A chemical mechanical polishing (CMP) composition comprising a glycoside

Description

This invention essentially relates to a chemical mechanical polishing (CMP) composition and its use in polishing substrates of the semiconductor industry. The CMP composition according to the invention comprises a specific glycoside and shows an improved polishing performance.

In the semiconductor industry, chemical mechanical polishing (abbreviated as CMP) is a well-known technology applied in fabricating advanced photonic, microelectromechanical, and microelectronic materials and devices, such as semiconductor wafers.

During the fabrication of materials and devices used in the semiconductor industry, CMP is employed to planarize metal and/or oxide surfaces. CMP utilizes the interplay of chemical and mechanical action to achieve the planarity of the to-be-polished surfaces. Chemical action is provided by a chemical composition, also referred to as CMP composition or CMP slurry. Mechanical action is usually carried out by a polishing pad which is typically pressed onto the to-be-polished surface and mounted on a moving platen. The movement of the platen is usually linear, rotational or orbital.

In a typical CMP process step, a rotating wafer holder brings the to-be-polished wafer in contact with a polishing pad. The CMP composition is usually applied between the to-be-polished wafer and the polishing pad.

In the state of the art, CMP compositions comprising a glycoside in general are known and described, for instance, in the following references.

US 6 616 514 discloses a CMP slurry comprising (a) an abrasive, (b) an aqueous medium, and (c) a further specified organic polyol that does not dissociate protons. Examples of such polyols include mannitol, sorbitol, mannose, xylitol, sorbose, sucrose, and dextrin.

US 6 866 793 discloses a CMP slurry comprising (a) bulk solution, (b) plurality of particles, and (c) at least one selective adsorption additive which is further specified in a specific concentration, wherein this adsorption additive may comprise a non-ionic surfactant. Examples of non-ionic surfactants include – inter alia – sugar alkylate and sugar ester.

US 6 974 777 discloses a method of polishing a substrate comprising:
(i) contacting a substrate comprising (A) a metal layer selected from the group consisting of copper, tantalum, titanium, tungsten, nickel, platinum, ruthenium, iridium, and rhodium, and (B) a dielectric layer with a CMP system comprising:

(a) (1) an abrasive selected from the group consisting of alumina, silica, co-formed products thereof, coated metal oxide particles, polymer particles, and combinations thereof, (2) a polishing pad, or (3) a combination of the items (1) and (2),

(b) an amphiphilic nonionic surfactant,
(c) an oxidizing agent, and
(d) a liquid carrier,
(ii) abrading at least a portion of the substrate to polish the substrate. The amphiphilic nonionic surfactant can be

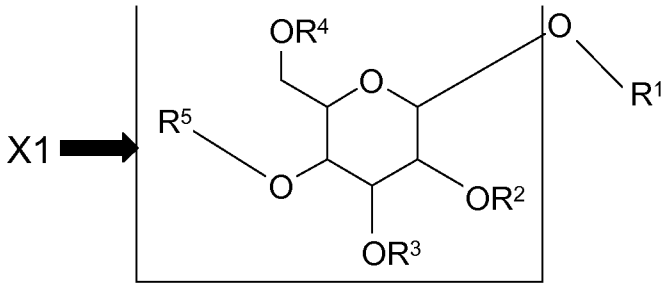
- a sorbitan alkyl acid ester or a polyoxyethylenesorbitan alkyl acid ester, or
- an alkyl polyglucose (e.g., Plantaren® surfactants available from Henkel), or an ethoxylate ester or diester of an alkyl glucose (e.g., PEG-120 methyl glucose dioleate and the like, available from Amerchol).

US 7 071 105 discloses a CMP system comprising (a) ceria, (b) a specific polishing additive bearing a functional group with a pK_a of about 4 to about 9, and (c) a liquid carrier, wherein the polishing system has a pH of about 7 or less and does not contain a significant amount of cross-linked polymer abrasive particles that are electrostatically associated with the inorganic abrasive. This CMP system may optionally further comprise a surfactant, and suitable non-ionic surfactants are for example sorbitan C_{6-30} alkyl acid esters or polyoxyethylenesorbitan C_{6-30} alkyl acid esters.

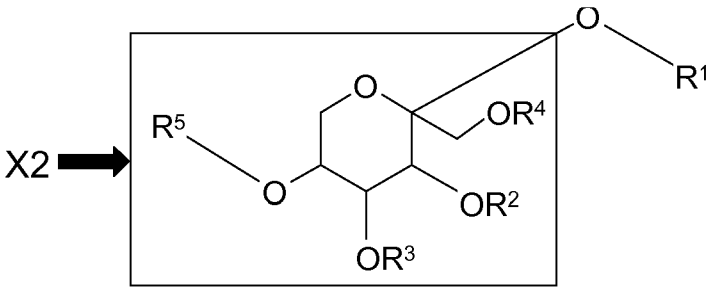
One of the objects of the present invention was to provide a CMP composition appropriate for the CMP of surfaces of dielectric substrates and/or showing an improved polishing performance, particularly the combination of high material removal rate (MRR) of silicon dioxide and low MRR of silicon nitride or polysilicon. Furthermore, A CMP composition was sought that would result in a high step height reduction (SHR) and would be ready-to-use.

Furthermore, a respective CMP process was to be provided.

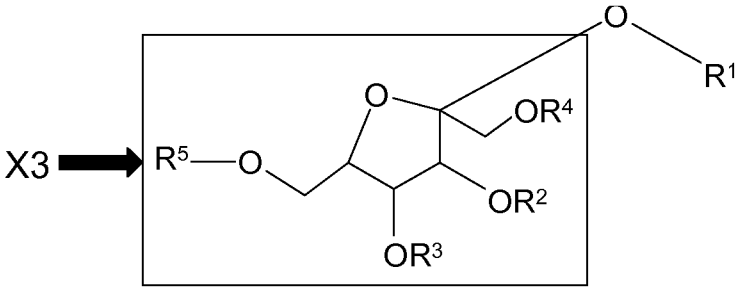
Accordingly, a CMP composition was found which comprises
(A) inorganic particles, organic particles, or a mixture or composite thereof,
(B) a glycoside of the formulae 1 to 6



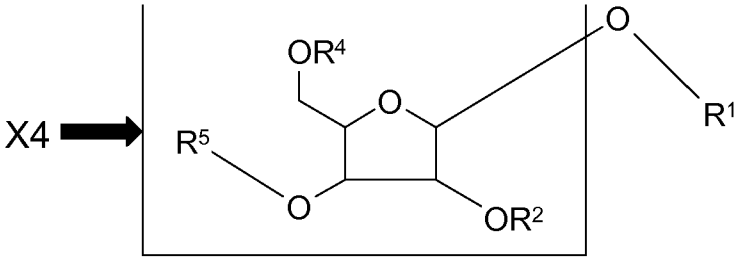
(formula 1)



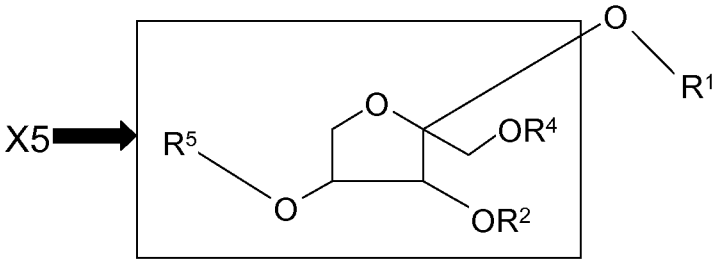
(formula 2)



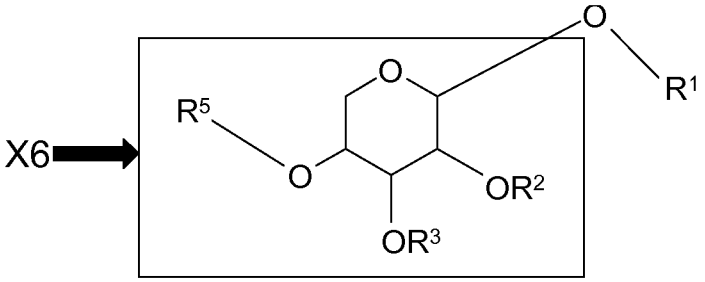
(formula 3)



(formula 4)



(formula 5)



(formula 6)

wherein R^1 is alkyl, aryl, or alkylaryl,
R^2 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^3 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^4 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,

R^5 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,

the total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) in the glycoside is in the range of from 1 to 20,

and X1 to X6 are the structural units as indicated in the rectangles in the corresponding formulae 1 to 6,

and

(C) an aqueous medium.

In addition, the above-mentioned objects of the invention are achieved by a process for the manufacture of a semiconductor device comprising the polishing of a substrate in the presence of said CMP composition.

Moreover, the use of the CMP composition of the invention for polishing substrates which are used in the semiconductor industry has been found, which fulfills the objects of the invention.

Preferred embodiments are explained in the claims and the specification. It is understood that combinations of preferred embodiments are within the scope of the present invention.

A semiconductor device can be manufactured by a process which comprises the CMP of a substrate in the presence of the CMP composition of the invention. Preferably, said process comprises the CMP of a dielectric substrate, that is a substrate having a dielectric constant of less than 6. Said process comprises more preferably the CMP of a substrate comprising silicon dioxide, most preferably the CMP of a substrate comprising silicon dioxide and silicon nitride or polysilicon, particularly the CMP of a silicon dioxide layer of a substrate which is a shallow trench isolation (STI) device or a part thereof, for example the CMP of a silicon dioxide layer of a substrate comprising silicon dioxide and silicon nitride or polysilicon.

If said process comprises the CMP of a substrate comprising silicon dioxide and silicon nitride, the selectivity of silicon dioxide to silicon nitride with regard to the material removal rate is preferably higher than 15:1, more preferably higher than 25:1, most preferably higher than 35:1, for example higher than 50:1. This selectivity can be adjusted by the type and concentration of glycoside (B) and by setting other parameters such as pH value.

If said process comprises the CMP of a substrate comprising silicon dioxide and polysilicon, the selectivity of silicon dioxide to polysilicon with regard to the material removal rate is preferably higher than 15:1, more preferably higher than 25:1, most preferably higher than 35:1, for example higher than 50:1. This selectivity can be adjusted by the type and concentration of glycoside (B) and by setting other parameters such as pH value.

The CMP composition of the invention is used for polishing any substrate used in the semiconductor industry. Said CMP composition is used preferably for polishing a dielectric substrate,

that is a substrate having a dielectric constant of less than 6, more preferably for polishing a substrate comprising silicon dioxide, most preferably for polishing a substrate comprising silicon dioxide and silicon nitride or polysilicon, particularly for polishing a silicon dioxide layer of a substrate which is a shallow trench isolation (STI) device or a part thereof, and for example for polishing a silicon dioxide layer of a substrate comprising silicon dioxide and silicon nitride or polysilicon.

If the CMP composition of the invention is used for polishing a substrate comprising silicon dioxide and silicon nitride, the selectivity of silicon dioxide to silicon nitride with regard to the material removal rate is preferably higher than 15:1, more preferably higher than 25:1, most preferably higher than 35:1, for example higher than 50:1.

If the CMP composition of the invention is used for polishing a substrate comprising silicon dioxide and polysilicon, the selectivity of silicon dioxide to polysilicon with regard to the material removal rate is preferably higher than 15:1, more preferably higher than 25:1, most preferably higher than 35:1, for example higher than 50:1.

According to the invention, the CMP composition contains inorganic particles, organic particles, or a mixture or composite thereof (A). (A) can be

- of one type of inorganic particles,
- a mixture or composite of different types of inorganic particles,
- of one type of organic particles,
- a mixture or composite of different types of organic particles, or
- a mixture or composite of one or more types of inorganic particles and one or more types of organic particles.

A composite is a composite particle comprising two or more types of particles in such a way that they are mechanically, chemically or in another way bound to each other. An example for a composite is a core-shell particle comprising one type of particle in the outer sphere (shell) and another type of particle in the inner sphere (core). If a core-shell particle is used as particles (A), a core-shell particle comprising a SiO_2 core and a CeO_2 shell is preferred, and particularly, a raspberry-type coated particle comprising a SiO_2 core with a mean core size of from 20 to 200 nm wherein the core is coated with CeO2 particles having a mean particle size below 10 nm is preferred. The particle sizes are determined using laser diffraction techniques and dynamic light scattering techniques.

Generally, the particles (A) can be contained in varying amounts. Preferably, the amount of (A) is not more than 10% by weight (referred to as “wt.%” in the following), more preferably not more than 5 wt.%, most preferably not more than 2 wt.%, for example not more than 0.75 wt.%, based on the total weight of the corresponding composition. Preferably, the amount of (A) is at

least 0.005 wt.%, more preferably at least 0.01 wt.%, most preferably at least 0.05 wt.%, for example at least 0.1 wt.%, based on the total weight of the corresponding composition.

Generally, the particles (A) can be contained in varying particle size distributions. The particle size distributions of the particles (A) can be monomodal or multimodal. In case of multimodal particle size distributions, bimodal is often preferred. In order to have an easily reproducible property profile and easily reproducible conditions during the CMP process of the invention, a monomodal particle size distribution is preferred for (A). It is most preferred for (A) to have a monomodal particle size distribution.

The mean particle size of the particles (A) can vary within a wide range. The mean particle size is the d_{50} value of the particle size distribution of (A) in the aqueous medium (C) and can be determined using dynamic light scattering techniques. Then, the d_{50} values are calculated under the assumption that particles are essentially spherical. The width of the mean particle size distribution is the distance (given in units of the x-axis) between the two intersection points, where the particle size distribution curve crosses the 50% height of the relative particle counts, wherein the height of the maximal particle counts is standardized as 100% height.

Preferably, the mean particle size of the particles (A) is in the range of from 5 to 500 nm, more preferably in the range of from 5 to 250 nm, most preferably in the range of from 50 to 150 nm, and in particular in the range of from 80 to 130 nm, as measured with dynamic light scattering techniques using instruments such as High Performance Particle Sizer (HPPS) from Malvern Instruments, Ltd. or Horiba LB550.

The particles (A) can be of various shapes. Thereby, the particles (A) may be of one or essentially only one type of shape. However, it is also possible that the particles (A) have different shapes. For instance, two types of differently shaped particles (A) may be present. For example, (A) can have the shape of cubes, cubes with chamfered edges, octahedrons, icosahedrons, nodules or spheres with or without protrusions or indentations. Preferably, they are spherical with no or only very few protrusions or indentations.

The chemical nature of particles (A) is not particularly limited. (A) may be of the same chemical nature or a mixture or composite of particles of different chemical nature. As a rule, particles (A) of the same chemical nature are preferred. Generally, (A) can be

- inorganic particles such as a metal, a metal oxide or carbide, including a metalloid, a metalloid oxide or carbide, or
- organic particles such as polymer particles,
- a mixture or composite of inorganic and organic particles.

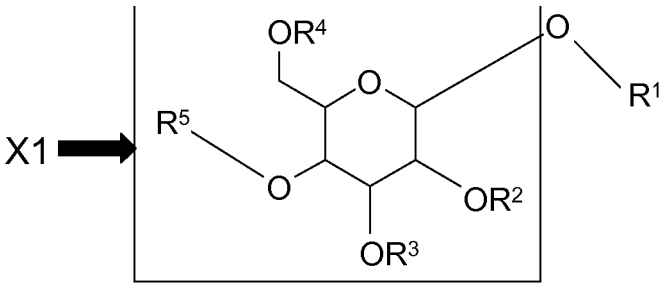
Particles (A) are preferably inorganic particles. Among them, oxides and carbides of metals or metalloids are preferred. More preferably, particles (A) are alumina, ceria, copper oxide, iron

oxide, nickel oxide, manganese oxide, silica, silicon nitride, silicon carbide, tin oxide, titania, titanium carbide, tungsten oxide, yttrium oxide, zirconia, or mixtures or composites thereof. Most preferably, particles (A) are alumina, ceria, silica, titania, zirconia, or mixtures or composites thereof. In particular, (A) are particles selected from the group consisting of ceria and composite particles comprising ceria. Particularly preferably, (A) are ceria. For example, (A) are colloidal ceria. Typically, colloidal ceria are produced by a wet precipitation process.

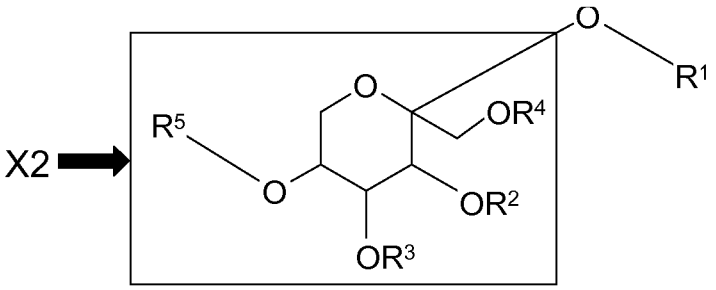
In another embodiment in which (A) are organic particles, or a mixture or composite of inorganic and organic particles, polymer particles are preferred. Polymer particles can be homo- or copolymers. The latter may for example be block-copolymers, or statistical copolymers. The homo- or copolymers may have various structures, for instance linear, branched, comb-like, dendrimeric, entangled or cross-linked. The polymer particles may be obtained according to the anionic, cationic, controlled radical, free radical mechanism and by the process of suspension or emulsion polymerisation. Preferably, the polymer particles are at least one of the polystyrenes, polyesters, alkyd resins, polyurethanes, polylactones, polycarbonates, poylacrylates, polymethacrylates, polyethers, poly(N-alkylacrylamide)s, poly(methyl vinyl ether)s, or copolymers comprising at least one of vinylaromatic compounds, acrylates, methacrylates, maleic anhydride acrylamides, methacrylamides, acrylic acid, or methacrylic acid as monomeric units, or mixtures or composites thereof. Among them, polymer particles with a cross-linked structure are preferred.

According to the invention, the CMP composition comprises

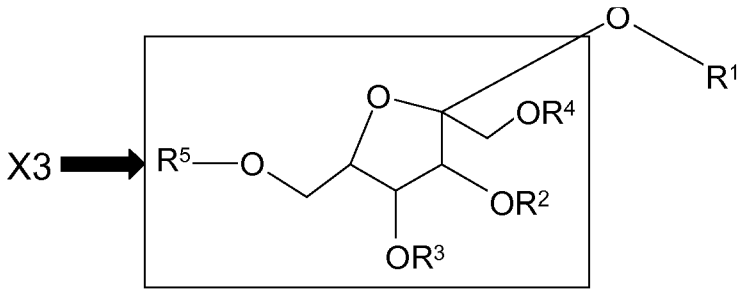
(B) a glycoside of the formulae 1 to 6:



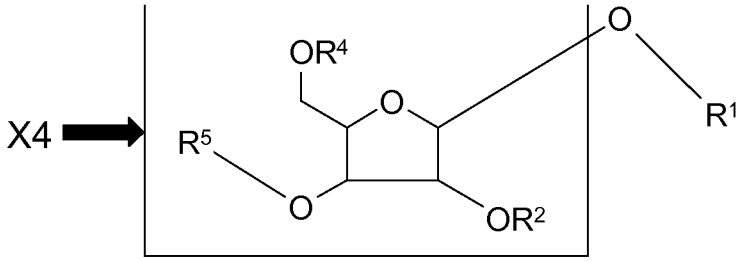
(formula 1)



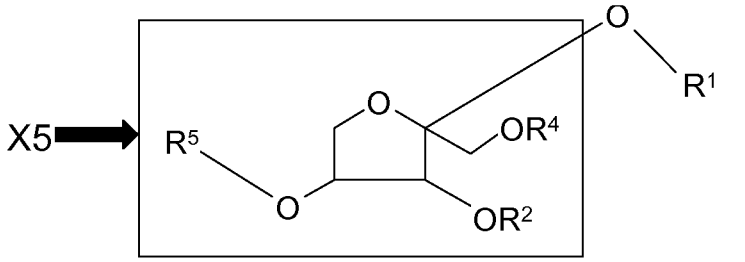
(formula 2)



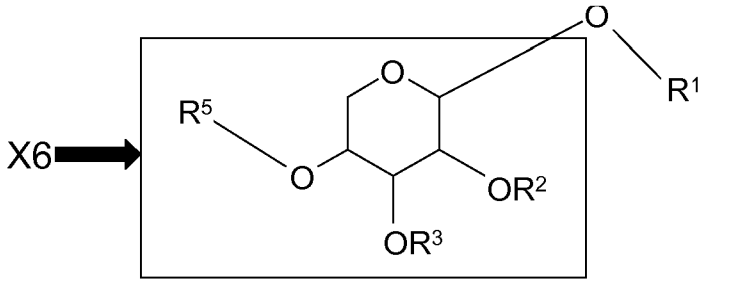
(formula 3)



(formula 4)



(formula 5)



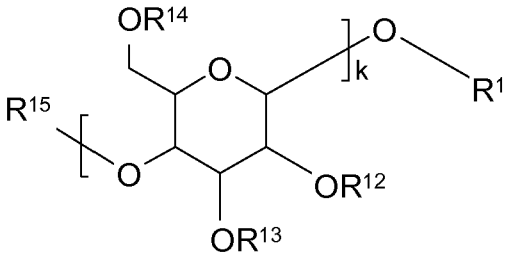
(formula 6)

wherein R^1 is alkyl, aryl, or alkylaryl,
R^2 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^3 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^4 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^5 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
the total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) in the glycoside is in the range of from 1 to 20,
and X1 to X6 are the structural units as indicated in the rectangles in the corresponding formulae 1 to 6.

The total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) in the glycoside is referred to as “monosaccharide-number” in the following.

The monosaccharide-number can vary within the range of from 1 to 20, and is preferably in the range of from 1 to 15, more preferably in the range of from 1 to 10, most preferably in the range of from 1 to 5, for example in the range of from 1 to 3.

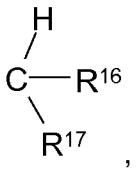
Preferably, (B) is a glycoside of the formulae 1 to 5. More preferably, (B) is a glycoside of the formulae 1 to 4. Most preferably, (B) is a glycoside of the formulae 1 to 3. Particularly preferably, (B) is a glycoside of the formulae 1 to 2. Particularly, (B) is a glycoside of formula 1. For example, (B) is a glycoside of formula 1a



(formula 1a)

wherein R^1 is alkyl, aryl or alkylaryl,
R^{12} is H, alkyl, aryl or alkylaryl,
R^{13} is H, alkyl, aryl or alkylaryl,
R^{14} is H, alkyl, aryl or alkylaryl,
R^{15} is H, alkyl, aryl or alkylaryl,
k is an integer from 1 to 20.

R^1 can generally be any substituted or unsubstituted alkyl, aryl or alkylaryl group. Preferably, R^1 is



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wherein R^{16} is H, alkyl, aryl or alkylaryl, and preferably alkyl,
R^{17} is H, alkyl, aryl or alkylaryl, and preferably alkyl.

More preferably, R^1 is CH_2R^{18}, wherein R^{18} is H, alkyl, aryl or alkylaryl, and preferably alkyl.

R^1 can generally be any substituted or unsubstituted alkyl, aryl or alkylaryl group having various numbers of carbon atoms. Preferably, R^1 is C_1-C_{30} alkyl, C_1-C_{30} alkylaryl, or C_1-C_{30} aryl, more preferably R^1 is a C_1-C_{30} alkyl, most preferably, R^1 is a C_7-C_{17} alkyl, particularly, R^1 is an unsubstituted C_{10}-C_{16} alkyl, for example, R^1 is an unsubstituted C_{12}-C_{14} alkyl.

R^2 can generally be H, X1, X2, X3, X4, X5, X6, or any substituted or unsubstituted alkyl, aryl or alkylaryl group. If (B) is a glycoside of formula # (# = 1, 2, 3, 4, 5, or 6), R^2 is preferably H, X# or alkyl, more preferably H, X# or unsubstituted alkyl, and most preferably H or X#. For example, if (B) is a glycoside of formula 1, R^2 is preferably H, X1 or alkyl, more preferably H, X1 or unsubstituted alkyl, and most preferably H or X1.

R^3 can generally be H, X1, X2, X3, X4, X5, X6, or any substituted or unsubstituted alkyl, aryl or alkylaryl group. If (B) is a glycoside of formula # (# = 1, 2, 3, 4, 5, or 6), R^3 is preferably H, X# or alkyl, more preferably H, X# or unsubstituted alkyl, and most preferably H or X#. For example, if (B) is a glycoside of formula 1, R^3 is preferably H, X1 or alkyl, more preferably H, X1 or unsubstituted alkyl, and most preferably H or X1.

R^4 can generally be H, X1, X2, X3, X4, X5, X6, or any substituted or unsubstituted alkyl, aryl or alkylaryl group. If (B) is a glycoside of formula # (# = 1, 2, 3, 4, 5, or 6), R^4 is preferably H, X# or alkyl, more preferably H, X# or unsubstituted alkyl, and most preferably H or X#. For example, if (B) is a glycoside of formula 1, R^4 is preferably H, X1 or alkyl, more preferably H, X1 or unsubstituted alkyl, and most preferably H or X1.

R^5 can generally be H, X1, X2, X3, X4, X5, X6, or any substituted or unsubstituted alkyl, aryl or alkylaryl group. If (B) is a glycoside of formula # (# = 1, 2, 3, 4, 5, or 6), R^5 is preferably H, X# or alkyl, more preferably H, X# or unsubstituted alkyl, and most preferably H or X#. For example, if (B) is a glycoside of formula 1, R^5 is preferably H, X1 or alkyl, more preferably H, X1 or unsubstituted alkyl, and most preferably H or X1.

R^{12} can generally be H or any substituted or unsubstituted alkyl, aryl or alkylaryl group. R^{12} is preferably H or alkyl, more preferably H or unsubstituted alkyl, and most preferably H.

R^{13} can generally be H or any substituted or unsubstituted alkyl, aryl or alkylaryl group. R^{13} is preferably H or alkyl, more preferably H or unsubstituted alkyl, and most preferably H.

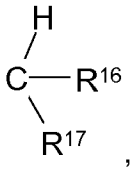
R^{14} can generally be H or any substituted or unsubstituted alkyl, aryl or alkylaryl group. R^{14} is preferably H or alkyl, more preferably H or unsubstituted alkyl, and most preferably H.

R^{15} can generally be H or any substituted or unsubstituted alkyl, aryl or alkylaryl group. R^{15} is preferably H or alkyl, more preferably H or unsubstituted alkyl, and most preferably H.

k is an integer from 1 to 20, preferably from 1 to 15, more preferably from 1 to 10, most preferably from 1 to 5, for example from 1 to 3.

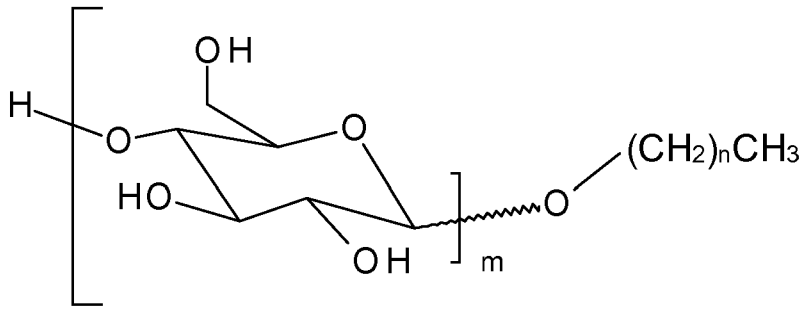
Generally, the glycoside (B) can be of one type or a mixture of different types of glycosides of the formulae 1 to 6. Preferably, (B) is one type of glycoside of the formulae 1 to 6. More preferably, (B) is a glycoside of the formulae 1 to 6, wherein R^2, R^3, R^4 and R^5 is – independently from

each other – H, X1, X2, X3, X4, X5, or X6. Most preferably, (B) is a glycoside of formula 1 wherein R^2 is H or X1, R^3 is H or X1, R^4 is H or X1, R^5 is H or X1. Particularly preferably, (B) is a glycoside of formula 1a wherein R^{12}, R^{13}, R^{14} and R^{15} is H and wherein R^1 is



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wherein R^{16} is H, alkyl, aryl or alkylaryl, R^{17} is H, alkyl, aryl or alkylaryl. Particularly, (B) is a glycoside of the formulae 1a wherein R^{12}, R^{13}, R^{14} and R^{15} is H and wherein R^1 is CH_2R^{18}, wherein R^{18} is H, alkyl, aryl or alkylaryl. For example, (B) is Lutensol GD70 (a BASF product, which is an aqueous solution of alkylglucoside of formula 7 with m = 1 to 3 and n = 9 to 15), Glucopon 600 CS UP (a Cognis product, which is an aqueous solution of alkylglucoside of formula 7 with m = 1 to 3 and n = 11 to 13), Glucopon 215 CS (215 UP) (a Cognis product, which is an aqueous solution of alkylglucoside of formula 7 with m = 1 to 3 and n = 7 to 9), methyl galactopyranoside, and n-dodecyl beta-D-maltopyranoside.



(formula 7)

Preferably, the glycoside (B) is a glucoside, galactoside or mannoside. More preferably, (B) is a glucoside or galactoside. Most preferably, (B) is a glucoside. For example, (B) is a D-glucoside.

In a further preferred embodiment, (B) is a glycoside of the formula 1, wherein R^1 is alkyl, aryl, or alkylaryl, R^2 is H or X1, R^3 is H or X1, R^4 is H or X1, R^5 is H or X1, and wherein the monosaccharide-number is within the range of from 1 to 10, more preferably from 1 to 5, most preferably from 1 to 3.

In yet a further preferred embodiment, (B) is a glycoside of the formula 1, wherein R^1 is alkyl, R^2 is H or X1, R^3 is H or X1, R^4 is H or X1, R^5 is H or X1, and wherein the monosaccharide-number is within the range of from 1 to 10, more preferably from 1 to 5, most preferably from 1 to 3.

In general, the glycoside (B) can be contained in varying amounts. Preferably, the amount of (B) is not more than 10 wt.%, more preferably not more than 5 wt.%, most preferably not more than 2 wt.%, for example not more than 1 wt.%, based on the total weight of the corresponding com-

position. Preferably, the amount of (B) is at least 0.001 wt.%, more preferably at least 0.005 wt.%, most preferably at least 0.01 wt.%, for example at least 0.05 wt.%, based on the total weight of the corresponding composition.

In general, the solubility of the glycoside of the formulae 1 to 6 (B) in an aqueous medium can vary within a wide range. The solubility of (B) in water at pH 7 at 25°C under atmospheric pressure is preferably at least 1 g/L, more preferably at least 10 g/L, most preferably at least 70 g/L, particularly at least 200 g/L, for example at least 350 g/L. Said solubility can be determined by evaporating the solvent and measuring the remaining mass in the saturated solution.

In one embodiment, (B) is preferably a glycoside of formula 2, more preferably a psicoside, a sorboside, a tagatoside, or a fructoside, most preferably a fructoside, for example a D-fructoside.

In another embodiment, (B) is preferably a glycoside of formula 3, more preferably a psicoside, a sorboside, a tagatoside, or a fructoside, most preferably a fructoside, for example a D-fructoside

In another embodiment, (B) is preferably a glycoside of formula 4, more preferably a arabinoside, a lyxoside, a riboside, or a xyloside, most preferably a riboside, for example a D-riboside.

In another embodiment, (B) is preferably a glycoside of formula 5, more preferably a ribuloside or a xyluloside, most preferably a ribuloside, for example a D-ribuloside.

In another embodiment, (B) is preferably a glycoside of formula 6, more preferably a arabinoside, a lyxoside, a riboside, or a xyloside, most preferably a riboside, for example a D-riboside.

According to the invention, the CMP composition contains an aqueous medium (C). (C) can be of one type or a mixture of different types of aqueous media.

In general, the aqueous medium (C) can be any medium which contains water. Preferably, the aqueous medium (C) is a mixture of water and an organic solvent miscible with water (e.g. an alcohol, preferably a C_1 to C_3 alcohol, or an alkylene glycol derivative). More preferably, the aqueous medium (C) is water. Most preferably, aqueous medium (C) is de-ionized water.

If the amounts of the components other than (C) are in total x % by weight of the CMP composition, then the amount of (C) is (100–x) % by weight of the CMP composition.

The CMP composition of the invention can further optionally contain at least one corrosion inhibitor (D), for example two corrosion inhibitors. Preferred corrosion inhibitors are diazoles, triazoles, tetrazoles and their derivatives, for example benzotriazole or tolyltriazole. Other examples

for preferred corrosion inhibitors are acetylene alcohols, or a salt or an adduct of an amine and a carboxylic acid comprising an amide moiety.

If present, the corrosion inhibitor (D) can be contained in varying amounts. Preferably, the amount of (D) is not more than 10 wt.%, more preferably not more than 5 wt.%, most preferably not more than 2.5 wt.%, for example not more than 1.5 wt.%, based on the total weight of the corresponding composition. Preferably, the amount of (D) is at least 0.01 wt.%, more preferably at least 0.1 wt.%, most preferably at least 0.3 wt.%, for example at least 0.8 wt.%, based on the total weight of the corresponding composition.

The CMP composition of the invention can further optionally contain at least one oxidizing agent (E), for example one oxidizing agent. In general, the oxidizing agent is a compound which is capable of oxidizing the to-be-polished substrate or one of its layers. Preferably, (E) is a per-type oxidizer. More preferably, (E) is a peroxide, persulfate, perchlorate, perbromate, periodate, permanganate, or a derivative thereof. Most preferably, (E) is a peroxide or persulfate. Particularly, (E) is a peroxide. For example, (E) is hydrogen peroxide.

If present, the oxidizing agent (E) can be contained in varying amounts. Preferably, the amount of (E) is not more than 20 wt.%, more preferably not more than 10 wt.%, most preferably not more than 5 wt.%, for example not more than 2 wt.%, based on the total weight of the corresponding composition. Preferably, the amount of (E) is at least 0.05 wt.%, more preferably at least 0.1 wt.%, most preferably at least 0.5 wt.%, for example at least 1 wt.%, based on the total weight of the corresponding composition.

The CMP composition of the invention can further optionally contain at least one complexing agent (F), for example one complexing agent. In general, the complexing agent is a compound which is capable of complexing the ions of the to-be-polished substrate or of one of its layers. Preferably, (F) is a carboxylic acid having at least two COOH groups, an *N*-containing carboxylic acid, *N*-containing sulfonic acid, *N*-containing sulfuric acid, *N*-containing phosphonic acid, *N*-containing phosphoric acid, or a salt thereof. More preferably, (F) is a carboxylic acid having at least two COOH groups, an *N*-containing carboxylic acid, or a salt thereof. Most preferably, (F) is an amino acid, or a salt thereof. For example, (F) is glycine, serine, alanine, hystidine, or a salt thereof.

If present, the complexing agent (F) can be contained in varying amounts. Preferably, the amount of (F) is not more than 20 wt.%, more preferably not more than 10 wt.%, most preferably not more than 5 wt.%, for example not more than 2 wt.%, based on the total weight of the corresponding composition. Preferably, the amount of (F) is at least 0.05 wt.%, more preferably at least 0.1 wt.%, most preferably at least 0.5 wt.%, for example at least 1 wt.%, based on the total weight of the corresponding composition.

The CMP composition of the invention can further optionally contain at least one biocide (G), for example one biocide. In general, the biocide is a compound which deters, renders harmless, or exerts a controlling effect on any harmful organism by chemical or biological means. Preferably, (G) is an quaternary ammonium compound, an isothiazolinone-based compound, an *N*-substituted diazenium dioxide, or an *N*'-hydroxy-diazenium oxide salt. More preferably, (G) is an *N*-substituted diazenium dioxide, or an *N*'-hydroxy-diazenium oxide salt.

If present, the biocide (G) can be contained in varying amounts. If present, the amount of (G) is preferably not more than 0.5 wt.%, more preferably not more than 0.1 wt.%, most preferably not more than 0.05 wt.%, particularly not more than 0.02 wt.%, for example not more than 0.008 wt.%, based on the total weight of the corresponding composition. If present, the amount of (G) is preferably at least 0.0001 wt.%, more preferably at least 0.0005 wt.%, most preferably at least 0.001 wt.%, particularly at least 0.003 wt.%, for example at least 0.006 wt.%, based on the total weight of the corresponding composition.

The properties of the CMP compositions used or according to the invention respectively, such as stability and polishing performance, may depend on the pH of the corresponding composition. Preferably, the pH value of the compositions used or according to the invention respectively is in the range of from 3 to 9, more preferably from 4 to 9, and most preferably from 5 to 8.5, for example from 7 to 8.5.

The CMP compositions according to the invention respectively may also contain, if necessary, various other additives, including but not limited to pH adjusting agents, stabilizers, surfactants etc. Said other additives are for instance those commonly employed in CMP compositions and thus known to the person skilled in the art. Such addition can for example stabilize the dispersion, or improve the polishing performance, or the selectivity between different layers.

If present, said additive can be contained in varying amounts. Preferably, the amount of said additive is not more than 10 wt.%, more preferably not more than 1 wt.%, most preferably not more than 0.1 wt.%, for example not more than 0.01 wt.%, based on the total weight of the corresponding composition. Preferably, the amount of said additive is at least 0.0001 wt.%, more preferably at least 0.001 wt.%, most preferably at least 0.01 wt.%, for example at least 0.1 wt.%, based on the total weight of the corresponding composition.

According to one embodiment, the CMP composition of the invention comprises:

(A) inorganic particles, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,
(B) a glycoside of the formula 1a, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,
(C) an aqueous medium.

According to a further embodiment, the CMP composition of the invention comprises:

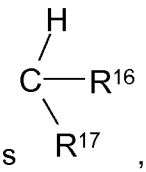
(A) particles selected from the group consisting of ceria and composite particles comprising ceria, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(B) a glycoside of the formula 1a which is a glucoside, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(C) an aqueous medium.

According to a further embodiment, the CMP composition of the invention comprises:

(A) alumina, ceria, silica, titania, zirconia, or a mixture or composite thereof, in a concentration of from 0.01 to 5 wt.% based on the total weight of the corresponding CMP composition,

(B) a glycoside of the formula 1a, wherein R^1 is ,
R^{16} is alkyl, aryl or alkylaryl,
R^{17} is alkyl, aryl or alkylaryl,
in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(C) an aqueous medium.

According to a further embodiment, the CMP composition of the invention comprises:

(A) particles selected from the group consisting of ceria and composite particles comprising ceria, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(B) a glycoside of the formula 1a, wherein R^1 is CH_2R^{18},
R^{18} is H, alkyl, aryl or alkylaryl,
in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(C) an aqueous medium.

According to a further embodiment, the CMP composition of the invention comprises:

(A) particles selected from the group consisting of ceria and composite particles comprising ceria, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(B) a glycoside of the formula 1a, wherein R^{12}, R^{13}, R^{14} and R^{15} is H, in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(C) an aqueous medium.

According to a further embodiment, the CMP composition of the invention comprises:

(A) ceria in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(B) a glycoside of the formula 1a in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(C) an aqueous medium.

According to a further embodiment, the CMP composition of the invention comprises:

(A) ceria in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(B) a glycoside of the formula 1a wherein R^1 is CH_2R^{18},
R^{18} is H, alkyl, aryl or alkylaryl,
R^{12}, R^{13}, R^{14} and R^{15} is H,
in a concentration of from 0.01 to 5 wt.%, based on the total weight of the corresponding CMP composition,

(C) an aqueous medium.

Processes for preparing CMP compositions are generally known. These processes may be applied to the preparation of the CMP composition of the invention. This can be carried out by dispersing or dissolving the above-described components (A) and (B) in the aqueous medium (C), preferably water, and optionally by adjusting the pH value through adding an acid, a base, a buffer or an pH adjusting agent. For this purpose the customary and standard mixing processes and mixing apparatuses such as agitated vessels, high shear impellers, ultrasonic mixers, homogenizer nozzles or counterflow mixers, can be used.

The CMP composition of the invention is preferably prepared by dispersing the particles (A), dispersing and/or dissolving a glycoside (B) and optionally further additives in the aqueous medium (C).

The polishing process is generally known and can be carried out with the processes and the equipment under the conditions customarily used for the CMP in the fabrication of wafers with integrated circuits. There is no restriction on the equipment with which the polishing process can be carried out.

As is known in the art, typical equipment for the CMP process consists of a rotating platen which is covered with a polishing pad. Also orbital polishers have been used. The wafer is mounted on a carrier or chuck. The side of the wafer being processed is facing the polishing pad (single side polishing process). A retaining ring secures the wafer in the horizontal position.

Below the carrier, the larger diameter platen is also generally horizontally positioned and presents a surface parallel to that of the wafer to be polished. The polishing pad on the platen contacts the wafer surface during the planarization process.

To produce material loss, the wafer is pressed onto the polishing pad. Both the carrier and the platen are usually caused to rotate around their respective shafts extending perpendicular from the carrier and the platen. The rotating carrier shaft may remain fixed in position relative to the rotating platen or may oscillate horizontally relative to the platen. The direction of rotation of the carrier is typically, though not necessarily, the same as that of the platen. The speeds of rotation for the carrier and the platen are generally, though not necessarily, set at different values. During the CMP process of the invention the CMP composition of the invention is usually applied onto the polishing pad as a continuous stream or in dropwise fashion. Customarily, the temperature of the platen is set at temperatures of from 10 to 70°C.

The load on the wafer can be applied by a flat plate made of steel for example, covered with a soft pad that is often called backing film. If more advanced equipment is being used a flexible membrane that is loaded with air or nitrogen pressure presses the wafer onto the pad. Such a membrane carrier is preferred for low down force processes when a hard polishing pad is used, because the down pressure distribution on the wafer is more uniform compared to that of a carrier with a hard platen design. Carriers with the option to control the pressure distribution on the wafer may also be used according to the invention. They are usually designed with a number of different chambers that can be loaded to a certain degree independently from each other.

For further details reference is made to WO 2004/063301 A1, in particular page 16, paragraph [0036] to page 18, paragraph [0040] in conjunction with the figure 2.

By way of the CMP process of the invention and/or using the CMP composition of the invention, wafers with integrated circuits comprising a dielectric layer can be obtained which have an excellent functionality.

The CMP composition of the invention can be used in the CMP process as ready-to-use slurry, they have a long shelf-life and show a stable particle size distribution over long time. Thus, they are easy to handle and to store. They show an excellent polishing performance, particularly with regard to the combination of high material removal rate (MRR) of silicon dioxide and low MRR of silicon nitride or polysilicon. Since the amounts of its components are held down to a minimum, the CMP composition according to the invention respectively can be used in a cost-effective way.

Figure 1 shows the correlation diagram regarding SiO_2/Si_3N_4 selectivity versus additive concentration in the CMP process using the compositions of the examples 4 to 6 and of the comparative examples V1 to V4; Data for the additive sorbitol (comparative examples) are shown as black rhombs, and data for the additive B1 which is Lutensol GD70 (examples of the invention) are shown as black squares; X is the concentration of the additive in weight percent, based on the total weight of the corresponding composition; Y1 is the SiO_2/Si_3N_4 selectivity; The data points for X = 0 corresponds to comparative Example V1; detailed data see table 1; The coeffi-

cient of determination R^2 for the linear extrapolation of the sorbitol data (see black bold line) is 0.94.

Figure 2 shows the Si_3N_4 material removal rate in the CMP process using the compositions of the examples 4 to 6 and of the comparative examples V1 to V5; Data for the additive sorbitol (comparative examples) are shown as black rhombs, and data for the additive B1 which is Lutensol GD70 (examples of the invention) are shown as black squares; X is the concentration of the additive in weight percent, based on the total weight of the corresponding composition; Y2 is the Si_3N_4 material removal rate in Angström per minute; The data points for X = 0 corresponds to comparative Example V1; detailed data see table 1.

Figure 3 shows the PolySi material removal rate in the CMP process using the compositions of the examples 4 to 6 and of the comparative examples V1 to V5; Data for the additive sorbitol (comparative examples) are shown as black rhombs, and data for the additive B1 which is Lutensol GD70 (examples of the invention) are shown as black squares; X is the concentration of the additive in weight percent, based on the total weight of the corresponding composition; Y3 is the polySi material removal rate in Angström per minute; The data points for X = 0 corresponds to comparative Example V1; detailed data see table 1.

Examples and Comparative Examples

The general procedure for the CMP experiments is described below.

Standard CMP process for 200 mm SiO_2 wafers:

Strasbaugh nSpire (Model 6EC), ViPRR floating retaining ring Carrier;

down pressure:	3.0 psi (210 mbar) for the CMP process using the compositions of all Examples other than Example 16; 2.0 psi (138 mbar) for the CMP proess using the composition of Example 16;
back side pressure:	0.5 psi (34.5 mbar);
retaining ring pressure:	2.5 psi (172 mbar);
polishing table / carrier speed:	95 / 85 rpm;
slurry flow rate:	200 ml / min;
polishing time:	60 s;
pad conditioning:	in situ, 6.0 lbs (27 N) for the CMP process using the compositions of all Examples other than Example 16; in situ, 4.0 lbs (18 N) for the CMP process using the composition of Example 16;
polishing pad:	IC1000 A2 on Suba 4 stacked pad, xy k or k grooved (R&H);

backing film:	Strasbaugh, DF200 (136 holes);
conditioning disk:	3M S60;

The pad is conditioned by three sweeps, before a new type of slurry is used for CMP. The slurry is stirred in the local supply station.

Standard analysis procedure for (semi) transparent blanket wafers:

The removal is determined by optical film thickness measurement using Filmmetrics F50. 49 points diameter scans (5 mm edge exclusion) are measured pre and post CMP for each wafer. For each point on the wafer that was measured with F50 the film thickness loss is calculated from the difference of the film thickness pre and post CMP The average of the resulting data from the 49 point diameter scans gives the total removal, the standard deviation gives the (non-) uniformity.

For the removal rate the quotient of the total material removal and the time of the main polishing step is used.
Standard films used for CMP experiments:

SiO_2 films:	PE TEOS;
Si_3N_4 films:	PE CVD for the CMP process using the compositions of all Examples other than Example 16; LP CVD for the CMP process using the composition of Example 16;
Poly Si films:	CVD;

Standard procedure for slurry preparation:

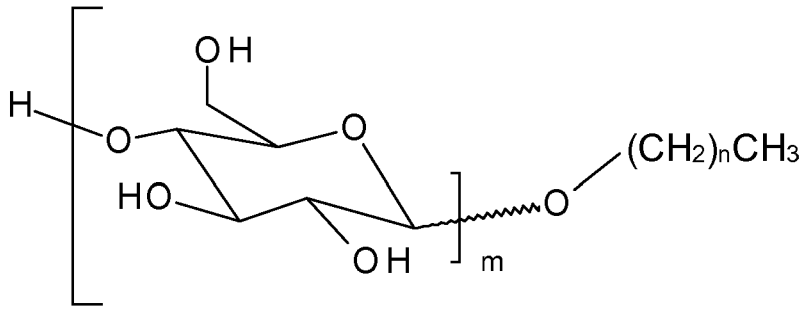
pH is adjusted by adding of aqueous ammonia solution (0.1%) or HNO_3 (0.1 %) to the slurry. The pH value is measured with a pH combination electrode (Schott, blue line 22 pH).

Inorganic particles (A) used in the Examples

Colloidal ceria particles (Rhodia HC60) having a mean primary particle size of 60 nm (as determined using BET surface area measurements) and having a mean secondary particle size (d50 value) of 99 nm (as determined using dynamic light scattering techniques via a Horiba instrument) were used.

Glycoside (B) used in the Examples

Glycosides B1 to B3 can be represented by the below formula (formula 7):



(formula 7)

Glycoside B1: Lutensol GD70, a BASF product, which is an aqueous solution of alkylglucoside of formula 7 with m = 1 to 3 and n = 9 to 15

Glycoside B2: Glucopon 600 CS UP, a Cognis product, which is an aqueous solution of alkylglucoside of formula 7 with m = 1 to 3 and n = 11 to 13

Glycoside B3: Glucopon 215 CS (215 UP), a Cognis product, which is an aqueous solution of alkylglucoside of formula 7 with m = 1 to 3 and n = 7 to 9

Glycoside B4: methyl galactopyranoside

Glycoside B5: n-dodecyl beta-D-maltopyranoside, obtained from Acros Organics.

Table 1: CMP compositions of the examples 1 to 15 and of the comparative examples V1 to V5, their pH values as well as their MRR (material removal rate) and selectivity data in the CMP process using these compositions, wherein the aqueous medium (C) is de-ionized water (B1 is Lutensol GD70, B2 is Glucopon 600 CS UP, B3 is Glucopon 215 CS (215 UP) and B4 is methyl galactopyranoside; conc. = concentration; wt% = percent by weight; polySi = polysilicon)

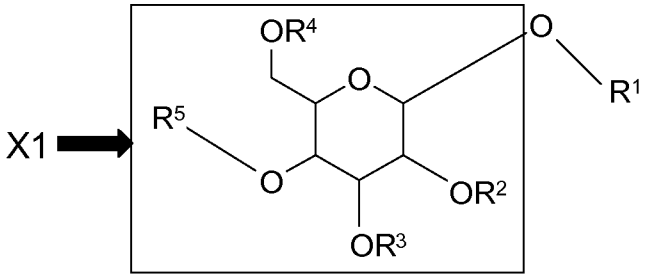
Example	Additive	Additive conc. [wt%]	pH [ ]	conc. of Rhodia HC60 [wt%]	MRR SiO_2 [Å/min]	MRR Si_3N_4 [Å/min]	MRR polySi [Å/min]	Selectivity Si_3N_4 [ ]	Selectivity poly-Si [ ]
Comparative Example V1	-	0	5.5	0.5	5480	475	441	12	12
Example 1	B1	0.1	4	0.5	5417	165	126	33	43
Example 2	B1	0.1	5	0.1	3453	56	90	62	38
Example 3	B1	0.5	5	0.5	4610	54	99	85	47
Example 4	B1	0.1	5.5	0.5	6274	134	124	47	51
Example 5	B1	0.25	5.5	0.5	5161	55	96	94	54
Example 6	B1	1.0	5.5	0.5	3070	43	83	71	37
Example 7	B1	0.5	5.5	0.1	2348	25	24	94	98
Example 8	B1	0.5	7.8	0.5	4172	66	96	63	43

Example 9	B1	0.5	7.8	0.1	1527	25	20	61	76
Example 10	B2	0.05	5.0	0.5	4737	177	149	27	32
Example 11	B2	0.1	5.5	0.5	5366	68	130	79	41
Example 12	B3	0.2	5.5	0.5	4001	53	84	75	48
Example 13	B3	0.5	5.5	0.1	1209	28	43	43	28
Example 14	B4	0.1	4	0.1	3238	62	450	52	7
Example 15	B4	0.2	5	0.1	2711	65	290	42	9
Example 16	B5	0.1	4	0.5	3032	17	–	178	–
Comparative Example V2	Sor-bitol	0.25	5.5	0.5	5608	360	461	16	12
Comparative Example V3	Sor-bitol	0.5	5.5	0.5	5330	303	440	18	12
Comparative Example V4	Sor-bitol	1	5.5	0.5	5249	255	448	21	12
Comparative Example V5	Sor-bitol	2	5.5	0.5	3853	198	453	19	9

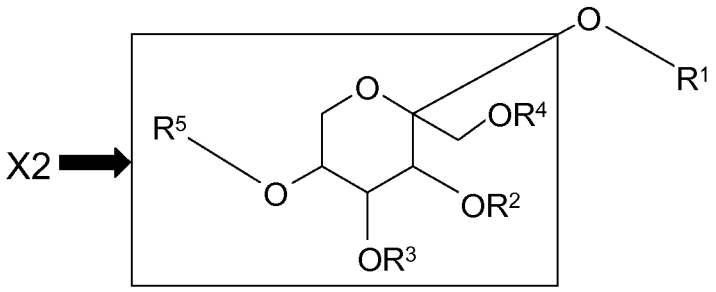
These examples of the CMP compositions of the invention improve the polishing performance.

Claims:

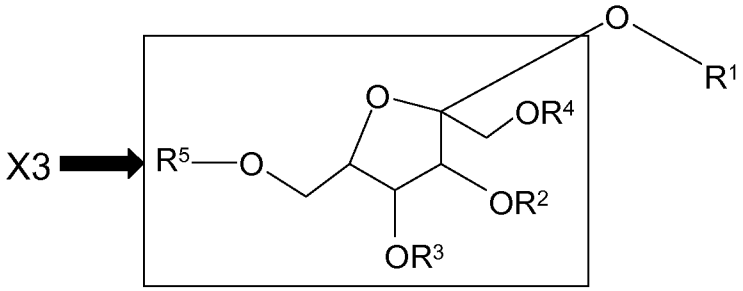
1. A chemical mechanical polishing (CMP) composition comprising
   (A) particles selected from the group consisting of ceria and composite particles comprising ceria,
   (B) a glycoside of the formulae 1 to 6



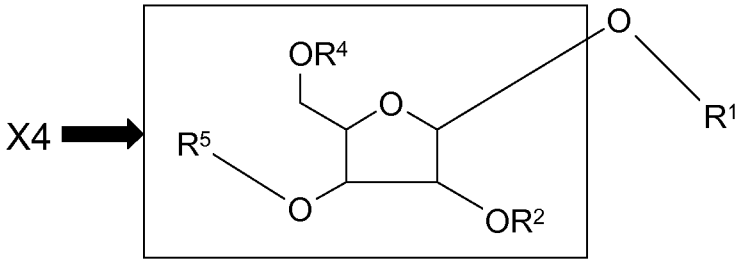
(formula 1)



(formula 2)

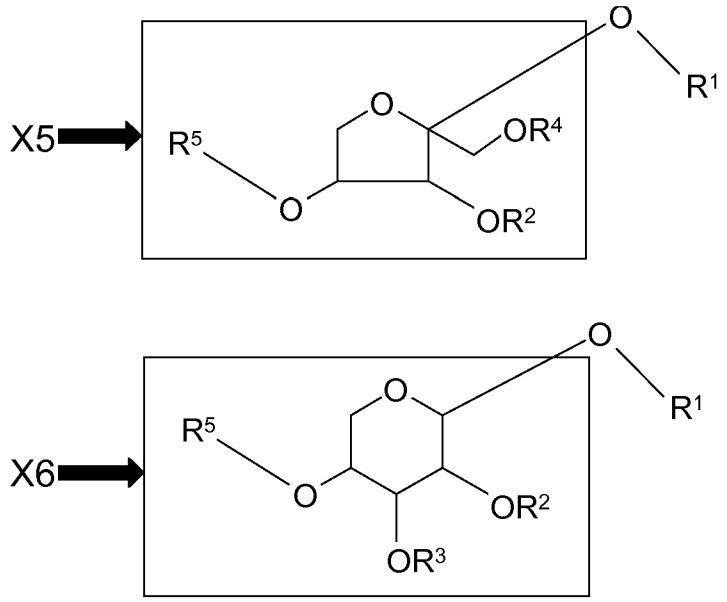


(formula 3)



(formula 4)

(formula 5)



(formula 6)

wherein R^1 is alkyl, aryl, or alkylaryl,
R^2 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^3 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^4 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
R^5 is H, X1, X2, X3, X4, X5, X6, alkyl, aryl, or alkylaryl,
the total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) in the glycoside is in the range of from 1 to 20,
and X1 to X6 are the structural units as indicated in the rectangles in the corresponding formulae 1 to 6,

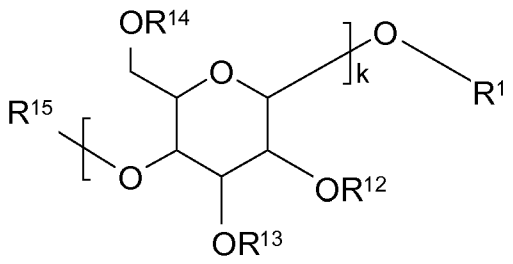
and

(C) an aqueous medium.

2. The CMP composition according to claim 1, wherein the total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) in the glycoside (B) is in the range of from 1 to 5.

3. The CMP composition according to claim 1 or 2, wherein the glycoside is a glycoside of formula 1 and wherein R^1 is alkyl, aryl, or alkylaryl, R^2 is H or X1, R^3 is H or X1, R^4 is H or X1, R^5 is H or X1.

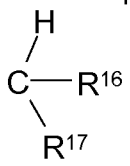
4. The CMP composition according to claim 1, wherein the glycoside is a glycoside of formula 1a



(formula 1a)

wherein R^1 is alkyl, aryl or alkylaryl,
R^{12} is H, alkyl, aryl or alkylaryl,
R^{13} is H, alkyl, aryl or alkylaryl,
R^{14} is H, alkyl, aryl or alkylaryl,
R^{15} is H, alkyl, aryl or alkylaryl,
k is an integer from 1 to 20,

5. The CMP composition according to claim 4, wherein



R^1 is
R^{16} is H, alkyl, aryl or alkylaryl,
R^{17} is H, alkyl, aryl or alkylaryl.

6. The CMP composition according to claim 4 wherein R^1 is CH_2R^{18}, and R^{18} is H, alkyl, aryl or alkylaryl.

7. The CMP composition according to anyone of the claims 4 to 6, wherein R^{12}, R^{13}, R^{14} and R^{15} is H.

8. The CMP composition according to anyone of the claims 4 to 7, wherein k is an integer from 1 to 5.

9. The CMP composition according to anyone of the claims 1 to 8, wherein the particles (A) is ceria.

10. The CMP composition according to anyone of the claims 1 to 9, wherein the concentration of the glycoside (B) is in the range of from 0.01 % to 2 % by weight of the CMP composition.

11. The CMP composition according to anyone of the claims 1 to 10, wherein the glycoside (B) is a glucoside.

12. The CMP composition according to anyone of the claims 1 to 11, wherein the pH value of the CMP composition is in the range of from 5 to 8.5.

13. The CMP composition according to claim 4, wherein
(A) is ceria,
(B) is a glycoside of the formula 1a
wherein R^1 is CH_2R^8, and R^8 is C_3-C_{29} alkyl, or phenyl,
R^2, R^3, R^4 and R^5 is H,
k is an integer from 1 to 5,
(C) is water.

14. A process for the manufacture of semiconductor devices comprising the chemical mechanical polishing of a substrate comprising silicon dioxide in the presence of a CMP composition as defined in anyone of the claims 1 to 13.

15. Use of a CMP composition as defined in anyone of the claims 1 to 13 for chemical mechanical polishing of a substrate comprising silicon dioxide and silicon nitride or polysilicon.