

POLISHING COMPOSITIONS AND METHODS OF USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims priority to U.S. Provisional Application Serial No. 63/071,711, filed on August 28, 2020, 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 through process and integration innovations. Chemical Mechanical Polishing/Planarization (CMP) is a powerful technology as it makes many complex integration
10 schemes at the transistor level possible, thereby facilitating increased chip density.

CMP is a process used to planarize/flatten a wafer surface by removing material using abrasion-based physical processes concurrently with surface-based chemical reactions. In general, a CMP process involves applying a CMP slurry (aqueous chemical formulation) to a
15 wafer surface while contacting the wafer surface with a polishing pad and moving the polishing pad in relation to the wafer. Slurries typically include an abrasive component and dissolved chemical components, which can vary significantly depending upon the materials (e.g., metals, metal oxides, metal nitrides, dielectric materials such as silicon oxide, silicon nitride, etc.) present on the wafer that will be interacting with the slurry and the polishing pad during the
20 CMP process.

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
25 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.

In one aspect, this disclosure features a polishing composition that includes at least one abrasive; at least one pH adjuster; and at least one biosurfactant selected from the group
30 consisting of glycolipids, lipopeptides, and mixtures thereof.

In another aspect, this disclosure features a method of polishing a substrate that includes the steps of applying a polishing composition described herein to 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 substrate.

DETAILED DESCRIPTION

The present disclosure relates to polishing compositions and methods for polishing semiconductor substrates using the same.

In some embodiments, this disclosure relates to polishing compositions that include at least one biosurfactant. As used herein, the term “biosurfactant” is intended to denote amphiphilic organic molecules, such as organic molecules that include both hydrophobic groups (e.g., an alkyl chain) and hydrophilic groups (e.g., a carboxylic acid group), which are produced by a biological organism (e.g., a microorganism). Commonly used surfactants in the CMP industry are produced using petroleum based precursors and/or energy intensive chemical reactions. In contrast, a biosurfactant can have a favorable environmental and energy profile (e.g., biodegradability and/or production by less energy intensive processes), while still being capable of providing the performance characteristics necessary to execute advanced CMP operations. Additionally, due to their unique chemical structures, biosurfactants can also impart enhanced performance (e.g., improved polishing selectivity between substrate constituents by reducing removing rates of certain dielectric and/or metal films) during CMP operations when used alone or in combination with surfactants that are not biosurfactants. Thus, the use of biosurfactants within the CMP industry presents an opportunity for improved or sustained performance combined with a significantly reduced environmental footprint.

In one or more embodiments, a polishing composition described herein can include at least one abrasive, at least one pH adjuster, and at least one biosurfactant. In one or more embodiments, a polishing composition according to the present disclosure can include from about 0.01% to about 50% by weight of at least one abrasive, from about 0.0001% to about 30% by weight of at least one pH adjuster, from about 0.0001% to about 10% by weight of at least

one biosurfactant, and the remaining percent by weight (e.g., from about 30% to about 99.99% by weight) of a solvent (e.g., deionized water).

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, or up to a factor of fifteen, or up to a factor of twenty. In other embodiments, the present disclosure provides a point-of-use (POU) polishing composition, comprising the above-described polishing composition, water, and optionally an oxidizer.

In one or more embodiments, a POU polishing composition can include from about 0.01% to about 25% by weight of at least one abrasive, from about 0.0001% to about 10% by weight of at least one pH adjuster, from about 0.0001% to about 5% by weight of at least one biosurfactant, and the remaining percent by weight (e.g., from about 65% to about 99.99% by weight) of a solvent (e.g., deionized water).

In one or more embodiments, a concentrated polishing composition can include from about 0.02% to about 50% by weight of at least one abrasive, from about 0.0002% to about 30% by weight of at least one pH adjuster, from about 0.0002% to about 10% by weight of at least one biosurfactant, and the remaining percent by weight (e.g., from about 35% to about 99.98% by weight) of a solvent (e.g., deionized water).

In one or more embodiments, the at least one (e.g., two or three) abrasive is selected from the group consisting of cationic abrasives, substantially neutral abrasives, and anionic abrasives.

In one or more embodiments, the at least one abrasive is selected from the group consisting of alumina, silica, titania, ceria, zirconia, co-formed products thereof (i.e., co-formed products of alumina, silica, titania, ceria, or zirconia), coated abrasives, surface modified abrasives, and mixtures thereof. In some embodiments, the at least one abrasive does not include ceria. In some embodiments, the at least one abrasive has a high purity, and can have less than about 100 ppm of alcohol, less than about 100 ppm of ammonia, and less than about 100 ppb of an alkali cation such as sodium cation. The abrasive can be present in an amount of from about 0.01% to

about 12% (e.g., from about 0.5% to about 10%), based on the total weight of a POU polishing composition, or any subranges thereof.

In one or more embodiments, the abrasive is a silica-based abrasive, such as one selected from the group consisting of colloidal silica, fumed silica, and mixtures thereof. In one or more embodiments, the abrasive can be surface modified with organic groups and/or non-siliceous inorganic groups. For example, the cationic abrasive can include terminal groups of formula (I):



in which m is an integer from 1 to 3; n is an integer from 1 to 10; X is Al, Si, Ti, Ce, or Zr; and Y is a cationic amino or thiol group. As another example, the anionic abrasive can include terminal groups of formula (I):



in which m is an integer from 1 to 3; n is an integer from 1 to 10; X is Al, Si, Ti, Ce, or Zr; and Y is an acid group.

In one or more embodiments, the abrasive described herein can have a mean particle size of 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, or at most about 200 nm). As used herein, the mean particle size (MPS) is determined by dynamic light scattering techniques.

In one or more embodiments, the at least one abrasive is in an amount of from at least about 0.01% (e.g., at least about 0.05%, at least about 0.06%, at least about 0.08%, 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%, at least about 1%, at least about 1.2%, at least about 1.5%, or at least about 2%) 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%, at most about 8%, at most about 6%, at most about 5%, at most

about 4%, %, at most about 2%, or %, at most about 1%,) by weight of the polishing compositions described herein.

In one or more embodiments, the polishing compositions described herein can include at least one (e.g., two or three) pH adjuster, if necessary, to adjust the pH to a desired value. In some embodiments, the at least one pH adjuster can be an acid (e.g., an organic or inorganic acid) or a base (e.g., an organic or inorganic base). For example, the pH adjuster can be selected from the group consisting of nitric acid, hydrochloric acid, sulfuric acid, propionic acid, citric acid, malonic acid, hydrobromic acid, hydroiodic acid, perchloric acid, ammonia, ammonium hydroxide, sodium hydroxide, potassium hydroxide, cesium hydroxide, monoethanolamine, diethanolamine, triethanolamine, methylethanolamine, 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 any combinations thereof.

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 0.002%, at least about 0.004%, at least about 0.005%, at least about 0.006%, at least about 0.008%, at least about 0.01%, at least about 0.02%, at least about 0.04%, at least about 0.05%, at least about 0.06%, at least about 0.08%, 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%, at least about 1%, at least about 1.5%, at least about 2%, at least about 2.5%, at least about 3%, at least about 4%, or at least about 5%) by weight to at most about 30% (e.g., at most about 25%, at most about 20%, at most about 15%, at most about 12%, 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 2.5%, at most about 2%, at most about 1.5%, 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 compositions described herein.

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In one or more embodiments, the polishing compositions described herein can be either acidic or basic. In some embodiments, the polishing compositions can have a pH ranging from at least about 1 to at most about 14. When the polish compositions are acidic, the pH can range from at least about 1 (e.g., at least about 1.5, at least about 2, at least about 2.5, at least about 3, at least about 3.5, at least about 4, at least about 4.5, or at least about 5) to at most about 7 (e.g., at most about 6.5, at most about 6, at most about 5.5, at most about 5, at most about 4.5, or at most about 4). When the polishing compositions are basic, the pH 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, or at most about 10).

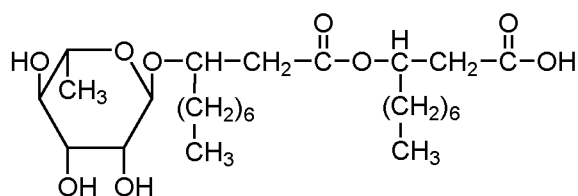
In one or more embodiments, the polishing compositions can include at least one (e.g., two or three) biosurfactant. In one or more embodiments, the at least one biosurfactant can be a microbial growth by-product (i.e., the biosurfactant can be produced by microorganisms), such as a microbial metabolite. The microbial growth by-product (i.e., the biosurfactant) can be collected from a cultivated yeast or fungus strain (i.e., the microorganisms) through a purification process that removes the microorganisms involved in producing the microbial growth by-product.

In one or more embodiments, the biosurfactant can be selected from the group consisting of glycolipids, lipopeptides, and mixtures thereof. In one or more embodiments, the biosurfactant includes a glycolipid selected from the group consisting of a rhamnolipid, a sophorolipid, a trehalose lipid, a mannosylerythritol lipid, and mixtures thereof. In one or more embodiments, the biosurfactant includes a lipopeptide selected from the group consisting of surfactin, iturin, fengycin, lichenysin, and mixtures thereof.

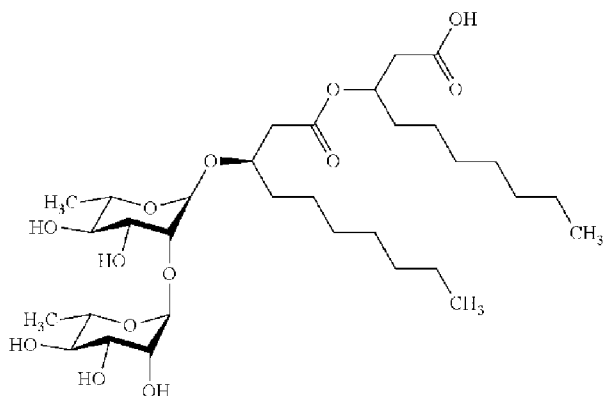
In one or more embodiments, the glycolipid is a rhamnolipid biosurfactant selected from a mono-rhamnolipid, a di-rhamnolipid, and mixtures thereof. Rhamnolipid biosurfactants are surface active compounds released by microorganisms. They are biodegradable, non-toxic, and eco-friendly materials. Their production depends on the fermentation conditions, environmental

factors and nutrient availability. In some embodiments, rhamnolipids have a glycosyl head group (i.e., a rhamnose moiety), and a fatty acid tail (e.g., containing one or more (e.g., two or three) C₁₀-C₁₄ 3-hydroxyalkanoic acid or ester group). In some embodiments, depending on the fermentation details, a rhamnolipid's fatty acid tail can be 10–28 (e.g., 20-28 or 24-28) carbons long. In some embodiments, the fatty acid tail can include a 3-(hydroxyalkanoyloxy)alkanoic acid (HAA) group. For example, the fatty acid tail can include a group of formula (II): -R₁-C(O)O-R₂-COOH, in which each of R₁ and R₂, independently, is a C₁₀-C₁₄ straight chained or branched alkylene group.

Structure I shows the structure of a typical mono-rhamnolipid, RLL or R1 (alpha-L-Rhamnopyranosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate, C₂₆H₄₈O₉ (504 g/mol):



Structure II shows a structure of a typical di-rhamnolipid, RRLL or R2 (2-O-alpha-L-rhamnopyranosyl-alpha-L-rhamnopyranosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate, C₃₂H₅₈O₁₃ (650 g/mol):



As mentioned above, there are two major groups of rhamnolipids; mono-rhamnolipids and di-rhamnolipids. Mono-rhamnolipids have a single rhamnose sugar ring. A common name for mono-rhamnolipid RLL (which is most often produced by *P. aeruginosa*) is: L-rhamnosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate (often referred to as Rha-C10-C10) with a
 5 formula of $C_{26}H_{48}O_9$. The IUPAC Name is 3-[3-[(2R,3R,4R,5R,6S)-3,4,5-trihydroxy-6-methyloxan-2-yl]oxydecanoyloxy]decanoic acid.

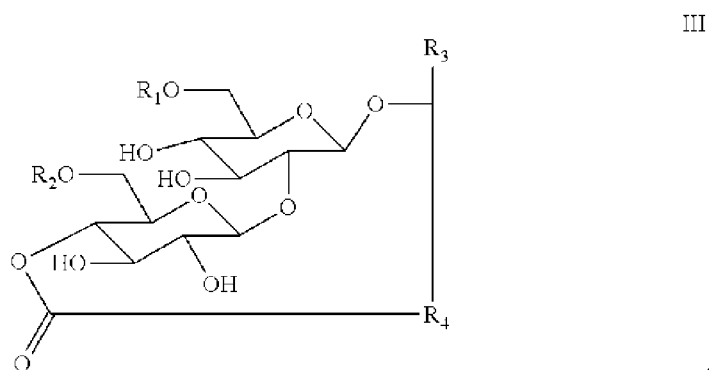
Di-rhamnolipids have two rhamnose sugar rings. A common name for di-rhamnolipid RRLL is: L-rhamnosyl-L-rhamnosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate (often
 10 referred to as Rha-Rha-C10-C10) with a formula of $C_{32}H_{58}O_{13}$. The IUPAC Name is: 3-[3-[4,5-dihydroxy-6-methyl-3-(3,4,5-trihydroxy-6-methyloxan-2-yl)oxyoxan-2-yl]oxydecanoyloxy]decanoic acid. Some other forms or names for the more common di-rhamnolipids include: L-rhamnopyranosyl-L-rhamnopyranosyl-beta-hydroxydecanoyl-beta-hydroxydecanoate (often referred to as Rha-Rha-C10-C10), L-rhamnopyranosyl-L-
 15 rhamnopyranosyl-beta-hydroxydecanoyl-beta-hydroxydodecanoate (often referred to as Rha-Rha-C10-C12), and L-rhamnopyranosyl-L-rhamnopyranosyl-beta-hydroxytetradecanoyl-beta-hydroxytetradecanoate (often referred to as Rha-Rha-C14-C14).

Rhamnolipid formulations for use as biosurfactants in the polishing compositions of the
 20 present disclosure can be crude or highly purified rhamnolipids. A crude rhamnolipid formulation contains a rhamnolipid, having many impurities which can include both external impurities (e.g., those arising from the biological production method), and/or a variety of various rhamnolipid mixtures, which can cause a reduced effect on the formulation. A highly purified rhamnolipid formulation contains rhamnolipids whose external impurities have been removed,
 25 and/or rhamnolipids (e.g., di-rhamnolipids, mono-rhamnolipids, or a mixture thereof) that have been purified to meet certain parameters (e.g., weight ratio of mono- to di-rhamnolipids) to cause an increased effect on the formulation. In one or more embodiments, the weight % ratio of mono-rhamnolipid to di-rhamnolipid in the polishing compositions is in the range of between about 0.1:99.9 and 99.9:0.1, respectively. For example, the weight % ratio of mono-rhamnolipid
 30 to di-rhamnolipid in the polishing compositions can be from at least about 0.1:99.9 (e.g., at least about 0.5:99.5, at least about 1:99, at least about 5:95, at least about 10:90, at least about 15:85,

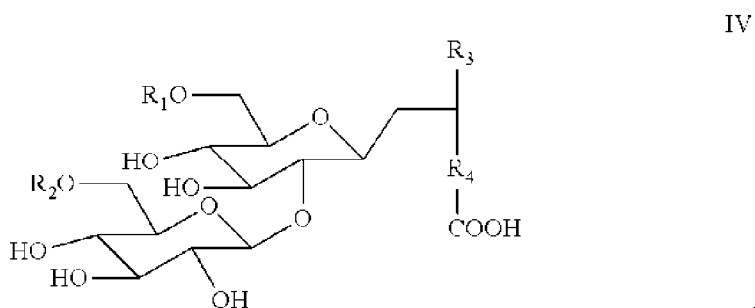
at least about 20:80, at least about 25:75, at least about 30:70, at least about 35:65, at least about 40:60, at least about 45:55, or at least about 50:50) to at most about 99.9:0.1 (e.g., at most about 99.5:0.5, at most about 99:1, at most about 95:5, at most about 90:10, at most about 85:15, at most about 80:20, at most about 75:25, at most about 70:30, at most about 65:35, at most about 60:40, at most about 55:45, or at most about 50:50).

In one or more embodiments, the rhamnolipid formulations are made by eliminating unwanted impurities from the initial mixture obtained from a microorganism and then establishing the percentage and type of rhamnolipid to be present in the final polishing composition, and simply diluting the rhamnolipid formulations by addition into/with the solvent used for the polishing composition. Crude rhamnolipid formulations and highly purified rhamnolipid formulations can be prepared by methods well-known to those of skill in the art. In some embodiments, rhamnolipid formulations for use as biosurfactants in the polishing compositions described herein can include at least about 50% (e.g., at least about 55%, 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 95%, at least about 98%, at least about 99%, at least about 99.5%, or at least about 99.9%) by weight rhamnolipid.

In one or more embodiments, the glycolipid is a sophorolipid biosurfactant. Sophorolipids (also known as sophorose lipids or SLs) are a group of biosurfactants consisting of a dimeric sugar (sophorose) and a hydroxyl fatty acid, linked by a beta-glycosidic bond. There are two types of SLs, namely, the acidic (non-lactonic) SLs and the lactonic SLs. The hydroxyl fatty acid moiety of the acidic SLs has a free carboxylic acid functional group, while that of the lactonic SLs forms a macrocyclic lactone ring with the 4''-hydroxyl group of the sophorose by intramolecular esterification. Sophorose lipids are generally categorized into two forms: (1) the lactone form represented by the following structural formula (III):



wherein R_1 and R_2 each represent H or COCH_3 ; R_3 represents H or CH_3 ; and R_4 represents a saturated or unsaturated C_{12-16} hydrocarbon group (e.g., a C_{12-16} alkylene group optionally containing one or more (e.g., 2, 3, 4, or 5) double bonds) when R_3 is H, and R_4 represents a saturated or unsaturated C_{11-15} hydrocarbon group (e.g., a C_{11-15} alkylene group optionally containing one or more (e.g., 2, 3, 4, or 5) double bonds) when R_3 is CH_3 , and (2) the acid form represented by the following formula (IV):



wherein R_1 to R_4 are as defined above. A commercial example of a sophorolipid biosurfactant is REWOFORM SL ONE available from Evonik (Essen, Germany), which includes a mixture of sophorolipids (i.e., lactone and acid forms) produced by fermenting glucose, fatty acids, and C18 unsaturated esters with glycerol in the presence of yeast *Candida Bombicola* and includes about 30-50 wt% sophorolipids.

As is clear from the above, sophorose lipids have a number of derivatives which are characterized by the positions and number of acetyl groups, the presence or absence of double bonds in the fatty acid side chain, the length of the carbon chain of the fatty acid side chain, the position of the glycosidic ether bond in the fatty acid side chain, the positions of hydroxyl groups on the sophorose moiety that is a part of a lactone ring, and other structural parameters.

Sophorose lipids generally occur as a mixture of these compounds. In general, sophorose lipids are produced in a highly viscous oil form that is difficult to handle. However, sophorose lipids in the diacetyl lactone form, which are comparatively high in hydrophobicity, can be produced in a solid form. In one or more embodiments, the glycolipid is a sophorolipid that includes at least about 5% (e.g., at least about 10%, at least about 15%, at least about 20%, at least about 25%, at least about 30%, at least about 35%, at least about 40%, at least about 45%, or at least about 50%) by weight to at most about 95% (e.g., at most about 90%, at most about 85%, at most about 80%, at most about 75%, at most about 70%, at most about 65%, at most about 60%, at most about 55%, at most about 50%) by weight acidic-type sophorolipid.

In one or more embodiments, the biosurfactant 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 0.002%, at least about 0.004%, at least about 0.005%, at least about 0.006%, at least about 0.008%, at least about 0.01%, at least about 0.02%, at least about 0.03%, at least about 0.04%, 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%, at least about 2.5%, at least about 3%, at least about 4%, or at least about 5%) by weight to at most about 10% (e.g., 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%, at most about 0.1%, or at most about 0.05%) by weight of the polishing compositions described herein.

In one or more embodiments, one or more (e.g., two or three) biosurfactants are the only surfactant(s) in the polishing compositions described herein. However, in some embodiments, the polishing compositions can also include one or more (e.g., two or three) additional surfactants, distinct from the biosurfactant, selected from the group consisting of anionic surfactants, non-ionic surfactants, amphoteric surfactants, cationic surfactants, and mixtures thereof.

The cationic surfactant is not particularly limited, but specific examples thereof include aliphatic amine salts and aliphatic ammonium salts.

The non-ionic surfactant is not particularly limited, but specific examples thereof include an ether-type surfactant, an ether ester-type surfactant, an ester-type surfactant, and an acetylene-based surfactant. The ether-type surfactant is not particularly limited, but specific examples thereof include polyethylene glycol mono-4-nonylphenyl ether, polyethylene glycol monooleyl ether, and triethylene glycol monododecyl ether. The ether ester-type surfactant is not particularly limited, but a specific example thereof is a polyoxyethylene ether of a glycerin ester. The ester-type surfactant is not particularly limited, but specific examples thereof include a polyethylene glycol fatty acid ester, a glycerin ester, and a sorbitan ester. The acetylene-based surfactant is not particularly limited, but specific examples thereof include ethylene oxide adducts of acetylene alcohol, acetylene glycol, and acetylene diol.

The amphoteric surfactant is not particularly limited, but specific examples thereof include betaine-based surfactants.

The anionic surfactant is not particularly limited, but specific examples thereof include carboxylic acid salts, sulfonic acid salts, sulfate salts, and phosphate salts. The carboxylic acid salts are not particularly limited, but specific examples thereof include fatty acid salts (e.g., soaps) and alkyl ether carboxylic acid salts. Examples of the sulfonic acid salts include alkylbenzenesulfonic acid salts, alkyl naphthalenesulfonic acid salts, and α -olefin sulfonic acid salts. The sulfate salts are not particularly limited, but specific examples thereof include higher alcohol sulfate salts and alkyl sulfate salts. The phosphates are not particularly limited, but specific examples thereof include alkyl phosphates and alkyl ester phosphates.

When the polishing compositions described herein include a second surfactant distinct from the biosurfactant described above, the amount of the second surfactant can range from at least about 0.001% (e.g., at least about 0.002%, at least about 0.003%, at least about 0.005%, at least about 0.01%, at least about 0.05%, or at least about 0.1%) 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%, or at most about 0.1%) by weight of the total mass of the polishing compositions.

In one or more embodiments, the polishing compositions described herein can further include at least one (e.g., two, three, or four) optional additive selected from the group consisting of an azole compound, a corrosion inhibitor, an oxidizer, a chelating agent, a water-soluble polymer, and a nitride removal rate reducing agent.

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The azole compound is not particularly limited, but specific examples thereof include substituted or unsubstituted triazoles (e.g., benzotriazoles), substituted or unsubstituted tetrazoles, substituted or unsubstituted diazoles (e.g., imidazoles, benzimidazoles, thiadiazoles, and pyrazoles), and substituted or unsubstituted benzothiazoles. Herein, a substituted diazole, triazole, or tetrazole refers to a product obtained by substitution of one or two or more hydrogen atoms in the diazole, triazole, or tetrazole with, for example, a carboxyl group, an alkyl group (e.g., a methyl, ethyl, propyl, butyl, pentyl, or hexyl group), a halogen group (e.g., F, Cl, Br, or I), an amino group, or a hydroxyl group. In one or more embodiments, the azole compound can be selected from the group consisting of 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, pyrazole, imidazole, aminotetrazole, adenine, benzimidazole, thiabendazole, 1,2,3-triazole, 1,2,4-triazole, 1-hydroxybenzotriazole, 2-methylbenzothiazole, 2-aminobenzimidazole, 2-amino-5-ethyl-1,3,4-thiadiazole, 3,5-diamino-1,2,4-triazole, 3-amino-5-methylpyrazole, 4-amino-4H-1,2,4-triazole, and combinations thereof. Without wishing to be bound by theory, it is believed that the azole compounds can be used as a corrosion inhibitor in the polishing compositions described herein to reduce the removal of certain materials (e.g., metals or dielectric materials) during the polishing process.

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In some embodiments, the azole compound can be from at least about 0.001% (e.g., at least about 0.002%, at least about 0.004%, at least about 0.005%, at least about 0.006%, at least about 0.008%, at least about 0.01%, at least about 0.02%, at least about 0.04%, at least about 0.05%, at least about 0.06%, at least about 0.08%, or at least about 0.1%) by weight to at most about 0.2% (e.g., at most about 0.18%, at most about 0.16%, at most about 0.15%, at most about 0.14%, at most about 0.12%, at most about 0.1%, at most about 0.08%, at most about 0.06%, at most about 0.05%, at most about 0.04%, at most about 0.03%, at most about 0.02%, or at most about 0.01%) by weight of the polishing compositions.

In some embodiments, the polishing compositions described herein can optionally include a non-azole corrosion inhibitor. Examples of non-azole corrosion inhibitors include alkylamines (e.g., ethylamine, propylamine, or butylamine) and organic phosphonic acids (e.g., ethylphosphonic acid).

In some embodiments, the non-azole corrosion inhibitor can be from at least about 0.001% (e.g., at least about 0.002%, at least about 0.004%, at least about 0.005%, at least about 0.006%, at least about 0.008%, at least about 0.01%, at least about 0.02%, at least about 0.04%, at least about 0.05%, at least about 0.06%, at least about 0.08%, or at least about 0.1%) by weight to at most about 0.2% (e.g., at most about 0.18%, at most about 0.16%, at most about 0.15%, at most about 0.14%, at most about 0.12%, at most about 0.1%, at most about 0.08%, at most about 0.06%, at most about 0.05%, at most about 0.04%, at most about 0.03%, at most about 0.02%, or at most about 0.01%) by weight of the polishing compositions described herein.

The oxidizing agent is not particularly limited, but specific examples thereof include ammonium persulfate, potassium persulfate, hydrogen peroxide, ferric nitrate, diammonium cerium nitrate, iron sulfate, hypochlorous acid, ozone, potassium periodate, and peracetic acid. Without wishing to be bound by theory, it is believed that the oxidizing agent can facilitate the removal of materials during the polishing process.

In some embodiments, the oxidizing agent can be from at least about 0.1% (e.g., at least about 0.2%, at least about 0.3%, at least about 0.4%, at least about 0.5%, at least about 0.6%, at

least about 0.7%, at least about 0.8%, at least about 0.9%, at least about 1%, at least about 1.5%, or at least about 2%) by weight to at most about 10% (e.g., 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%, or at most about 1%) by weight of the polishing compositions described herein.

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In one or more embodiments, the chelating agent can be 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, ammonia, 1,2-ethanedisulfonic acid, 4-amino-3-hydroxy-1-naphthalenesulfonic acid, 8-hydroxyquinoline-5-sulfonic acid, aminomethanesulfonic acid, benzenesulfonic acid, hydroxylamine O-sulfonic acid, methanesulfonic acid, m-xylene-4-sulfonic acid, poly(4-styrenesulfonic acid), polyanetholesulfonic acid, p-toluenesulfonic acid, trifluoromethane-sulfonic acid, salts thereof, and mixtures thereof. Without wishing to be bound by theory, it is believed that the chelating agent can serve as a removal rate enhancer to facilitate removal of certain materials on a substrate.

In some embodiments, the chelating agent can be from at least about 0.1% (e.g., at least about 0.2%, at least about 0.3%, at least about 0.4%, at least about 0.5%, at least about 0.6%, at least about 0.7%, at least about 0.8%, at least about 0.9%, or at least about 1%) by weight to at most about 10% (e.g., at most about 8%, at most about 6%, at most about 5%, at most about 4%, at most about 2%, at most about 1%, at most about 0.8%, at most about 0.6%, or at most about 0.5%) by weight of the polishing compositions described herein.

25

The water-soluble polymer is not particularly limited, but specific examples thereof include polyacrylamide, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylic acid, and hydroxyethyl cellulose. Without wishing to be bound by theory, it is believed that the water-soluble polymer can serve as a removal rate inhibitor to reduce the removal rate of certain exposed materials on a substrate that do not intend to be removed or should be removed at a lower removal rate during the polishing process.

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In some embodiments, the water-soluble polymer can be from at least about 0.01% (e.g., at least about 0.02%, at least about 0.03%, at least about 0.04%, at least about 0.05%, at least about 0.06%, at least about 0.07%, at least about 0.08%, at least about 0.09%, or at least about 0.1%) 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 0.08%, at most about 0.06%, or at most about 0.05%) by weight of the polishing compositions described herein.

In one or more embodiments, the nitride removal rate reducing agent is a compound that includes a hydrophobic portion containing a C₁₂ to C₄₀ hydrocarbon group (e.g., containing an alkyl group and/or an alkenyl group); and a hydrophilic portion containing at least one group selected from the group consisting of a sulfinite group, a sulfate group, a sulfonate group, a carboxylate group, a phosphate group, and a phosphonate group. In one or more embodiments, the hydrophobic portion and the hydrophilic portion are separated by zero to ten (e.g., 1, 2, 3, 4, 5, 6, 7, 8, or 9) alkylene oxide groups (e.g., -(CH₂)_nO- groups in which n can be 1, 2, 3, or 4). In one or more embodiments, the nitride removal rate reducing agent has zero alkylene oxide groups separating the hydrophobic portion and the hydrophilic portion. Without wishing to be bound by theory, it is believed that the presence of alkylene oxide groups within the nitride removal rate reducing agent may not be preferred in some embodiments as they may create slurry stability issues and increase silicon nitride removal rate.

In one or more embodiments, the nitride removal rate reducing agent has a hydrophobic portion containing a hydrocarbon group that includes at least 12 carbon atoms (C₁₂) (e.g., at least 14 carbon atoms (C₁₄), at least 16 carbon atoms (C₁₆), at least 18 carbon atoms (C₁₈), at least 20 carbon atoms (C₂₀), or at least 22 carbon atoms (C₂₂)) and/or at most 40 carbon atoms (C₄₀) (e.g., at most 38 carbon atoms (C₃₈), at most 36 carbon atoms (C₃₆), at most 34 carbon atoms (C₃₄), at most 32 carbon atoms (C₃₂), at most 30 carbon atoms (C₃₀), at most 28 carbon atoms (C₂₈), at most 26 carbon atoms (C₂₆), at most 24 carbon atoms (C₂₄), or at most 22 carbon atoms (C₂₂)). The hydrocarbon groups mentioned herein refer to groups that contain only carbon and hydrogen atoms and can include both saturated groups (e.g., linear, branched, or cyclic alkyl groups) and

unsaturated groups (e.g., linear, branched, or cyclic alkyenyl groups; linear, branched, or cyclic alkynyl groups; or aromatic groups (e.g., phenyl or naphthyl)). In one or more embodiments, the hydrophilic portion of the nitride removal rate reducing agent contains at least one group selected from a phosphate group and a phosphonate group. It is to be noted that the term “phosphonate group” is expressly intended to include phosphonic acid groups.

In one or more embodiments, the nitride removal rate reducing agent is selected from the group consisting of naphthalenesulfonic acid-formalin condensate, lauryl phosphate, myristyl phosphate, stearyl phosphate, octadecylphosphonic acid, oleyl phosphate, behenyl phosphate, octadecyl sulfate, lacceryl phosphate, oleth-3-phosphate, and oleth-10-phosphate.

In one or more embodiments, the nitride removal rate reducing agent is included in a polishing composition described herein in an amount from at least about 0.1 ppm (e.g., at least about 0.5 ppm, at least about 1 ppm, at least about 5 ppm, at least about 10 ppm, at least about 25 ppm, at least about 50 ppm, at least about 75 ppm, or at least about 100 ppm) to at most about 1000 ppm (e.g., at most about 900 ppm, at most about 800 ppm, at most about 700 ppm, at most about 600 ppm, at most about 500 ppm, or at most about 250 ppm) based on the total weight of the composition.

In one or more embodiments, the polishing compositions described herein can be substantially free of one or more of certain ingredients, such as organic solvents, pH adjustors (e.g., acids or bases), fluorine containing compounds (e.g., fluoride compounds or fluorinated polymers/surfactants), silicon containing compounds such as silanes (e.g., alkoxysilanes), nitrogen containing compounds (e.g., amino acids, amines, or 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., non-ionic, cationic, or anionic polymers) such as polyols, inorganic acids (e.g., hydrochloric acid, sulfuric acid, phosphoric acid, or nitric acid), surfactants (e.g., cationic surfactants, anionic surfactants, non-ionic surfactants, or those other than the biosurfactant described herein), plasticizers, oxidizing agents (e.g., H₂O₂), quaternary ammonium compounds (e.g., salts such as tetraalkylammonium salts or hydroxides such as tetramethylammonium hydroxide), corrosion inhibitors (e.g., azole or non-azole corrosion

inhibitors), electrolytes (e.g., polyelectrolytes), and/or certain abrasives (e.g., ceria abrasives or non-ionic abrasives). The halide salts that can be 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
5 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 compositions described herein can have at 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
10 substantially free from the polishing compositions. In some embodiments, the polishing compositions described can be completely free of one or more of the above ingredients.

In one or more embodiments, this disclosure features a method of polishing that can include applying a polishing composition according to the present disclosure to a surface of a
15 substrate (e.g., a wafer); and bringing a pad (e.g., a polishing pad) into contact with the surface of the substrate and moving the pad in relation to the substrate. In one or more embodiments, the substrate can include at least one of silicon oxides (e.g., tetraethyl orthosilicate (TEOS), high density plasma oxide (HDP), high aspect ratio process oxide (HARP), or borophosphosilicate glass (BPSG)), spin on films (e.g., films based on inorganic particle or films based on cross-
20 linkable carbon polymer), silicon nitride, silicon carbide, high-K dielectrics (e.g., metal oxides of hafnium, aluminum, or zirconium), silicon (e.g., polysilicon, single crystalline silicon, or amorphous silicon), carbon, metals (e.g., tungsten, copper, cobalt, ruthenium, molybdenum, titanium, tantalum, or aluminum), metal nitrides (e.g., titanium nitride or tantalum nitride), and mixtures or combinations thereof.

25 In some embodiments, the method that uses a polishing composition described herein can further include one or more additional steps (e.g., metal or dielectric deposition on a substrate) to produce a semiconductor device from the substrate treated by the polishing composition. For example, the method can include one or more of the following steps prior to the polishing
30 method described above: (1) depositing silicon oxide (e.g., thermal silicon oxide) on a substrate (e.g., a silicon wafer) to form a silicon oxide layer, (2) depositing silicon nitride on the silicon

oxide layer to form a silicon nitride layer, (3) etching the substrate to form trenches and non-trench areas, and (4) depositing silicon oxide to the etched substrate to fill the trenches with silicon oxide. As another example, the method can include at least one additional step after the polishing method described above, such as etching the substrate (e.g., to remove silicon nitride and silicon oxide) to expose silicon and/or silicon oxide or other heterogeneous films on the wafer substrate.

In one or more embodiments, the method that uses a polishing composition described 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 used to produce a semiconductor device from the substrate treated by the polishing composition described herein.

EXAMPLES

In these examples, the polishing was performed on 200 mm wafers using a Mirra CMP polisher with a Fujibo H804 pad and a slurry flow rate between 150 mL/min and 250 mL/min.

The general compositions used in the examples are shown in Table 1 below. The specific details on the differences in the compositions tested will be explained in further detail when discussing the respective examples.

TABLE 1

Component	% By Weight of the Composition
Organic Acid	0.001 – 2
Nitride Removal Rate Reducing Agent (C ₁₂ -C ₂₀ phosphate)	0.001 – 0.5 (if used)
Biosurfactant	0.001 – 0.5 (if used)
Abrasive (silica)	0.1 – 5
Solvent (DI Water)	75-99
pH	1-4

Example 1

The removal rates (RR) for silicon nitride, silicon oxide (TEOS), and polysilicon blanket wafers were measured when polishing the wafers using Compositions 1-6. Compositions 1-6 were the same except for the differences indicated in Table 2 below. Table 2 also summarizes the test results.

TABLE 2

	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6
NRRR/BS Concentration	0/0	0/2X	0/10X	1X/0	1X/2X	1X/10X
TEOS RR (Å/min)	522	527	305	357	410	390
SiN RR (Å/min)	88	88.2	87.5	3.81	5.51	8.21
Polysilicon RR (Å/min)	90.9	98.6	320	107	110	304
TEOS/SiN RR ratio	5.93	5.97	3.49	93.7	74.4	47.5
Polysilicon/SiN RR ratio	1.03	1.12	3.66	28.1	20	37
Normalized Defects on silicon nitride	N/A	N/A	N/A	1	0.59	0.45

NRRR = Nitride Removal Rate Reducing Agent; BS = Biosurfactant

The results show that the biosurfactant increased the polysilicon removal rate at the highest loading. Further, the addition of the biosurfactant resulted in only a modest increase in silicon nitride rates, while silicon nitride rates typically increase significantly when a secondary surfactant/polymer that is not a biosurfactant is added to the above polishing compositions (see Example 2 below). Further, the NRRR produces high organic defect counts on silicon nitride (see Comp. 4), but the addition of the biosurfactant appears to perform as an in-situ cleaner during polishing, resulting in much lower organic defects counts on silicon nitride.

Example 2

The removal rates for silicon nitride, silicon oxide (TEOS), and polysilicon blanket wafers were measured when polishing the wafers using Compositions 7-11. Compositions 7-11 each included 1X NRRR (i.e., a surfactant) and were the same except for Composition 7 did not

include any surfactant other than the NRRR, Composition 8 included 10X biosurfactant, Composition 9 included 10X anionic polymer, and Compositions 10-11 included 10X of one of two chemically distinct non-ionic surfactants that are not biosurfactants. Table 3 summarizes the test results.

5

TABLE 3

	Comp. 7	Comp. 8	Comp. 9	Comp. 10	Comp. 11
TEOS RR (Å/min)	836	765	611	695	532
SiN RR (Å/min)	10.9	14.6	82.3	40	110
TEOS/SiN RR ratio	76.7	52.4	7.42	17.4	4.84

10

The results show that, as mentioned above, the inclusion of a co-surfactant/polymer that is not a biosurfactant to a polishing composition using the NRRR commonly results in a significant increase in the silicon nitride removal rate, thereby decreasing the TEOS/SiN removal rate ratio (Compositions 9-11). These compositions have a decreased TEOS/SiN removal selectivity, which is undesirable when these compositions are designed to remove TEOS but stop on SiN. By contrast, the inclusion of biosurfactant in Composition 8 results in only a slight increase in the silicon nitride removal rate and a slight decrease in the TEOS/SiN removal rate ratio, but a significant decrease in the defects left behind by the NRRR (See Comp. 6 in Table 2 above).

15

Example 3

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The removal rate for silicon nitride, silicon oxide (TEOS), and polysilicon blanket wafers was measured when polishing the wafers using Compositions 12-20. Compositions 12-20 did not include the NRRR and were otherwise the same except for the differences indicated in Table 4 below. Table 4 also summarizes the test results.

TABLE 4

	Comp. 12	Comp. 13	Comp. 14	Comp. 15	Comp. 16	Comp. 17	Comp. 18	Comp. 19	Comp. 20
Abrasive	Anionic	Anionic	Anionic	Cationic	Cationic	Cationic	Neutral	Neutral	Neutral
Biosurfactant	0	10X	20X	0	10X	20X	0	10X	20X
TEOS RR (Å/min)	227	195	212	746	698	862	1354	1316	752
SiN RR (Å/min)	481	490	502	97	108	50.1	153	136	87.6

Polysilicon RR (Å/min)	43.7	90.9	120	162	404	464	68	465	489
TEOS/SiN RR ratio	0.47	0.40	0.42	7.69	6.46	17.2	8.85	9.68	8.58
Polysilicon/SiN RR ratio	0.09	0.19	0.24	1.67	3.74	9.26	0.44	3.42	5.58

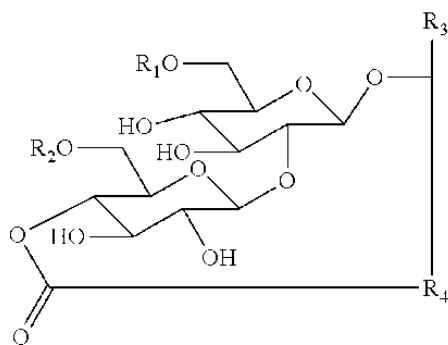
The results show that including a biosurfactant in a polishing composition resulted in a significant enhancement of polysilicon removal rate with increasing amounts of biosurfactant across all abrasive types. Additionally, there was a reduction in silicon nitride removal rate when using the neutral and cationic abrasive, which makes the biosurfactant a suitable replacement for the NRRR given that the NRRR leaves organic residue defects behind when included in a polishing composition. Such polishing compositions can be advantageous as they can be used to remove TEOS but stop on SiN without generating a large amount of defects on silicon nitride.

While this disclosure has been described with respect to the examples set forth herein, it is understood that other modifications and variations are possible without departing from the spirit and scope of the disclosure as defined in the appended claims.

CLAIMS

1. A polishing composition, comprising:
at least one abrasive;
at least one pH adjuster; and
5 at least one biosurfactant selected from the group consisting of glycolipids, lipopeptides, and mixtures thereof,
wherein the polishing composition is free of non-ionic polymers.
2. The polishing composition of claim 1, wherein the at least one abrasive is selected
10 from the group consisting of alumina, silica, titania, ceria, zirconia, co-formed products of alumina, silica, titania, ceria, or zirconia, coated abrasives, surface modified abrasives, and mixtures thereof.
3. The polishing composition of claim 1, wherein the at least one abrasive is in an
15 amount of from 0.01% to 50% by weight of the composition.
4. The polishing composition of claim 1, wherein the at least one biosurfactant
comprises a glycolipid selected from the group consisting of a rhamnolipid, a sophorolipid, a
trehalose lipid, a mannosylerythritol lipid, and mixtures thereof.
20
5. The polishing composition of claim 4, wherein the at least one biosurfactant
comprises a rhamnolipid selected from the group consisting of a mono-rhamnolipid, a di-
rhamnolipid, or a mixture thereof.
- 25 6. The polishing composition of claim 4, wherein the at least one biosurfactant
comprises a sophorolipid of formula (III):

III

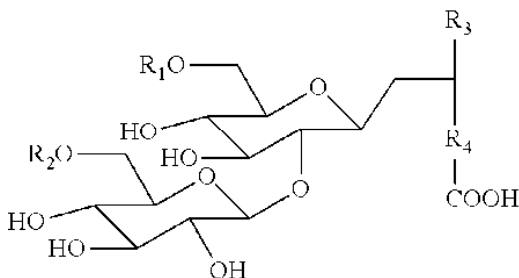


in which R_1 and R_2 each represent H or COCH_3 ; R_3 represents H or CH_3 ; and R_4 represents a saturated or unsaturated C_{12-16} hydrocarbon group when R_3 is H, and R_4 represents a saturated or unsaturated C_{11-15} hydrocarbon group when R_3 is CH_3 .

5

7. The polishing composition of claim 4, wherein the at least one biosurfactant comprises a sophorolipid of formula (IV):

IV



in which R_1 and R_2 each represent H or COCH_3 ; R_3 represents H or CH_3 ; and R_4 represents a saturated or unsaturated C_{12-16} hydrocarbon group when R_3 is H, and R_4 represents a saturated or unsaturated C_{11-15} hydrocarbon group when R_3 is CH_3 .

10

8. The polishing composition of claim 4, wherein the glycolipid comprises at least 5% to at most 95% by weight acidic-type sophorolipid.

15

9. The polishing composition of claim 1, wherein the at least one biosurfactant comprises a lipopeptide selected from the group consisting of surfactin, iturin, fengycin, lichenysin, mixtures thereof.

10. The polishing composition of claim 1, wherein the at least one biosurfactant is the only surfactant in the polishing composition.

11. The polishing composition of claim 1, wherein the at least one biosurfactant is in an amount from 0.0001% to 10% by weight of the composition.

12. The polishing composition of claim 1, further comprising:
a second surfactant, distinct from the at least one biosurfactant, selected from the group consisting of anionic surfactants, non-ionic surfactants, and cationic surfactants.

13. The polishing composition of claim 1, wherein the at least one pH adjustor is in an amount of from 0.0001% to 30% by weight of the composition.

14. The polishing composition of claim 1, further comprising:
at least one additive selected from the group consisting of an azole compound, a corrosion inhibitor, an oxidizer, a chelating agent, and a water-soluble polymer, wherein the water-soluble polymer is selected from the group consisting of polyacrylamide, polyvinylpyrrolidone, polyacrylic acid, and hydroxyethyl cellulose.

15. The polishing composition of claim 1, wherein the composition has a pH of from 1 to 14.

16. A method of polishing a substrate, comprising the steps of:
applying the polishing composition of claim 1 to 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 substrate.

17. The method of claim 16, wherein the substrate is a wafer having a surface comprising SiN, SiC, TiN, TaN, W, silicon oxides, Cu, Co, Ru, Mo, Ti, Ta, Al, carbon, silicon, hafnium oxide, aluminum oxide, zirconium oxide, or p-Si, or a combination thereof.