium removal rate enhancer can include ammonium hydroxide or its salts, thiocyanate salts, nitric acid or its salts, and/or halide salts. In some embodiments, the at least one ruthenium removal rate enhancer is selected from the group consisting of ammonium hydroxide, ammonium chloride, ammonium fluoride, ammonium bromide, ammonium sulfate, ammonium carbonate, ammonium hydrogen carbonate, ammonium nitrate, ammonium phosphate, ammonium acetate, ammonium thiocyanate, potassium thiocyanate, sodium thiocyanate, sulfuric acid, sulfurous acid, phosphoric acid, phosphonic acid, hydrochloric acid, periodic acid, nitric acid, sodium nitrate, potassium nitrate, rubidium nitrate, cesium nitrate,

sodium fluoride, potassium fluoride, rubidium fluoride, cesium fluoride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride, and mixtures thereof.

In one or more embodiments, the ruthenium removal rate enhancer is in an amount of
5 from about 0.0001% to about 5% by weight of the composition. In one or more embodiments, the ruthenium removal rate enhancer is at least about 0.0001% (e.g., at least about 0.0002%, at least about 0.0005%, at least about 0.001%, at least about 0.002%, at least about 0.005%, at least about 0.01%, at least about 0.02%, at least about 0.05%, at least about 0.1%, at least about 0.2%, or at least about 0.5%) by weight to at most about 5% (e.g., at most about 4%, at most about 3%,
10 at most about 2%, at most about 1%, at most about 0.8%, at most about 0.6%, at most about 0.5%, at most about 0.4%, at most about 0.2%, at most about 0.1%, at most about 0.05%, at most about 0.02%, at most about 0.01%, or at most about 0.005%) by weight of the polishing composition described herein.

15 In one or more embodiments, the polishing composition described herein can optionally include at least one (e.g., two or three) barrier film removal rate enhancer. In some embodiments, the at least one barrier film removal rate enhancer is an organic acid (such as a carboxylic acid, an amino acid, a sulfonic acid, or a phosphonic acid) or a salt thereof. In some
20 embodiments, the barrier film removal rate enhancer can be an organic acid or a salt thereof selected from the group consisting of gluconic acid, lactic acid, citric acid, tartaric acid, malic acid, glycolic acid, malonic acid, formic acid, oxalic acid, acetic acid, propionic acid, peracetic acid, succinic acid, lactic acid, amino acetic acid, phenoxyacetic acid, bicine, diglycolic acid, glyceric acid, tricine, alanine, histidine, valine, phenylalanine, proline, glutamine, aspartic acid, glutamic acid, arginine, lysine, tyrosine, benzoic acid, salts thereof, and mixtures thereof. In
25 some embodiments, if the polishing composition described herein includes both a barrier film removal rate enhancer and a pH adjuster (or other acidic materials such as a chelating agent or an amino acid), the barrier film removal rate enhancer is different from the pH adjuster (or the other acidic materials). Without wishing to be bound by theory, it is believed that an organic acid or a salt thereof (such as those described above) can be used as an effective barrier removal rate

enhancer in the polishing composition described herein to improve the removal rate of a barrier film (e.g., a Ta or TaN film) in a semiconductor substrate.

In one or more embodiments, the barrier film rate removal rate enhancer is in an amount of from at least about 0.002% (e.g., at least about 0.005%, at least about 0.01%, at least about 0.05%, at least about 0.1%, at least about 0.15%, at least about 0.2%, at least about 0.5%, at least about 1%, at least about 1.5%, or at least about 2%) by weight to at most about 4% (e.g., at most about 3.5%, at most about 3%, at most about 2.5%, at most about 2%, at most about 1.5%, or at most about 1%) by weight of the polishing composition described herein.

In one or more embodiments, the polishing composition described herein can optionally include at least one (e.g., two or three) azole-containing corrosion inhibitor. In some embodiments, the at least one azole-containing corrosion inhibitor is selected from the group consisting of substituted or unsubstituted triazoles, substituted or unsubstituted tetrazoles, substituted or unsubstituted benzotriazoles, substituted or unsubstituted pyrazoles, and substituted or unsubstituted imidazoles. In some embodiments, suitable substituents include halo (e.g., F, Cl, Br, or I), amino, aryl, or C₁-C₆ alkyl optionally substituted by aryl. In one or more embodiments, the azole-containing corrosion inhibitor can be selected from the group consisting of 1,2,4-triazole, 1,2,3-triazole, tetrazole, benzotriazole, tolyltriazole, methyl benzotriazole (e.g., 1-methyl benzotriazole, 4-methyl benzotriazole, and 5-methyl benzotriazole), ethyl benzotriazole (e.g., 1-ethyl benzotriazole), propyl benzotriazole (e.g., 1-propyl benzotriazole), butyl benzotriazole (e.g., 1-butyl benzotriazole and 5-butyl benzotriazole), pentyl benzotriazole (e.g., 1-pentyl benzotriazole), hexyl benzotriazole (e.g., 1-hexyl benzotriazole and 5-hexyl benzotriazole), dimethyl benzotriazole (e.g., 5,6-dimethyl benzotriazole), chloro benzotriazole (e.g., 5-chloro benzotriazole), dichloro benzotriazole (e.g., 5,6-dichloro benzotriazole), chloromethyl benzotriazole (e.g., 1-(chloromethyl)-1-H-benzotriazole), chloroethyl benzotriazole, phenyl benzotriazole, benzyl benzotriazole, aminotriazole, aminobenzimidazole, aminotetrazole, isothiazole, and mixtures thereof. In one or more embodiments, the polishing composition can include both benzotriazole and a benzotriazole derivative (e.g., a substituted benzotriazole). Without wishing to be bound by theory, it is believed that an azole-containing

corrosion inhibitor (such as those described above) can significantly reduce or minimize the removal rate of copper in a semiconductor substrate.

In one or more embodiments, the azole-containing corrosion inhibitor is in an amount of
5 from at least about 0.0001% (e.g., at least about 0.0002%, at least about 0.0005%, at least about 0.001%, at least about 0.002%, at least about 0.005%, at least about 0.01%, at least about 0.02%, at least about 0.05%, at least about 0.1%, at least about 0.2%, or at least about 0.5%) by weight to at most about 1% (e.g., at most about 0.8%, at most about 0.6%, at most about 0.5%, at most about 0.4%, at most about 0.2%, at most about 0.1%, at most about 0.05%, at most about 0.02%,
10 at most about 0.01%, or at most about 0.005%) by weight of the polishing composition described herein.

In one or more embodiments, the polishing composition described herein can optionally include at least one (e.g., two or three) chelating agent. In some embodiments, the at least one
15 optional chelating agent can be an amino-containing carboxylic acid (e.g., a polyaminopolycarboxylic acid) or a phosphonic acid. In some embodiments, the chelating agent is selected from the group consisting of ethylenediaminetetracetic acid, iminodiacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid, nitrilotriacetic acid, diethylenetriaminepentacetic acid, hydroxyethylethylenediaminetriacetic acid, triethylenetetraaminehexaacetic acid,
20 diaminocyclohexanetetraacetic acid, nitrilotrimethylphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), 1-hydroxyl ethylidene-1,1,-diphosphonic acid, diethylenetriamine penta (methylene phosphonic acid), hydroxyethylidene diphosphonic acid, 2-phosphono-1,2,4-butane tricarboxylic acid, aminotrimethylene phosphonic acid, hexamethylenediamine tetra(methylenephosphonic acid), bis(hexamethylene)triamine
25 phosphonic acid, amino acetic acid, and combinations thereof. In some embodiments, if the polishing composition described herein includes both a chelating agent and a pH adjuster (or other acidic materials such as a barrier film removal rate enhancer or an amino acid), the chelating agent is different from the pH adjuster (or the other acidic materials). Without wishing to be bound by theory, it is believed that including a chelating agent (such as those described
30 above) in the polishing composition described herein can significantly reduce or minimize the

observed defects on a semiconductor substrate (such as the defects on a surface of a copper wafer).

In one or more embodiments, the chelating agent is in an amount of from at least about
5 0.001% (e.g., at least about 0.002%, at least about 0.005%, at least about 0.01%, at least about
0.02%, at least about 0.05%, at least about 0.1%, at least about 0.2%, or at least about 0.5%) by
weight to at most about 1% (e.g., at most about 0.8%, at most about 0.6%, at most about 0.5%, at
most about 0.4%, at most about 0.2%, at most about 0.1%, at most about 0.05%, at most about
10 0.02%, at most about 0.01%, or at most about 0.005%) by weight of the polishing composition
described herein.

An optional oxidizer (or oxidizing agent) can be added when diluting a concentrated
slurry to form a POU slurry. The oxidizer can be selected from the group consisting of hydrogen
peroxide, orthoperiodic acid, metaperiodic acid, dimesoperiodic acid, diorthoperiodic acid,
15 ammonium periodate, potassium periodate, sodium periodate, ammonium persulfate, iodic acid,
iodate salt, perchloric acid, perchloroate salt, hydroxylamine and hydroxylamine salts, and any
combinations thereof. In one or more embodiments, the oxidizer can be hydrogen peroxide.

In one or more embodiments, the oxidizer is in an amount of from at least about 0.001%
20 (e.g., at least about 0.002%, at least about 0.004%, at least about 0.005%, at least about 0.01%, at
least about 0.025%, at least about 0.05%, at least about 0.075%, at least about 0.1%, at least
about 0.5%, at least about 1%, or at least about 2%) by weight to at most about 5% (e.g., at most
about 4.5%, at most about 4%, at most about 3.5%, at most about 3%, at most about 2.5%, at
most about 2%, at most about 1.5%, at most about 1%, at most about 0.5%, or at most about
25 0.1%) by weight of the polishing composition described herein. In some embodiments, without
wishing to be bound by theory, it is believed that the oxidizer can help remove a hard mask
material in a hard mask containing substrate.

In one or more embodiments, the polishing composition described herein can include a
30 solvent (e.g., a primary solvent), such as water. In some embodiments, the solvent (e.g., water)

is in an amount of from at least about 20% (e.g., at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45%, at least about 50%, at least about 55%, at least about 60%, at least about 65%, at least about 70%, at least about 75%, at least about 80%, at least about 85%, at least about 90%, at least about 92%, at least about 94%, at least about 95%, or at least about 97%) by weight to at most about 99% (e.g., at most about 98%, at most about 96%, at most about 94%, at most about 92%, at most about 90%, at most about 85%, at most about 80%, at most about 75%, at most about 70%, or at most about 65%) by weight of the polishing composition described herein.

10 In one or more embodiments, an optional secondary solvent (e.g., an organic solvent) can be used in the polish composition (e.g., the POU or concentrated polishing composition) of the present disclosure, which can help with the dissolution of components such as an azole-containing corrosion inhibitor. In one or more embodiments, the secondary solvent can include one or more alcohols, alkylene glycols, or alkylene glycol ethers. In one or more embodiments, 15 the secondary solvent includes one or more solvents selected from the group consisting of ethanol, 1-propanol, 2-propanol, n-butanol, propylene glycol, 2-methoxyethanol, 2-ethoxyethanol, propylene glycol propyl ether, dimethyl sulfoxide, and ethylene glycol.

In one or more embodiments, the secondary solvent is in an amount of from at least about 20 0.0025% (e.g., at least about 0.005%, at least about 0.01%, at least about 0.02%, at least about 0.05%, at least about 0.1%, at least about 0.2%, at least about 0.4%, at least about 0.5%, at least about 0.6%, at least about 0.8%, or at least about 1%) by weight to at most about 5% (e.g., at most about 4%, at most about 3%, at most about 2%, at most about 1%, at most about 0.8%, at most about 0.6%, at most about 0.5%, or at most about 0.1%) by weight of the polishing 25 composition described herein.

In one or more embodiments, the polishing composition described herein can be substantially free of one or more of certain ingredients, such as organic solvents, pH adjusting agents or pH adjusters, quaternary ammonium compounds (e.g., salts or hydroxides), amines, 30 alkali bases (such as alkali hydroxides), fluorine containing compounds (e.g., fluoride

compounds or fluorinated compounds (e.g., polymers/surfactants)), silicon-containing compounds such as silanes (e.g., alkoxysilanes or inorganic silicates), imines (e.g., amidines such as 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)), salts (e.g., halide salts or metal salts), polymers (e.g., cationic or anionic polymers),
5 surfactants (e.g., cationic surfactants, anionic surfactants, or non-ionic surfactants), plasticizers, oxidizing agents (e.g., H₂O₂ or periodic acid), corrosion inhibitors (e.g., azole or non-azole corrosion inhibitors), electrolytes (e.g., polyelectrolytes), and/or certain abrasives (e.g., polymeric abrasives, ceria abrasives, non-ionic abrasives, surface modified abrasives, ceramic abrasive composites, or negatively/positively charged abrasive). The halide salts that can be
10 excluded from the polishing compositions include alkali metal halides (e.g., sodium halides or potassium halides) or ammonium halides (e.g., ammonium chloride), and can be fluorides, chlorides, bromides, or iodides. As used herein, an ingredient that is “substantially free” from a polishing composition refers to an ingredient that is not intentionally added into the polishing composition. In some embodiments, the polishing composition described herein can have at
15 most about 1000 ppm (e.g., at most about 500 ppm, at most about 250 ppm, at most about 100 ppm, at most about 50 ppm, at most about 10 ppm, or at most about 1 ppm) of one or more of the above ingredients that are substantially free from the polishing composition. In some embodiments, the polishing compositions described herein can be completely free of one or more of the above ingredients.

20

The present disclosure also contemplates a method of using any of the above-described polishing compositions (e.g., concentrates or POU slurries). With the concentrate, the method can comprise the steps of diluting the concentrate to form a POU slurry (e.g., by a factor of at least two), and then contacting a surface at least partially comprising ruthenium and/or a hard
25 mask material with the POU slurry. In some embodiments, an oxidizer can be added to the slurry before, after, or during the dilution. With the POU slurry, the method comprises the step of contacting the surface at least partially comprising ruthenium and/or a hard mask material with the slurry.

In one or more embodiments, this disclosure features a polishing method that can include applying a polishing composition according to the present disclosure to a substrate (e.g., a wafer) having at least ruthenium and/or a hard mask material on a surface of the substrate; and bringing a pad into contact with the surface of the substrate and moving the pad in relation to the
5 substrate. In some embodiments, when the substrate includes at least one or more of silicon oxides, ruthenium, copper, hard mask material and/or barrier materials (e.g., Ta and/or TaN), the above method can effectively polish the substrate without significant corrosion or undesirable removal rate selectivity. In one or more embodiments, the copper removal rate is less than about 500 Å/min, (e.g., less than about 400 Å/min, less than about 300 Å/min, less than about 200
10 Å/min, less than about 150 Å/min, less than about 125 Å/min, less than about 100 Å/min, less than about 90 Å/min, less than about 80 Å/min, or less than about 70 Å/min). In one or more embodiments, the static etch rate (SER) for a 2 cm x 2 cm copper coupon incubated with a polishing composition for 5 minutes at 45°C according to the present disclosure is less than about 10 Å/min (e.g., less than about 8 Å/min, less than about 6 Å/min, less than about 5 Å/min,
15 less than about 4 Å/min, less than about 3.5 Å/min, less than about 2 Å/min, or less than about 2.5 Å/min). In one or more embodiments, the ruthenium removal rate is at least about 3 Å/min (e.g., at least about 5 Å/min, at least about 15 Å/min, at least about 25 Å/min, at least about 35 Å/min, at least about 45 Å/min, or at least about 55 Å/min).

20 In one or more embodiments, the compositions and/or methods described herein can have appropriate copper/ruthenium removal rate ratio. For example, the ratio of the copper removal rate to the ruthenium removal rate (Cu:Ru) is at most about 35:1 (e.g., at most about 30:1, at most about 25:1, at most about 20:1, at most about 15:1, at most about 10:1, at most about 5:1, at most about 4:1, at most about 3:1, at most about 2.5:1, at most about 2:1, at most about 1.5:1, or
25 at most about 1:1).

It is to be noted that the term “silicon oxide” described herein is expressly intended to include both un-doped and doped versions of silicon oxide. For example, in one or more
embodiments, the silicon oxide can be doped with at least one dopant selected from carbon,
30 nitrogen (for silicon oxide), oxygen, hydrogen, or any other known dopants for silicon oxide.

Some examples of silicon oxide film types include TEOS (tetra-ethyl orthosilicate), SiOC, SiOCN, SiOCH, SiOH and SiON.

In one or more embodiments, the method that uses a polishing composition described
5 herein can further include producing a semiconductor device from the substrate treated by the
polishing composition through one or more steps. For example, photolithography, ion
implantation, dry/wet etching, plasma etching, deposition (e.g., PVD, CVD, ALD, ECD), wafer
mounting, die cutting, packaging, and testing can be performed to produce a semiconductor
device from the substrate treated by the polishing composition described herein.

10 The specific examples below are to be construed as merely illustrative, and not limitative
of the remainder of the disclosure in any way whatsoever. Without further elaboration, it is
believed that one skilled in the art can, based on the description herein, utilize the present
invention to its fullest extent.

15 EXAMPLES

The polishing was performed on 200 mm wafers, using a AMAT Mirra CMP polisher, a
Fujibo soft pad, a downforce pressure of 1.5 psi, and a slurry flow rate between 100 and 400
mL/min.

20 Example 1

Figure 1 shows a plot of the change in Zeta Potential as the pH is changed for aqueous
dispersions of three different types of silica abrasives indicated in the figure. Other than water
and the abrasive, no other components were included in the aqueous dispersions. Figure 1 shows
25 that the carboxylic acid modified abrasive has a more negative zeta potential than the unmodified
abrasive and the sulfonic acid modified abrasive in the roughly pH 5 to pH 8.5 range. The more
negative zeta potential within this range indicates that the carboxylic acid modified abrasive
dispersion has more stability than the unmodified or sulfonic acid modified abrasive dispersion.

30 Example 2

Figure 2 shows a plot of the change in the mean particle size (MPS) over time for aqueous dispersions of unmodified silica, cationic modified silica, sulfonic acid modified silica, and carboxylic acid modified silica. The aqueous dispersions each had the same amount of abrasive, a barrier film removal rate enhancer, an azole, and a ruthenium removal rate enhancer. The aqueous dispersions had a pH of 10 and were aged at 45°C for the time period indicated. Table 1 below shows summarized data from the plot in Figure 2.

Table 1

Abrasive	Day 0 MPS (nm)	Day 35 MPS (nm)	MPS change (%)
Unmodified Silica	70.08	72.54	3.51
Carboxylic Acid Modified Silica	68.92	68.46	-0.67
Cationic Modified Silica	67.91	73.8	8.67
Sulfonic Acid Modified Silica	68.06	69.85	2.63

The results show that the carboxylic acid modified abrasive displays the most stable MPS over the 35 day test period, indicating a very high stability for the dispersed particle solution.

Example 3

Table 2 below shows particle stability for three different aqueous abrasive dispersions (i.e., containing unmodified silica, carboxylic acid modified silica, and sulfonic acid modified silica) with or without copper ions present in the aqueous dispersion. The aqueous dispersions each had the same amount of abrasive, a barrier film removal rate enhancer, an azole, and a ruthenium removal rate enhancer. The particle stability was measured by determining a “Transmission Stability Index” (TSI), which is determined by measuring the light transmission and backscattering of the samples. Higher TSI values suggest that the sample is less stable and has more particle agglomeration and poorer dispersion. The measurement was performed at 35°C.

Table 2

Abrasive	w/o Cu ions	w/ Cu ions (50 ppm)	Change in TSI
Unmodified Silica	0.39	10.2	9.77
Carboxylic Acid Modified Silica	0.38	9.01	8.63
Sulfonic Acid Modified Silica	0.34	10.3	9.96

The silica particle stability during metal polishing is critical from a defectivity point of view. Specifically, silica-metal agglomerates can form from interactions between the abrasive and metal ions created during the action of polishing a metal substrate. Once these agglomerates form, they can cause scratching and/or residue issues on a polished substrate. The carboxylic acid modified abrasive exhibited the best stability in the presence of the Cu ions, indicating that the carboxylic acid modified abrasive would be more stable during a polishing process and have less potential for defect formation.

Example 4

Table 3 below shows the removal rate for Cu, Co, and CVD-Ru using blanket wafers when polished by a polishing composition including unmodified silica abrasive, carboxylic acid modified silica abrasive, or sulfonic acid modified silica abrasive. All other components of the polishing compositions were the same.

Table 3

	Unmodified Silica	Carboxylic Acid Modified Silica	Sulfonic Acid Modified Silica
Cu RR (Å/Min)	66	65	53
Co RR (Å/Min)	55	56	51
CVD-Ru RR (Å/Min)	5	9	8
Total Defect Counts on Cu	1077	699	1150

The results show that the carboxylic acid modified silica was able to achieve as high of Cu and Co removal rates as the unmodified silica, while also increasing the CVD-Ru removal rate roughly two times. In contrast, the sulfonic acid modified silica abrasive only increased the CVD-Ru removal rate relative to the unmodified abrasive, while the Cu and Co removal rates were lower. Moreover, the carboxylic acid modified silica surprisingly produced at least 35% less defects on Cu than either the unmodified silica or the sulfonic acid modified silica.

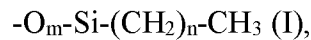
Although only a few example embodiments have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from this invention. Accordingly, all such modifications are intended to be included within the scope of this disclosure as defined in the

following claims.

WHAT IS CLAIMED IS:

1. A polishing composition, comprising:

an anionic silica abrasive, wherein the anionic silica abrasive comprises terminal groups
5 of formula (I):



in which m is an integer from 1 to 3; n is an integer from 0 to 10; and the $-(\text{CH}_2)_n\text{-CH}_3$ group is substituted by at least one carboxylic acid group;

a pH adjuster;

10 a low-k removal rate inhibitor;

a ruthenium removal rate enhancer; and

water;

wherein the polishing composition has a pH of about 7 to about 14.

15 2. The polishing composition of claim 1, wherein the anionic silica abrasive is in an amount of from about 0.01 wt% to about 50 wt% of the composition.

3. The polishing composition of claim 1, wherein the pH adjuster is selected from the group consisting of formic acid, acetic acid, malonic acid, citric acid, propionic acid, malic
20 acid, adipic acid, succinic acid, lactic acid, oxalic acid, peracetic acid, potassium acetate, phenoxyacetic acid, benzoic acid, nitric acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphonic acid, hydrochloric acid, periodic acid, lithium hydroxide, potassium hydroxide, sodium hydroxide, cesium hydroxide, ammonium hydroxide, triethanolamine, diethanolamine, monoethanolamine, methylethanolamine, methyldiethanolamine, tetrabutylammonium
25 hydroxide, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetramethylammonium hydroxide, ethyltrimethylammonium hydroxide, diethyltrimethylammonium hydroxide, dimethyldipropylammonium hydroxide, benzyltrimethylammonium hydroxide, tris(2-hydroxyethyl)methylammonium hydroxide, choline hydroxide, and mixtures thereof.

30

4. The polishing composition of claim 1, wherein the pH adjuster is in an amount of from about 0.0001 wt% to about 30 wt% of the composition.

5. The polishing composition of claim 1, wherein the low-k removal rate inhibitor is a nonionic surfactant.

6. The polishing composition of claim 5, where the nonionic surfactant is selected from the group consisting of alcohol alkoxyates, alkylphenol alkoxyates, tristyrylphenol alkoxyates, sorbitan ester alkoxyates, polyalkoxyates, polyalkylene oxide block copolymers, tetrahydroxy oligomers, alkoxyated diamines, and mixtures thereof.

7. The polishing composition of claim 1, wherein the low-k removal rate inhibitor is in an amount of from about 0.0005% to about 5% by weight of the composition.

8. The polishing composition of claim 1, wherein the ruthenium removal rate enhancer is selected from the group consisting of ammonium hydroxide, ammonium chloride, ammonium fluoride, ammonium bromide, ammonium sulfate, ammonium carbonate, ammonium hydrogen carbonate, ammonium nitrate, ammonium phosphate, ammonium acetate, ammonium thiocyanate, potassium thiocyanate, sodium thiocyanate, nitric acid, sulfuric acid, sulfurous acid, phosphoric acid, phosphonic acid, hydrochloric acid, periodic acid, sodium nitrate, potassium nitrate, rubidium nitrate, cesium nitrate, sodium fluoride, potassium fluoride, rubidium fluoride, cesium fluoride, sodium chloride, potassium chloride, rubidium chloride, cesium chloride and mixtures thereof.

9. The polishing composition of claim 1, wherein the ruthenium removal rate enhancer is in an amount of from about 0.0001% to about 5% by weight of the composition.

10. The polishing composition of claim 1, further comprising:
a chelating agent selected from the group consisting of ethylenediaminetetracetic acid, iminodiacetic acid, N-hydroxyethyl-ethylenediaminetriacetic acid, nitrilotriacetic acid,

diethylenetriaminepentacetic acid, hydroxyethylethylenediaminetriacetic acid,
triethylenetetraaminehexaacetic acid, diaminocyclohexanetetraacetic acid,
nitrilotrimethylphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), 1-hydroxyl
ethylidene-1,1-diphosphonic acid, diethylenetriamine penta (methylene phosphonic acid),
5 hydroxyethylidene diphosphonic acid, 2-phosphono-1,2,4-butane tricarboxylic acid,
aminotrimethylene phosphonic acid, hexamethylenediamine tetra(methylenephosphonic acid),
bis(hexamethylene)triamine phosphonic acid, amino acetic acid, and combinations thereof.

11. The polishing composition of claim 10, wherein the chelating agent is in an
10 amount of from about 0.001% to about 1% by weight of the composition.

12. The polishing composition of claim 1, further comprising an oxidizing agent
selected from the group consisting of hydrogen peroxide, orthoperiodic acid, metaperiodic acid,
dimesoperiodic acid, diorthoperiodic acid, ammonium periodate, potassium periodate, sodium
15 periodate, ammonium persulfate, iodic acid, iodate salts, perchloric acid, perchlorate salts,
hydroxylamine and hydroxylamine salts, and mixtures thereof.

13. The polishing composition of claim 12, wherein the oxidizing agent is in an
amount of from about 0.001% to about 5% by weight of the composition.

20 14. The polishing composition of claim 1, further comprising an azole-containing
corrosion inhibitor selected from the group consisting of triazole, tetrazole, benzotriazole,
tolyltriazole, 1,2,4-triazole, ethyl benzotriazole, propyl benzotriazole, butyl benzotriazole, pentyl
benzotriazole, hexyl benzotriazole, dimethyl benzotriazole, chloro benzotriazole, dichloro
25 benzotriazole, chloromethyl benzotriazole, chloroethyl benzotriazole, phenyl benzotriazole,
benzyl benzotriazole, aminotriazole, aminobenzimidazole, pyrazole, imidazole, aminotetrazole,
isothiazole, and mixtures thereof.

15. The polishing composition of claim 14, wherein the azole-containing corrosion
30 inhibitor is in an amount of from about 0.0001% to about 1% by weight of the composition.

16. The composition of claim 1, wherein the water is in an amount of from about 20 wt% to about 99 wt% of the composition.

5 17. A method of polishing a substrate, comprising the steps of:
applying the polishing composition of claim 1 to a surface of a substrate, wherein the surface comprises ruthenium or a hard mask material; and
bringing a pad into contact with the surface of the substrate and moving the pad in relation to the substrate.

10 18. The method of claim 17, further comprising producing a semiconductor device from the substrate treated by the polishing composition.

15

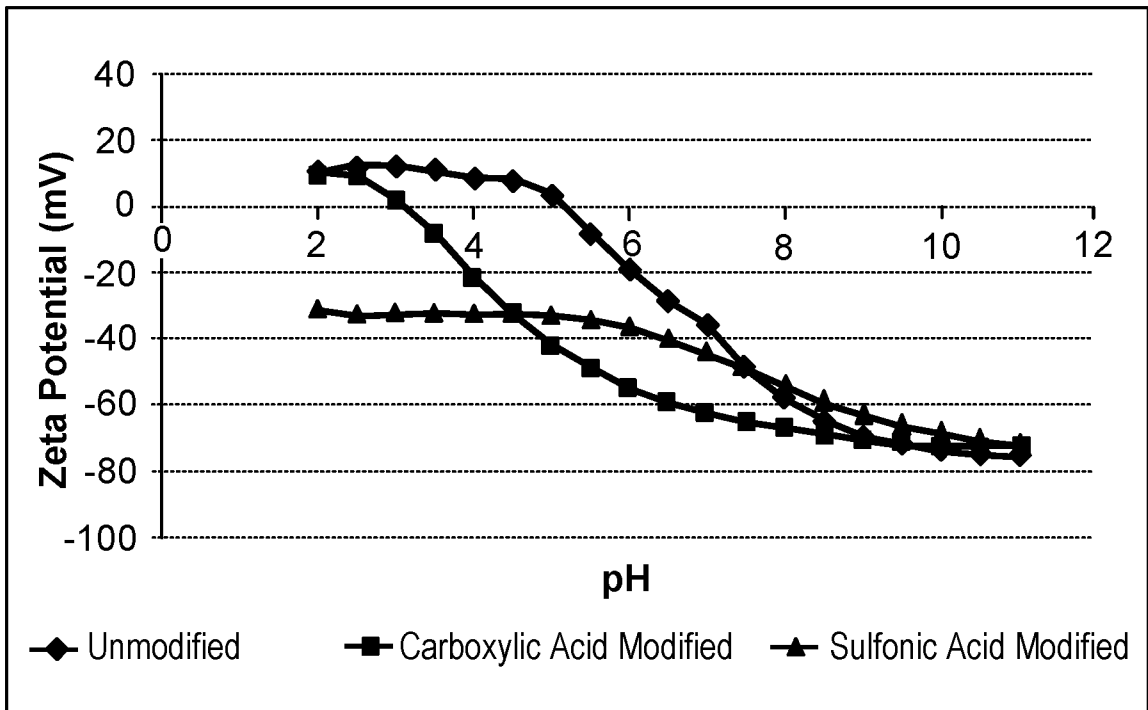


FIG. 1

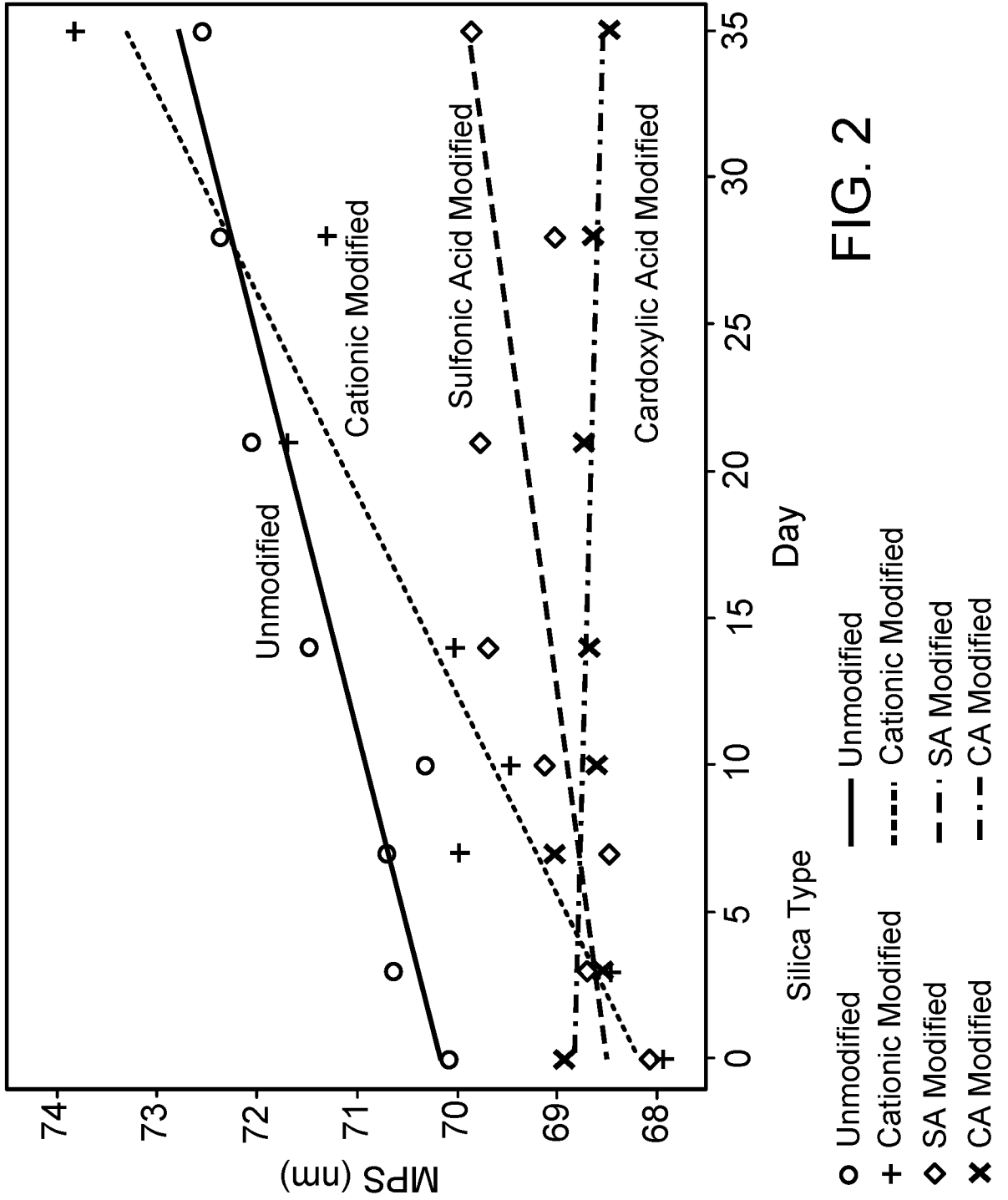


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US22/47391

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. C09G 1/02; C23F 3/04 (2022.01)
ADD.
CPC - INV. C09G 1/02; C23F 3/04; H01L 21/30625; H01L 21/3212
ADD.

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)
See Search History document

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

Electronic database consulted during the international search (name of database and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2019/0359858 A1 (FUJIFILM ELECTRONIC MATERIALS U.S.A., INC.) 28 November 2019; page 2 paragraph [0008], page 2 paragraph [0017]-[0018], claim 1, page 3 paragraph [0031], page 5 paragraph [0040], page 6 paragraph [0050], page 6 paragraph [0051], page 6 paragraph [0052], page 8 paragraph [0072], page 10 paragraph [0084]; claim 1, claim 7	1-18
Y	US 2021/0253904 A1 (FUJIFILM ELECTRONIC MATERIALS U.S.A., INC.) 19 August 2021; page 2 paragraph [0013], page 3 paragraph [0024], page 4 paragraph [0028], page 4 paragraph [0030], page 5 paragraph [0039], page 5 paragraph [0041], claim 1	1-18

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
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 "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
30 December 2022 (30.12.2022)

Date of mailing of the international search report

JAN 27 2023

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