CMP composition comprising abrasive particles containing ceria

Description

The present invention relates to a chemical-mechanical polishing (CMP) composition comprising abrasive particles containing ceria, a process for preparing a CMP composition according to the present invention, a process for the manufacture of a semiconductor device comprising chemical mechanical polishing of a substrate in the presence of a chemical mechanical polishing (CMP) composition according to the present invention, to the use of specific polymers for suppressing the agglomeration and/or adjusting the zeta potential of ceria containing particles dispersed in aqueous medium and to a process for suppressing the agglomeration and/or adjusting the zeta potential of ceria containing particles dispersed in aqueous medium.

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 planarize surfaces. Chemical action is provided by a chemical composition, also referred to as a CMP slurry or a CMP composition. 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, and by abrasive particles which are dispersed in the CMP composition. 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 substrate in contact with a polishing pad. The CMP composition is usually applied between the substrate' s surface to-be-polished and the polishing pad.

Particularly in the fabrication of integrated circuits and microelectromechanical devices, very high requirements have to be met for the CMP process step, which is carried out at each level of a multileveled structure. One important parameter describing these requirements is the material removal rate (MRR) i.e. the speed with which the to-be-polished material is removed.

The CMP compositions typically used in this field contain particles of inorganic materials, which serve as abrasives, and various further components. For certain CMP applications, colloidal ceria containing particles are used as abrasive. Ceria-based CMP compositions have received considerable attention in STI (shallow trench isolation) applications because of their ability to achieve a comparatively high oxide-to-nitride selectivity due to the high chemical affinity of ceria to silicon dioxide which is also referred to in the art as the chemical tooth action of ceria.

The stability of a dispersed colloid is determined by the zeta-potential of the colloid particles. The zeta potential of a particle is the potential at the plane where shear with respect to the bulk solution is postulated to occur. This plane, named shear plane, is located in the diffuse part of the electrical double layer and is interpreted as a sharp boundary between the hydrodynamically mobile and the immobile fluid (see Measurement and Interpretation of Electrokinetic Phenomena by A. V. Delgado et al., Journal of Colloid and Interface Science 309 (2007), p. 194-224). As an indicator for the colloid stability of a dispersion, the zeta potential can be considered as an estimation for the surface charge of a particle and depends on the composition and pH, temperature, ionic strength, and ionic species in the liquid.

Within a colloid comprising only one sort of particles, e.g. particles of ceria, at a given set of conditions (pH, temperature, ionic strength, and ionic species in the liquid) the zeta potential of all particles has the same sign. Thus, when the particles carry significant charges, electrostatic repulsion prevents them from coagulation (flocculation).

For colloidal oxides, the zeta potential strongly depends on the pH of the liquid. At a pH in the acidic region, the particles of a colloidal oxide usually have H^+ ions adsorbed on their surfaces. When the pH is increased, the adsorbed H^+ ions are neutralized, resulting in a decrease of the surface charge until the isoelectric point is reached where the overall charge of each colloid oxide particle is zero. Accordingly, the electrostatic repulsion between particles ceases, so that the particles can coagulate into larger particles (agglomerated particles) due to the action of Van der Waals forces. For colloidal ceria, in the absence of stabilizing additives, the zeta potential is significantly above 30 mV at a pH of 5.5 or lower, but significantly decreases when the pH rises above 6, resulting in coagulation of the particles.

Another issue is that in the case of dielectric substrates the surface of the substrate to be polished by the CMP composition is charged, too. If the charge of the substrate to be polished is opposite to the charge of the abrasive particle, due to electrostatic attraction the abrasive particles adsorb on the oppositely charged surface and are hardly removable after polishing. On the other hand, if the charge of the material to be polished is of the same sign like of the abrasive particle, polishing is hindered due to electrostatic repulsion. Accordingly, the material removal rate and selectivity strongly depends on the interaction between the zeta potential of the abrasive and the charge of the material to be polished. For this reason, it is preferred that the abrasive particles carry no significant charge. Unfortunately, reducing the absolute value of the surface charge of the abrasive particles promotes coagulation of said particles for the reasons described above.

In order to at least partially solve the above-explained problems, several additives for CMP compositions have been proposed which shall minimize agglomeration of the abrasive particles and/or improve the material removal rate and selectivity of the respective CMP composition.

In EP 1 844 122 B1 an adjuvant for use in simultaneous polishing of a cationically charged material like silicon nitride and an anionically charged material like silicon dioxide is disclosed. It is assumed that said adjuvant forms an adsorption layer on the cationically charged material in order to increase the polishing selectivity of the anionically charged material over the cationically charged material. The adjuvant comprises a polyelectrolyte salt containing: (a) a graft type polyelectrolyte that has a weight average molecular weight of 1,000 to 20,000 and comprises a backbone and a side chain having a specific structure as defined in EP 1 844 122 B1; and (b) a basic material. Said adjuvant shall also minimize agglomeration of abrasive particles. However, the examples of EP 1 844 122 B1 show that said objects are not always achieved with the proposed adjuvants. In some cases the material removal selectivity of silicon dioxide over silicon nitride is not increased, compared to CMP compositions with prior art adjuvants. Furthermore, in the CMP compositions comprising an adjuvant according to EP 1 844 122 B1 the average agglomerated particle size of the ceria particles is higher than 500 nm which is not acceptable for a plurality of CMP applications. The influence of said adjuvant on the zeta potential of the ceria particles is not discussed in EP 1 844 122 B1.

US 7,381,251 B2 discloses a liquid composition comprising a mixture of a liquid medium, a colloidal dispersion of mineral particles and a phosphonate terminated poly(oxyalkene) polymer.

One of the objects of the present invention is to provide a chemical mechanical polishing (CMP) composition and a CMP process showing an improved polishing performance especially for dieletric substrates. More specifically it is an object of the present invention to provide a chemical mechanical polishing (CMP) composition and a CMP process showing

(i) a high material removal rate (MRR) of silicon dioxide, or

(ii) an adjustable selectivity between silicon dioxide and silicon nitride, or

(iii) an adjustable selectivity between silicon dioxide and polycrystalline silicon,

(iv) a high surface quality of the polished surfaces

(v) preferably the combination of (i), (ii), (iii) and (iv).

It is a further object of the present invention to provide a chemical mechanical polishing (CMP) composition comprising ceria particles wherein agglomeration of the ceria particles at a pH value of 6 and higher, preferably up to a pH value of 10, is suppressed.

It is a further object of the present invention to provide a chemical mechanical polishing (CMP) composition comprising ceria particles wherein the ceria particles carry low charges, i.e. have a low zeta potential.

According to a first aspect of the present invention, a chemical-mechanical polishing (CMP) composition is provided comprising the following components:

(A) abrasive particles containing ceria

(B) one or more polymers, wherein each macromolecule of said polymers (B) comprises

(i) one or more anionic functional groups

and

(ii) one or more structure units $-(AO)_a-R$

wherein in each structure unit $-(AO)_a-R$ independently from each other structure unit $-(AO)_a-R$

A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is (independently from each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2

wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different

a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135,

R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein in said polymer (B) the sum of the molar masses of all structure units (ii) is at least 50 % of the molar mass of said polymer (B).

Further details, modifications and advantages of the present invention are explained in the following detailed description and the examples.

(A) Abrasive particles containing ceria

The CMP composition according to the present invention comprises as component (A) abrasive particles containing ceria. In the CMP process, said ceria particles act (A) as an abrasive towards the surface to be polished.

Preferably, the abrasive particles (A) consist of ceria. Preferably, a chemical-mechanical polishing (CMP) composition according to the present invention does not contain other abrasive particles than (A) abrasive particles containing ceria or consisting of ceria.

Within the CMP composition of the present invention, the ceria particles are typically dispersed in a colloidal state.

Suitable ceria containing abrasive particles (A) are commercially available, for instance under the trade name Rhodia.

Suitable ceria containing abrasive particles (A) are obtainable e.g. by a wet precipitation process or by a plasma process. In the later case the ceria is also referred to as fumed ceria. In some cases, wet-precipitated ceria is preferred because of it has very good dispersion properties. In other cases, fumed ceria is preferred because it has a very strong abrasive action.

In a CMP composition according to the present invention, it is preferred that the abrasive particles containing ceria have a particle size distribution characterized by a D_{50} value of 500 nm lower, preferably of 250 nm or lower, further preferably 200 nm or lower, particularly preferably 180 nm or lower, most preferably 150 nm or lower. The particle size distribution can be measured for example with DLS (dynamic light scattering) or SLS (static light scattering) methods. These and other methods are well known in the art, see e.g. Kuntzsch, Timo; Witnik, Ulrike; Hollatz, Michael Stintz; Ripperger, Siegfried; Characterization of Slurries Used for Chemical-Mechanical Polishing (CMP) in the Semiconductor Industry; Chem. Eng. Technol; 26 (2003), volume 12, page 1235. Typically a Horiba LB550 V (DLS, dynamic light scattering, measurement according to manual) or any other DLS instrument is used. The particle size distribution of a ceria dispersion is usually measured in a plastic cuvette at 0.1 to 1.0 % solid concentration. Dilution, if necessary, is carried out with the dispersion medium or ultra pure water. The D_{50} value of the volume based particle size distribution is shown as representation of the particle size distribution.

The particle size distribution of the abrasive particles containing ceria (A) can be monomodal, bimodal or multimodal. Preferably, the particle size distribution is monomodal in order to have an easily reproducible property profile of the abrasive particles containing ceria (A) and easily reproducible conditions during the process of the invention.

Moreover, the particle size distribution of the abrasive particles containing ceria (A) can be narrow or broad. Preferably, the particle size distribution is narrow with only small amounts of small particles and large particles in order to have an easily reproducible property profile of the abrasive particles containing ceria (A) and easily reproducible conditions during the process of the invention.

The abrasive particles containing ceria (A) can have various shapes. Thus, they may be of one or essentially one type of shape. However, it also possible that the abrasive particles containing ceria (A) have different shapes. In particular, two types of differently shaped abrasive particles containing ceria (A) may be present in a given composition of the invention. As regards the shapes themselves, they can be cubes, cubes with chamfered edges, octahedrons, icosahedrons, nodules and spheres with or without protrusions or indentations. Most preferably, the shape is spherical with no or only very few protrusions or indentations. This shape, as a rule, is preferred because it usually increases the resistance to the mechanical forces the abrasive particles containing ceria (A) are exposed to during a CMP process.

The abrasive particles (A) which contain ceria can contain minor amounts of other rare earth metal oxides.

The abrasive particles (A) which consist of ceria can have a hexagonal, cubic or face-centered cubic crystal lattice.

In certain specific cases, the abrasive particles (A) which contain ceria are composite particles comprising a core containing or consisting of at least one other abrasive particulate material which is different from ceria, in particular alumina, silica, titania, zirconia, zinc oxide, and mixtures thereof.

Such composite particles are known, for example, from WO 2005/035688 A1, US 6,110,396, US 6,238,469 B1, US 6,645,265 B1, K. S. Choi et al., Mat. Res. Soc. Symp. Proc., Vol. 671, 2001 Materials Research Society, M5.8.1 to M5.8.10, S.-H. Lee et al., J. Mater. Res., Vol. 17, No. 10 (2002), pages 2744 to 2749, A. Jindal et al., Journal of the Electrochemical Society, 150 (5), G314-G318 (2003), Z. Lu, Journal of Materials Research, Vol. 18, No. 10, October 2003, Materials Research Society, or S. Hedge et al., Electrochemical and Solid-State Letters, 7 (12), G316-G318 (2004).

Most preferably, the composite particles are raspberry-type coated particles comprising a core selected from the group consisting of alumina, silica titania, zirconia, zinc oxide, and mixtures thereof with a core size of from 20 to 100 nm wherein the core is coated with ceria particles having a particle size below 10 nm.

Particularly preferred is a chemical-mechanical polishing (CMP) composition according to the present invention, wherein the total amount of (A) abrasive particles containing ceria is in a range of from 0.01 wt.-% to 5 wt.-%, preferably 0.1 wt.-% to 1.0 wt.-%, for example 0.5 wt.-%, in each case based on the total weight of the respective CMP composition.

(B) Polymers

A CMP composition according to the present invention comprises one or more polymers (B), wherein each macromolecule of said polymers (B) comprises

(i) one or more anionic functional groups

and

(ii) one or more structure units $-(AO)_a-R$

wherein in each structure unit $-(AO)_a-R$ independently from each other structure unit $-(AO)_a-R$

A is C_xH_{2x} wherein for each A in said structure units -$(AO)_a$-R, x (is independently from each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2

wherein within each structure unit -$(AO)_a$-R the groups A are the same or different

a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135,

R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein in said polymer (B) the sum of the molar masses of all structure units (ii) is at least 50 % of the molar mass of said polymer (B).

The polymers (B) to be used according to the present invention are water-soluble.

The structure units – $(AO)_a$-R are hereinbelow also referred to as structure units (ii). The group R is preferably selected from the group consisting of hydrogen and methyl.

Anionic functional groups are functional groups which in the dissociated state carry a negative charge. Preferably, in the macromolecules of said polymer (B) or of at least one of said polymers (B) said one or more anionic functional groups are selected from the group consisting of the carboxylic group, the sulfonic group, the sulfate group, the phosphoric group and the phosphonic group.

A carboxylic group has the structure -COOM (wherein M is H or one cation equivalent) in the undissociated state and -COO^- in the dissociated state.

A sulfate group has the structure – O-SO_3M (wherein M is H or one cation equivalent) in the undissociated state and – O-SO_3^- in the dissociated state.

A sulfonic group has the structure -SO_3M (wherein M is H or one cation equivalent) in the undissociated state and -SO_3^- in the dissociated state.

A phosphoric group has the structure -O-PO_3M_2 (wherein M is H or one cation equivalent) in the undissociated state, -O-PO_3M^- (wherein M is H or one cation equivalent) in the first dissociated state and -O-PO_3^{2-} in the second dissociated stage.

In the context of the present application, the term phosphoric group includes phosphoric groups wherein one of the two hydroxy groups is esterified by an alcohol R^x-OH, resulting in a structure – O-$P(OR^x)O_2M$ (wherein M is H or one cation equivalent) in the undissociated state, and – O-$P(OR)O_2^-$ in the dissociated state.

A phosphonic group has the structure – PO_3M_2 (wherein M is H or one cation equivalent) in the undissociated state, $-PO_3M^-$ (wherein M is H or one cation equivalent) in the first dissociated state and $-PO_3^{2-}$ in the fully dissociated stage.

In the context of the present application, the term phosphonic group includes phosphonic groups wherein one of the two hydroxy groups is esterified by an alcohol R^x-OH, resulting in a structure – $P(OR^x)O_2M$ (wherein M is H or one cation equivalent) in the undissociated state and – $P(OR^x)O_2^-$ in the dissociated state.

The structure units -AO- defined above are preferably selected from the group consisting of $-O-CH_2-CH_2-$, $-O-CH_2-CH(CH_3)-$, $-O-CH(CH_3)-CH_2-$ and $-O-CH_2-CH_2-CH_2-CH_2-$, wherein $-O-CH_2-CH_2-$ (a structure unit derived from ethylene oxide) is preferred.

Preferably, in the polymers (B) to be used according to the present invention, the molar mass of each of said one or more structure units (ii) $-(AO)_a-R$ is 500 g/mol or more, preferably 1000 g/mol or more, more preferably 2000 g/mol or more, most preferably 3000 g/mol or more

and/or

the sum of the molar masses of all of said structure units (ii) $-(AO)_a-R$ is 60 % or more, preferably 70 % or more, most preferably 80 % or more of the molar mass of said polymer (B).

Preferably, said polymer (B) or at least one of said polymers (B) is selected from the group consisting of comb polymers and block copolymers.

Block copolymers are copolymers whose macromolecules each consist of adjacent blocks which are constitutionally different, i.e. the adjacent blocks in each case comprise either constitutional units derived from different species of monomer or from the same species of monomer but with a different composition or sequence distribution of constitutional units.

Comb polymers are polymers whose macromolecules are comb macromolecules each comprising a main chain (typically referred to as the backbone) with a plurality of trifunctional branch points from each of which a linear side-chain emanates. Comb polymers are obtainable by homopolymerisation or copolymerisation of long-chained α -olefines, alkyloxiranes, vinyl ethers, vinyl esters, alkyl(meth)acrylates or *N*-alkyl(meth)acrylamides. The long-chained monomers are also referred to as macromers. Alternatively, they are obtainable by graft copolymerisation.

In preferred CMP composition of the present invention, said polymer (B) or at least one of said polymers (B) is a comb polymer comprising

(i) a backbone to which one or more anionic functional groups are linked

and

(ii) one or more side chains each comprising or consisting of a structure unit $-(AO)_a-R$ (wherein A, a and R have the above-defined meaning)

wherein in said comb polymer the sum of the molar masses of all said structure units (ii) $-(AO)_a-R$ is at least 50 % of the molar mass of said comb polymer.

Hereinbelow, specific types of preferred polymers (B) are described in more detail, e.g. by means of general formulae. Insofar as in different general formulae identical variables are used and such variables have different meanings in said respective formulae, in each case the meaning defined specifically for the respective formulae is binding.

A preferred comb polymer (B) comprises

- building units each comprising one or more anionic functional groups

and

- side chains each comprising a structure unit (ii) $-(AO)_a-R$ wherein

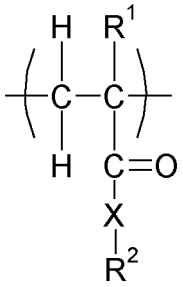
  A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is (independently from each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2

  wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different

  a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135

  R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein one or more of the building units comprising an anionic functional group are selected from general formulae (7.1), (7.2), (7.3) and (7.4):



(7.1)

in which

R^1 is H or an unbranched or branched C_1-C_4 alkyl group, CH_2COOH or CH_2CO-X-R^2;

R^2 is PO_3M_2, O-PO_3M_2, (C_6H_4)-PO_3M_2 or (C_6H_4)-OPO_3M_2;

X is NR^7-(C_nH_{2n}) or O-(C_nH_{2n}) with n = 1, 2, 3 or 4, the nitrogen atom or the oxygen atom, respectively, being attached to the CO group;

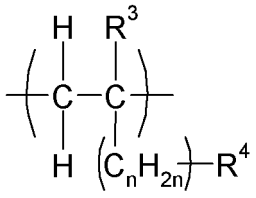
R^7 is H, C_1-C_6 alkyl, (C_nH_{2n})-OH, (C_nH_{2n})-PO_3M_2, (C_nH_{2n})-OPO_3M_2, (C_6H_4)-PO_3M_2, (C_6H_4)-OPO_3M_2 or (C_nH_{2n})-O-(A^2O)$_\alpha$ -R^9 with n = 1, 2, 3 or 4

A^2 is C_zH_{2z} with z = 2, 3, 4 or 5 or is $CH_2CH(C_6H_5)$;

α is an integer from 1 to 350; and

R^9 is H or an unbranched or branched C_1-C_4 alkyl group;

or X is a chemical bond and R^2 is OM;



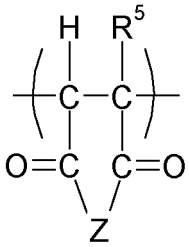
(7.2)

in which

R^3 is H or an unbranched or branched C_1-C_4 alkyl group;

n is 0, 1, 2, 3 or 4;

R^4 is PO_3M_2, or O-PO_3M_2;



(7.3)

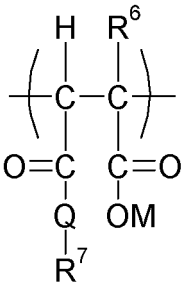
in which

R^5 is H or an unbranched or branched C_1-C_4 alkyl group;

Z is O or NR^7; and

R^7 is H, (C_nH_{2n})-OH, (C_nH_{2n})-PO_3M_2, (C_nH_{2n})-OPO_3M_2, (C_6H_4)-PO_3M_2, or (C_6H_4)-OPO_3M_2, wherein

n is 1, 2, 3 or 4;



(7.4)

in which

R^6 is H or an unbranched or branched C_1-C_4 alkyl group;

Q is NR^7 or O;

R^7 is H, (C_nH_{2n})-OH, (C_nH_{2n})-PO_3M_2, (C_nH_{2n})-OPO_3M_2, (C_6H_4)-PO_3M_2, (C_6H_4)-OPO_3M_2 or (C_nH_{2n})-O-$(A^2O)_\alpha$ -R^9,

n is 1, 2, 3 or 4;

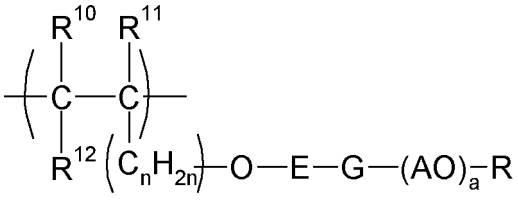
A^2 is C_zH_{2z} with z = 2, 3, 4 or 5 or is $CH_2CH(C_6H_5)$;

α is an integer from 1 to 350;

R^9 is H or an unbranched or branched C_1-C_4 alkyl group;

wherein in formulae (7.1), (7.2), (7.3) and (7.4) each M independently of any other M is H or one cation equivalent

and/or wherein one or more of the side chains comprising a structure unit (ii) $-(AO)_a-R$ are selected from general formulae (7.5), (7.6), (7.7) and (7.8):



(7.5)

in which

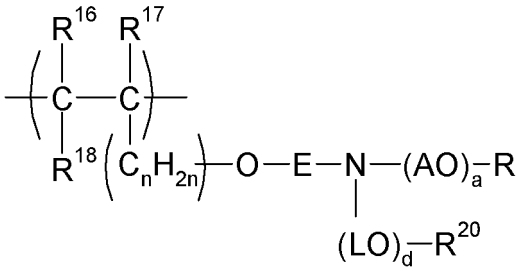
R^{10}, R^{11} and R^{12} independently of one another are H or an unbranched or branched C_1-C_4 alkyl group;

n is 0, 1, 2, 3, 4 and/or 5;

E is an unbranched or branched C_1-C_6 alkylene group, a cyclohexylene group, CH_2-C_6H_{10}, 1,2-phenylene, 1,3-phenylene or 1,4-phenylene;

G is O, NH or CO-NH; or

E and G together are a chemical bond;



(7.6)

in which

R^{16}, R^{17} and R^{18} independently of one another are H or an unbranched or branched C_1-C_4 alkyl group;

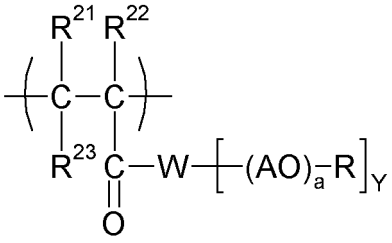
n is 0, 1, 2, 3, 4 or 5;

E is an unbranched or branched C_1-C_6 alkylene group, a cyclohexylene group, CH_2-C_6H_{10}, 1,2-phenylene, 1,3-phenylene or 1,4-phenylene or is a chemical bond;

L is C_zH_{2z} with z = 2, 3, 4 or 5 or is CH_2-$CH(C_6H_5)$;

d is an integer from 1 to 350;

R^{20} is H or an unbranched C_1-C_4 alkyl group;



(7.7)

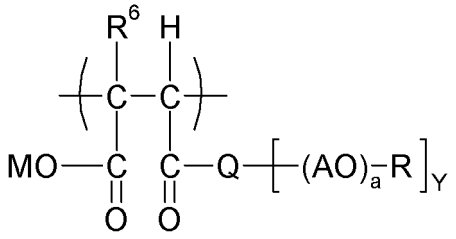
in which

R^{21}, R^{22} and R^{23} independently of one another are H or an unbranched or branched C_1-C_4 alkyl group;

W is O, NR^{25} or N

R^{25} is H or an unbranched or branched C_1-C_4 alkyl group;

Y is 1, if W = O or NR^{25}, and is 2 if W = N;



(7.8)

in which

R^6 is H or an unbranched or branched C_1-C_4 alkyl group;

Q is NR^{10}, N or O;

R^{10} is H or an unbranched or branched C_1-C_4 alkyl group;

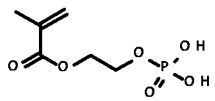
Y is 1 if Q = O or NR^{10} , and is 2 if Q = N.

Particularly preferably the building unit of formula (7.1) is a methacrylic acid or acrylic acid unit, the buidling unit of formula (7.3) is a maleic anhydride unit, and the building unit of formula (7.4) is a maleic acid or maleic monoester unit.

Particularly preferable the building unit of formula (7.5) is an alkoxylated isoprenyl unit, alkoxylated hydroxybutyl vinyl ether unit, alkoxylated (meth)allyl alcohol unit or is a vinylated methylpolyalkylene glycol unit.

In the above-defined comb-polymer, preferably the molar ratio between the total amount of building units of formulae (7.1), (7.2), (7.3) and (7.4) and the total amount of building units of formulae (7.5), (7.6), (7.7) and (7.8) is 1:4 to 15:1, preferably 1:1 to 10:1.

Such comb polymers are obtainable by copolymerization of a monomer selected from the group consisting of acrylic acid; hydroxyalkyl acrylates; methacrylic acid; hydroxyalkyl methacrylates, maleic acid, itaconic acid, 2-Acrylamido-2-methylpropane sulfonic acid (AMPS); acrylamide and phosphoric acid hydroxalkylmethacrylate



with one or more macromers selected from the group consisting of alkoylated vinyl ethers (e.g. ethoxylated hydroxybutyl vinyl ester), alkoxylated allyl ethers, alkoxylated methallyl ethers, alkoxylated Isoprenyl ethers, methacrylic acid esters of polyalkyleneoxide monoalkylethers, acrylic acid esters of polyalkyleneoxide monoalkylethers, maleic acid esters of polyalkyleneoxide monoalkyl ethers. Said alkoxylated macromers each comprise a structure unit $-(AO)_a-R$ whrein A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is (independently from

each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2.

Preferably, electron-rich macromers are reacted with electron-deficient monomers, i.e. vinyl ether monomers with acrylic or maleic monomers.

Suitable ways for obtaining the above-defined comb polymer are disclosed in the European patent application having the application number 13156752.1.

A preferred comb polymer of this type is available under the trade name MelPers 0045 from BASF SE. In said comb polymer, the back bone is formed of acrylic and maleic acid monomers, the structure units $-(AO)_a-R$ each have a molar mass of 5800 g/mol, A is $-CH_2-CH_2-$, R is H and the sum of the molar masses of all said structure units $-(AO)_a-R$ is 94 % of the molar mass of said comb polymer.

A further kind of polymer (B) suitable for the present invention is a comb polymer obtainable by copolymerisation of the monomers

(8.1) acrylic acid and

(8.2) one or more macromers each comprising a polymerizable double bond, preferably a double bond of a vinyl group, an allyl group, an isoprenyl group, an acrylate group, a methacrylate group or a maleic ester group,

A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is (independently from each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2

wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different

a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135

R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein the amounts of the monomers (8.1) and (8.2) are selected so that a comb polymer is obtained wherein in said comb polymer the sum of the molar masses of all said structure units (ii) $-(AO)_a-R$ is at least 70 % of the molar mass of said comb polymer.

In a preferred comb polymer of this type, the backbone is formed of polyacrylic acid, the structure units $-(AO)_a-R$ each have a molar mass of 1100 g/mol, A is $-CH_2-CH_2-$, R is H and the sum of the molar masses of all said structure units $-(AO)_a-R$ is 75 % of the molar mass of said comb polymer.

A further kind of polymer (B) suitable for the present invention is a comb polymer which is a polycondensate containing

(9.1) at least one building unit comprising an aromatic or heteroaromatic system Ar^1 and a side chain comprising or consisting of a structure unit (ii) $-(AO)_a-R$

wherein in each building unit (9.1) independently from each other building unit (9.1)

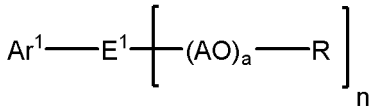
A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is (independently from each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2

wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different

a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135

R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein preferably the building units (9.1) are represented by general formula (9.1)



(9.1)

wherein for each building unit of formula (9.1) independently from each other building unit of formula (9.1)

Ar^1 is selected from the group consisting of unsubstituted aromatic or heteroaromatic systems having 5 to 10 carbon atoms in each case

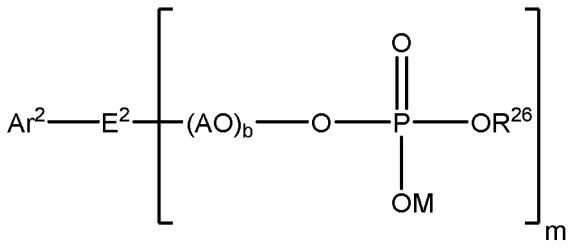
E^1 is selected from the group consisting of N, NH and O, preferably O

n = 2 if E^1 = N and n = 1 if E^1 = NH or O

A, a and R are as defined above

(9.2) at least one building unit comprising an aromatic or heteroaromatic system Ar^1 and a phosphoric group

wherein preferably one or more of the building units (9.2) are represented by general formula (9.2)



(9.2)

wherein for each building unit of formula (9.2) independently from each other building unit of formula (9.2)

Ar^2 is selected from the group consisting of unsubstituted aromatic or heteroaromatic system having 5 to 10 carbon atoms in each case

E^2 is selected from the group consisting of N, NH and O, preferably O

m = 2 if E^2 = N and m = 1 if E^2 = NH or O

A is as defined above for building unit (9.1)

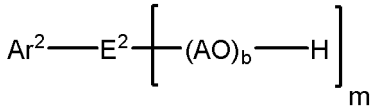
b is an integer selected from the range of from 0 to 300, preferably 1 to 5

M independently of any other M is H or one cation equivalent,

R^{26} is M or Ar^1-O-$(AO)_a$-

(9.3) at least one building unit comprising an aromatic or heteroaromatic system Ar^2, wherein building unit (9.3) differs from building unit (9.2) exclusively in that the phosphonic group of the building unit (9.2) is replaced by H in building unit (9.3), and building unit (9.3) is not the same as building unit (9.1)

wherein preferably the building unit (9.3) is represented by general formula (9.3)

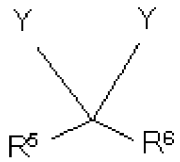


(9.3)

wherein for each building unit of formula (9.3) independently from each other building unit of formula (9.3) Ar^2, E^2, m, A and b are as defined for building unit (9.2)

In the building units (9.1), (9.2) and (9.3) of said polycondensates the aromatic or heteroaromatic systems Ar^1 and Ar^2, resp., are preferably represented by or derived from phenyl, 2-hydroxyphenyl, 3-hydroxyphenyl, 4-hydroxyphenyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, naphthyl, 2-hydroxynaphthyl, 4-hydroxynaphthyl, 2-methoxynaphthyl, 4-methoxynaphthyl. Preferably, the aromatic or heteroaromatic systems Ar^1 and Ar^2, are phenyl.

The above-defined polycondensate preferably contains a further building unit (9.4) which is represented by the following formula



(9.4)

where

Y, independently of one another, are identical or different and are building units (9.1), (9.2), (9.3) or further constituents of the polycondensate

where

R^5 are identical or different and are represented by H, CH_3, COOH or a substituted or unsubstituted aromatic or heteroaromatic system having 5 to 10 C atoms

where

R^6 are identical or different and are represented by H, CH_3, COOH or a substituted or unsubstituted aromatic or heteroaromatic system having 5 to 10 carbon atoms. Preferably R^5 and R^6 in building unit (9.4) independently of one another, are identical or different and are represented by H, COOH and/or methyl.

In said polycondensate, preferably

the molar ratio of the building units [(9.1) + (9.2) + (9.3)]:(9.4) is in the range of from 1:0.8 to 3, preferably 1:0.9 to 2 and particularly preferably 1:0.95 to 1.2.
and/or

the molar ratio of the building units (9.1):[(9.2) + (9.3)] is in the range of from 1:10 to 10:1, preferably 1:7 to 5:1 and particularly preferably 1:5 to 3:1.
and/or

the molar ratio of the building units (9.2):(9.3) is in the range of from 1 :0.005 to 1:10, preferably 1:0.01 to 1:1, in particular 1:0.01 to 1:0.2 and particularly preferably 1:0.01 to 1:0.1.

In the process for the preparation of said polycondensate, polycondensation and the introduction of the phosphoric group (phosphatizing) are preferably carried out in a reaction mixture. Preferably, the reaction mixture used in this process contains at least

(9.1a) a monomer having aromatic or heteroaromatic system Ar^1 and a side chain comprising or consisting of a structure unit (ii) $-(AO)_a-R$

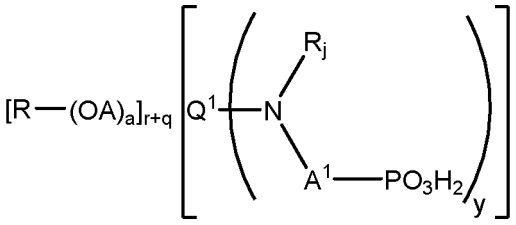
(9.3a) a monomer having an aromatic or heteroaromatic system, said monomer (9.3a) being partially phosphatized during the reaction and thus forming a monomer (9.2a) and/or, in the polycondensate, the building unit (9.2),

(9.4a) a monomer having an aldehyde group, e.g. fomaldehyde, and a phosphatizing agent, e.g. polyphosphoric acid and/or phosphorous pentoxide.

Suitable ways for obtaining the above-defined polycondensates are disclosed in WO2010/040612.

A preferred comb polymer of this type is available under the trade name EPPR 312 from BASF SE. In said comb polymer, the structure units $-(AO)_a-R$ each have a molar mass of 5000 g/mol, A is $-CH_2-CH_2-$, R is H and the sum of the molar masses of all said structure units (ii) $-(AO)_a-R$ is 83 % of the molar mass of said comb polymer, and the molar ratio of the building units (9.1):[(9.2) + (9.3)] is 1:4.

A further kind of polymer (B) suitable for the present invention is disclosed in US 5,879,445 and has a structure of the formula (10)

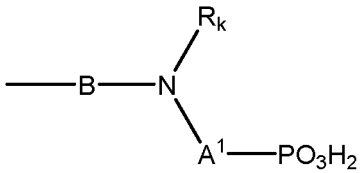


(10)

wherein

- A is C_xH_{2x} wherein for each A in said structure units -$(AO)_a$-R, x is (independently from each other x) selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2, wherein within each structure unit -$(AO)_a$-R the groups A are the same or different
- a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135
- R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms, wherein R is preferably selected from the group consisting of hydrogen and methyl,
- Q^1 is a hydrocarbon group comprising 2 to 18 carbon atoms and possibly one or more heteroatoms,
- A^1 is an alkylene group comprising 1 to 5 carbon atoms,
- the R_j groups are independently from each other selected from the group consisting of:
  - the A^1-PO_3H_2 group, wherein A^1 has the above-defined meaning,
  - the alkyl group comprising 1 to 18 carbon atoms and able to carry -$(AO)_a$-R groups

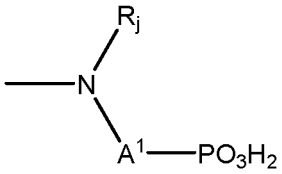
  and
  - the group



wherein B designates an alkylene group having 2 to 18 carbon atoms,

- r is the number of structure units -$(AO)_a$-R carried by all the R_j groups,
- q is the number of structure units -$(AO)_a$-R carried by Q,

- the sum "r+q" is selected so that in said polymer (B) the sum of the molar masses of all said structure units $-(AO)_a-R$ is at least 50 % of molar mass of said polymer (B) preferably 90 % or more, based on the molar mass of said polymer
- y is an integer in the range of from 1 to 3, wherein when y > 1, the groups



are the same or different

- Q^1, N, and the R_j groups can form together one or more rings, this ring or these rings moreover able to contain one or more other heteroatoms.

Suitable ways for obtaining polymers (B) of formula (10) are disclosed in US 5,879,445.

The group Q^1 preferably has 2 to 12 carbon atoms (inclusive), and more preferably, it has 2 to 6 carbon atoms (inclusive). Advantageously, Q^1 is chosen from among ethylene, cyclohexene or n-hexene.

The alkylene group A^1 which is the carrier of one divalent carbon atom has preferably 1 to 3 carbon atoms (inclusive). It is particularly advantageous that A^1 is the methylene group.

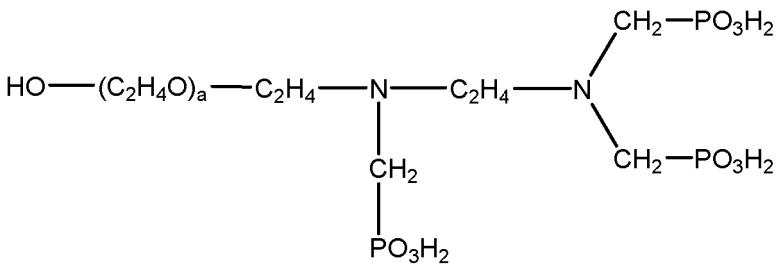
The R_j group, which is possibly combined in salt form, is chosen preferably from among the $-CH_2-PO_3H_2$, methyl, and $-C_2H_4N(CH_2-PO_3H_2)_2$ groups. More preferably still, R_j represents the $-CH_2-PO_3H_2$ group.

The sum "r+q" corresponds to the total number of polyoxyalkylated chains. Preferably, this sum is less than 3. More preferably, it is equal to 1.

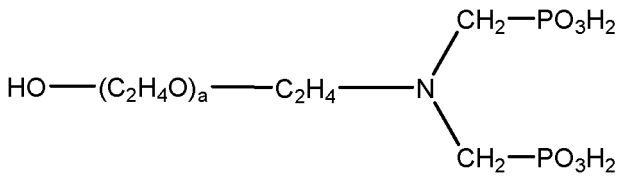
"y" is a number comprised between 1 and 3 inclusive. It is preferably equal to 1.

R is preferably H, A is preferably $-CH_2-CH_2-$ and a is preferably 50.

According to US 5,879,445, preferred compounds of formula (10) as defined above are



and



wherein a is preferably 50.

A preferred polymer (B) of this type is hereinbelow referred to as Stab 100. In said polymer Stab 100 the structure units $-(AO)_a-R$ each have a molar mass of 3000 g/mol, A is $-CH_2-CH_2-$, R is H and the sum of the molar masses of all said structure units $-(AO)_a-R$ is 92 % of the molar mass of said polymer.

Without wishing to be bound to any specific theory, it is presently assumed that the structure units (ii) $-(AO)_a-R$ (wherein A, a and R are as defined above) present in the polymers (B) stabilize the ceria-containing abrasive particles (A) in a non-ionic steric manner while the negatively charged anionic functional groups anchor the polymers (B) to the positively charged ceria-containing abrasive particles (A). The steric stabilization is assumed to be due to a screening (shielding) effect of the structure units $-(AO)_a-R$ present on the surface of the ceria-containing abrasive particles (A). Accordingly, it is important that in the polymers (B) to be used according to the present invention a significant part of each macromolecule is formed of screening structure units $-(AO)_a-R$. This steric stabilization effect could not be achieved with polymers having no or not a sufficient fraction of screening structure units, e.g. polymers wherein the fraction of anionic groups in the macromolecules is significantly larger than in the above-defined polymers to be used according to the invention (e.g. carboxylic acid homopolymers like polyacrylic acid and polyaspartic acid, which form polyanions with a large amount of negative charge). At least for this reason it is important that in said polymer (B) the sum of the molar masses of the structure units $-(AO)_a-R$ which provide for the screening effect is at least 50 % of the molar mass of said polymer (B). On the other hand, the presence of anionic groups (i) is necessary in order to enable anchoring of the polymer (B) to the positively charged surface of the abrasive particles (A) containing ceria. Furthermore, in order to provide for reliable and efficient anchoring by the anionic functional groups (i) and screening by the structure units (ii) $-(AO)_a-R$, it is important that there is no random distribution of anionic functional groups (i) and structure units (ii) $-(AO)_a-R$ within the polymer.

In this way, the charge of the ceria-containing abrasive particles (A) is minimized and at the same time agglomeration (flocculation) of the abrasive particles is suppressed, even at a pH in the range of 6 to 10, preferably up to 10.8 or at least in a significant subrange of this pH range.

Abrasive particles carrying a low charge are especially preferably for polishing surfaces of dielectric materials like silicon dioxide and silicon nitride, because when the charge of the abrasive

particles is low, electrostatic interaction between the abrasive particles and the charged surface of the to-be-polished dielectric which is detrimental to the CMP process (see above) is reduced.

Especially for chemical-mechanical polishing of silicon dioxide, a CMP composition having a pH of more than 6 is desirable because it allows for alkaline chemical hydrolysis of silicon dioxide which supports the removal mechanism and helps in preventing scratches which are visible after the chemical mechanical polishing process.

Accordingly, it is preferred that in a chemical-mechanical polishing (CMP) composition according to the present invention the concentration of said one or more polymers (B) as defined hereinabove is selected so that

- no flocculation of ceria containing particles (A) occurs in the pH range of from 6 to 10, preferably up to 10.8

and/or

- at a pH in the range of from 6 to 10 the zeta potential of the particles containing ceria is in the range between +30 mV and - 30 mV, preferably between + 20 mV and - 20 mV.

Particularly preferred is a chemical-mechanical polishing (CMP) composition according to the present invention, wherein the total amount of polymers (B) as defined hereinabove is in a range of from 0.0002 to 1.0 wt.-%, preferably 0.001 wt.-% to 0.1 wt.-%, more preferably 0.005 wt.-% to 0.025 wt.-%, further preferably 0.0075 wt.-% to 0.01 wt.-%, in each case based on the total weight of the respective CMP composition.

In this regard, further aspects of the present invention are directed to

- the use of a polymer (B) as defined hereinabove for suppressing the agglomeration of ceria containing particles dispersed in aqueous medium and/or for adjusting the zeta potential of ceria containing particles

and

- a process for suppressing the agglomeration and/or adjusting the zeta potential of ceria containing particles dispersed in aqueous medium, said process comprising the step of adding an effective amount of one or more polymers (B) as defined hereinabove to said aqueous medium wherein the containing ceria particles are dispersed.

(C) Polyhydroxy compounds

For certain applications, a chemical mechanical polishing (CMP) composition according to the present invention preferably further comprises

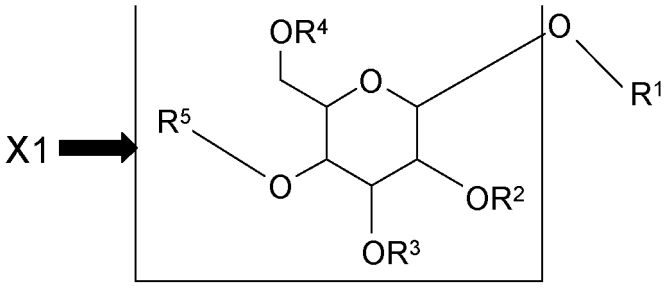
(C) one or more polyhydroxy compounds.

Including one or more polyhydroxy compounds (C) in the CMP composition of the present invention in preferred cases is helpful in improving the polishing performance, particularly the combination of high material removal rate of silicon dioxide and low material removal rate of silicon nitride and/or polycrystalline silicon.

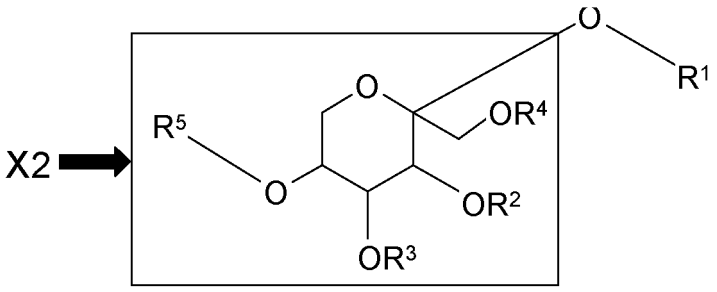
Polyhydroxy compounds (also referred to as polyols) are organic compounds comprising two or more alcoholic hydroxy groups per molecule. Typical representatives of polyhydroxy compounds are diols (e.g. glycols, including polyalkylene glycols), glycerol, carbohydrates and sugar alcohols.

Preferred polyhydroxy compounds (C) are selected from the group consisting of mannitol, sorbitol, xylitol, mannose, sorbose, dextrin, glucose, gelatin, taragum, cationic guar gum, collagen, dextrin, tragacanth, propylene glycol alginate, cyclodextrin, chitin, hyaluronic acid, carmelose, starch, cyprogum, bee gum, pullulan, "LAPONITE® (manufactured by Rockwood Additives Limited)", pectin, trehalose, casein, saccharose, maltose, fructose, mannose, glucuronic acid, glucosamine, glucosan, cationic cellulose, glucosidase, glucose phenylosazone, hydroxyethylcellulose,
chitosan, starch phosphate, soybean lecithin, xanthan gum, tamalind gum, locust bean gum, tamalindsy gum, arabic gum, cyliumseed gum, caragynan, gelan gum, guar gum polyglycerol fatty acid ester, polysaccharides, such as starch, chitosan, algenic acid, carboxy methyl cellulose, methyl cellulose, curdlan and derivatives thereof, Xanthan Gum, Guaiac gum, Mastic Gum and Rosin Gumgluconic acid, glucono (acid) delta lacton, and glycosides, especially alkyl poly glycosides.

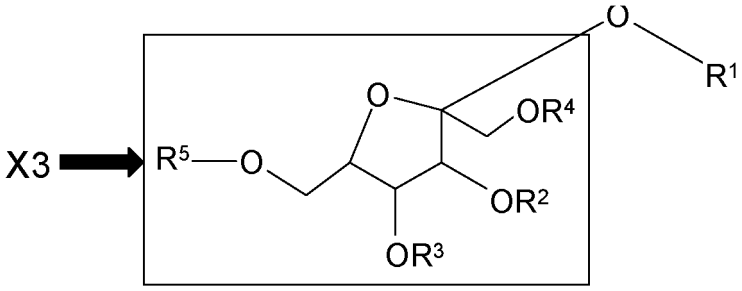
In preferred cases the polyhydroxy compound (C) or one of the polyhydroxy compounds (C) is a glycoside of the formulae 1 to 6



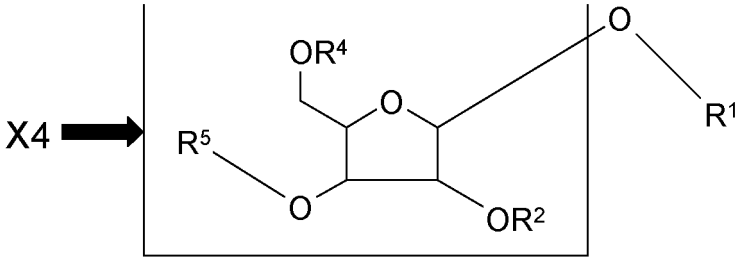
(formula 1)



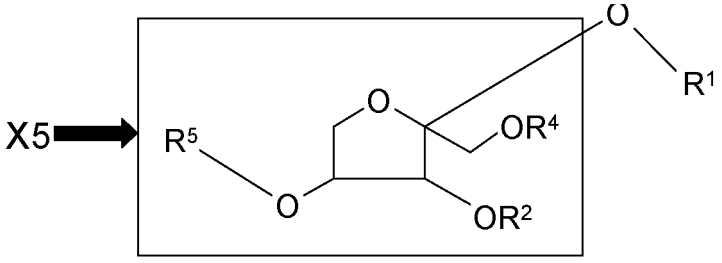
(formula 2)



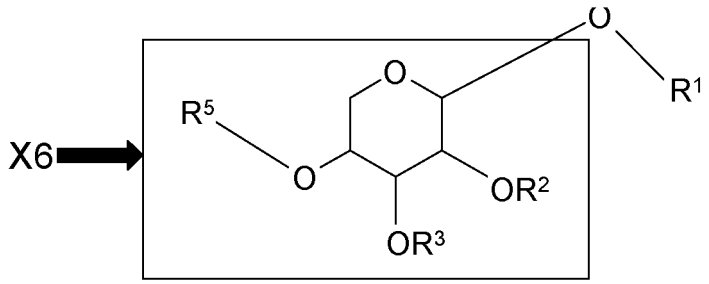
(formula 3)



(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,

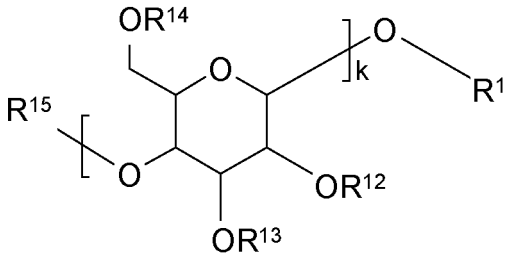
the total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) in the glycoside is in the range of from 1 to 20,

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

In the glycosides of formulae 1 to 6, the total number of monosaccharide units (X1, X2, X3, X4, X5, or X6) is preferably in the range of from 1 to 5.

Further preferably, 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.

Particularly preferably, 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, preferably H,

R^{13} is H, alkyl, aryl or alkylaryl, preferably H,

R^{14} is H, alkyl, aryl or alkylaryl, preferably H,

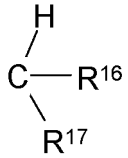
R^{15} is H, alkyl, aryl or alkylaryl, preferably H,

and k is an integer from 1 to 20, preferably from 1 to 5.

Preferably, in formula (1a), R^{12}, R^{13}, R^{14} and R^{15} are H.

Preferably, in formula (1a),

R^1 is



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

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

Particularly preferred is a chemical-mechanical polishing (CMP) composition according to the present invention, wherein the total amount of polyhydroxy compounds (C) as defined hereinabove is in a range of from 0.001 wt.-% to 2 wt.-%, preferably 0.01 wt.-% to 1 wt.-%, for example 0,02 wt.-% to 0.05 wt.-%% in each case based on the total weight of the respective CMP composition.

(D) pH adjustors

Further preferably, a chemical-mechanical polishing (CMP) composition according to the present invention further comprising

(D) one or more pH adjustors.

Suitable pH adjustors are selected from the group consisting of ammonia, KOH, NaOH; M_2CO_3, $M(HCO_3)_2$, where in each case M is selected from the group consisting of K, Na, NH_4 and tetraalkyl-ammonium, tetraakylammonium hydroxides like etramethylammonium hydroxide (TMAH) and tetraethylammonium hydroxide (TEMH), alkyl substitued amines like tri-methyhl-amine, triethyl-amine, di-methyl-amine, di-ethyl-amine, methyl-amine; ethyl-aminpolyamines like diethylen-tri-amine, hexamethylene-tri-amine or urotropin, polymeric imines like polyethylenimine, nitric acid, phosphoric acid, sulfuric acid, hydrochloric acid, formic acid, phosphonic acids, sulfonic acids, wherein ammonia, KOH, TMAH, TEAH; nitric acid, formic acid are poreferred.

The pH value of the CMP composition according to the present invention is in the range of from 5 to 10.8, preferably from 6 to 10, more preferably from 6.5 to 9.5, further preferably from 7 to 9, still further preferably from 7.5 to 8.5, for example 8.

Particularly preferred is a chemical-mechanical polishing (CMP) composition according to the present invention, wherein

(A) the total amount of abrasive particles containing ceria is in a range of from 0.01 wt.-% to 5 wt.-%, preferably 0.1 wt.-% to 1.0 wt.-%, for example 0.5 wt.-%, in each case based on the total weight of the respective CMP composition,

and

(B) the total amount of polymers (B) as defined hereinabove is in a range of from 0.0002 wt.-% to 1 wt.-%, preferably 0.001 wt.-% to 0.1 wt.-%, more preferably 0.005 wt.-% to 0.025 wt.-%, further preferably 0.0075 wt.-% to 0.01 wt.-%, in each case based on the total weight of the respective CMP composition.

and

(C) the total amount of polyhydroxy compounds is in a range of from 0.001 wt.-% to 2 wt.-%, preferably 0.01 wt.-% to 1 wt.-% in each case based on the total weight of the respective CMP composition.

Further components of the CMP composition

The CMP compositions according to the invention may further contain, if necessary, various other coomponents, including but not limited to biocides. The biocide is different from the components (A), (B), (C) and (D) as defined hereinabove. 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, the biocide is a quaternary ammonium compound, an isothiazolinone-based compound, an *N*-substituted diazenium dioxide, or an *N*'-hydroxy-diazenium oxide salt. More preferably, the biozide is an *N*-substituted diazenium dioxide, or an *N*'-hydroxy-diazenium oxide salt.

Preparation of a CMP composition according to the present invention

In a further aspect, the present invention relates to a process for preparing a CMP composition according to the present invention (as defined hereinabove). The process comprises the step of combining

(A) abrasive particles containing ceria

(B) one or more polymers as defined hereinabove

in an aqueous medium.

Processes for preparing CMP compositions are generally known. These processes may be applied to the preparation of the CMP composition used according to the present invention. This can be carried out by dispersing the above-described component (A) and dissolving the above-

described component (B), and if appropriate the above-described optional further component (C) in water, and optionally by adjusting the pH value through adding a pH adjustor (D) as defined hereinabove or hereinbelow. 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 pH value of the CMP composition according to the present invention is preferably adjusted in the range of from 5 to 10.8, preferably from 6 to 10, more preferably from 6.5 to 9.5, further preferably from 7 to 9, still further preferably from 7.5 to 8.5, for example 8.

Preferably, a process for preparing a CMP composition according to the present invention (as defined hereinabove) comprises the step of adding one or more polymers (B) as defined hereinabove to an aqueous suspension comprising abrasive particles containing ceria (A).

Chemical mechanical polishing using the CMP composition of the present invention

In a further aspect the present invention relates to a process for the manufacture of a semiconductor device comprising the step of chemical mechanical polishing of a substrate in the presence of a chemical mechanical polishing (CMP) composition according to the present invention as defined hereinabove. In the step of chemical mechanical polishing, the pH value of the CMP composition is in the range of from 5 to 10.8, preferably from 6 to 10, more preferably from 6.5 to 9.5, further preferably from 7 to 9, still further preferably from 7.5 to 8.5, for example 8.

The chemical-mechanical polishing step 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.

In a preferred process according to the present invention, the substrate comprises

- a surface region or a layer consisting of silicon dioxide

and

- a surface region or a layer consisting of silicon nitride or polycrystalline silicon.

In preferred cases, the silicon dioxide layer to be polished by the CMP composition according to the present invention is a silicon dioxide layer of a substrate which is a shallow trench isolation (STI) device or a part thereof.

Examples

The invention is hereinafter further illustrated by means of examples and comparison examples.

Preparation of the CMP compositions:

The polymer (B) as defined hereinbelow and optionally a polyhydroxy compound (C) as defined hereinbelow are added to a commercially available solution of colloidal ceria.

The following polymers (B) are used

polymer (B)	supplier	Anionic group (i)	molar mass of structure unit (ii)	Percentage of molar mass of all structure units (ii) based on the molar mass of polymer (B)
EPPR 312	BASF SE	phosphoric group	5000	83
Melpers 0045	BASF SE	carboxylic group	5800	94
Stab 0557 (comb polymer having a backbone formed of poly-acrylic acid)		carboxylic group	1100	75 %
Stab100		phosphonic group	3000	92 %

For comparison, CMP compositions not containing any polymer (B) are also tested.

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

The concentration of ceria (either wet-precipitated, tradename HC 60 from Rhodia, or fumed, tradename NanoArc 6440 from NanoPhase) is in each case 0.5 wt.-%, based on the weight of the respective CMP composition.

Wet-precipitated ceria particles (for example Rhodia HC60) as obtained from supplier have a mean primary particle size of 60 nm (as determined using BET surface area measurements) and a mean secondary particle size (d50 value) of 99 nm (as determined using dynamic light scattering techniques via a Horiba instrument).

Fumed ceria particles (for example NanoArc 6440) as obtained from supplier have a mean primary particle size of 30 nm (as determined using BET surface area measurements) and a mean secondary particle size (d50 value) of 130 nm (as determined using dynamic light scattering techniques via a Horiba instrument).

If not indicated otherwise, wet-precipitated ceria is used. For further information about the components of the CMP compositions, see the tables in the section " results" hereinbelow.

CMP experiments

Several comparative CMP compositions (see the tables in the result section) were used for chemical mechanical polishing 200 mm diameter wafers coated with either silicon dioxide, silicon nitride and polycrystalline silicon.

The polishing parameters are as follows:

CMP device:	Strasbaugh nSpire (Model 6EC) with ViPRR floating retaining ring Carrier;
down pressure:	2.0 psi (140 mbar);
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 (4 lbs, 17,8 N);
polishing pad:	IC1000 A2 stacked pad, x,y k or k grooved (R&H);
backing film:	Strasbaugh, DF200 (136 holes);
conditioning disk:	3M S60;

For studying the material removal of silicon dioxide (SiO_2), substrates coated with a silicon dioxide layer obtained by plasma-enhanced chemical vapor deposition using tetra ethyl ortho silicate (TEOS) as the precursor were used.

For studying the material removal of silicon nitride (Si_3N_4), substrates coated with a silicon nitride layer obtained by plasma-enhanced chemical vapor deposition were used.

For studying the material removal of polycrystalline silicon (poly-Si), substrates coated with a polycrystalline silicon layer obtained from chemical vapor deposition were used.

For silicon dioxide, the material removal is determined based on the difference of weight before and after the chemical mechanical polishing, based on a density of SiO_2 of 1.9 kg/l. The weight is measured by means of a Sartorius LA310 S scale. For silicon nitride and polycrystalline silicon, the material removal is determined based on the difference of the film thickness of the substrates before and after the chemical mechanical polishing. The film thickness (average thickness of diameter scan) is measured by means of a Filmmetrics F50 reflectometer. For calculating the material removal rate (MRR) the total material removal as determined above is divided by the time of the main polishing step.

The selectivity for removing silicon dioxide vs. silicon nitride (SiO_2/Si_3N_4) is the ratio between the material removal rates of silicon dioxide and silicon nitride. The selectivity for removing silicon dioxide vs. polycrystalline silicon (SiO_2/poly-Si) is the ratio between the material removal rates of silicon dioxide and polycrystalline silicon.

Results of the CMP experiments

The results of the CMP experiments are given in tables 1-8 hereinbelow.

Table 1 CMP compositions comprising EPPR 312 as polymer (B)

Concentration of EPPR 312 [wt.-%]	pH	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0	5.5	3293	7	11
0.01	4	1280	5	11
0.01	5	2432	23	22
0.01	6	2768	24	15
0.005	6	1280	5	11
0.005	8	2432	23	22

CMP compositions comprising EPPR312 as polymer (B) in the above-indicated amounts are stable at the pH values given in table 1. In some cases the selectivities SiO_2/Si_3N_4 and/or SiO_2/poly-Si are improved in the presence of EPPR312.

Table 2 CMP compositions comprising EPPR 312 as polymer (B) ans a polyhydroxy compound (C)

concentration of EPPR 312 [wt.-%]	pH	polyhydroxy compound (C)	concentration of (C) [wt.-%]	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0.01	6	alkylpolyglycoside (Glucopon 225 DK)	0.01	2262	103	84
0.0075	5.5		0.075	2221	53	26
0.005	5		0.05	1991	50	39
0.01	6	galactose	0.5	1852	154	36
0.005	6		0.5	2967	106	11
0.01	6	innositol	0.5	1551	67	39

Combination of EPPR312 as polymer (B) with polyhydroxy compounds (C) at the pH values as listed in table 2 results in a significant improvements of the selectivities SiO_2/Si_3N_4 and SiO_2/poly-Si, compared to CMP compositions comprising either no polymer (B) or EPPR312 as polymer (B) but no polyhydroxy compound (C).

Table 3: CMP compositions comprising Melpers 0045 as polymer (B)

Concentration of MelPers 0045 [wt.-%]	pH	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0	5.5	3293	7	11
0.05	9	1725	72	173
0.025	7	2044	21	76
0.025	9	2478	38	165

CMP compositions comprising Melpers 0045 as polymer (B) in the above-indicated amounts are stable at the pH values given in table 3. The selectivities SiO_2/Si_3N_4 and/or SiO_2/poly-Si are remarkably improved in the presence of Melpers 0045, especially at pH = 9.

Table 4: CMP compositions comprising Melpers 0045 as polymer (B) and polyhydroxy compounds (C)

concentration of Melpers 0045 [wt.-%]	pH	conc.of PEG [wt.-%]	further polyhydroxy compound (C)	conc. of (C) [wt.-%]	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0	5.5	0	-	0	3293	7	11
0	5	0.4	-	0	2804	7	47
0.025	7	0.2	-	0	1791	24	128
0.025	9	0.2	-	0	1872	33	69
0.025	9	0.2	sucralose	0.1	1938	55	323
0.025	5	0	alkylpolyglycoside (Glucopon 225 DK)	0.05	1902	59	Not measured
0.025	7	0		0	2220	10	62
0.025	7	0		0.05	2922	66	97

The PEG is a polyethylene glycol having a molar mass of 10000 g/mol, available from Aldrich. In the last two CMP compositions of table 4, the abrasive particles (A) are fumed ceria.

Combination of Melpers 0045 as polymer (B) with polyhydroxy compounds (C) as listed above at the pH values given in table 4 results in suitable selectivities SiO_2/Si_3N_4 and SiO_2/poly-Si, compared to CMP compositions comprising no polymer (B).

Table 5: CMP compositions comprising Stab 100 as polymer (B)

Concentration of Stab 100 [wt.-%]	pH	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0	5.5	3293	7	11
0.01	8	2565	6	13

CMP compositions comprising Stab 100 as polymer (B) in the above-indicated amount are stable at pH = 8, see table 5. The selectivities SiO_2/Si_3N_4 and SiO_2/poly-Si are not significantly changed in the presence of Stab 100.

Table 6: CMP compositions comprising Stab 100 as polymer (B) and polyhydroxy compounds (C)

concentration of Stab 100 [wt.-%]	pH	polyhydroxy compound (C)	concentration of (C) [wt.-%]	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0.01	8	galactose	0.25	2338	37	21
0.01	8	Alkylpoly-glycoside (Glucopon 225 DK)	0.1	2660	106	121

Combination of Stab 100 as polymer (B) with a polyhydroxy compound (C) as listed in table 6 at pH =8 results in improved selectivities SiO_2/Si_3N_4 and SiO_2/poly-Si, compared to CMP compositions comprising no polymer (B) or Stab 100 as polymer (B) but no polyhydroxy compound (C).

Table 7: CMP compositions comprising Stab0557 as polymer (B)

Concentration of Stab0557 [wt.-%]	pH	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0	5.5	3293	7	11
0.01	8	1763	35	80

CMP compositions comprising Stab 100 as polymer (B) in the above-indicated amount are stable at pH = 8, see table 7. The selectivities SiO_2/Si_3N_4 and SiO_2/poly-Si are significantly increased in the presence of Stab 100.

Table 8: CMP compositions comprising Stab0557 as polymer (B) and a polyhydroxy compound (C)

concentration of Stab0557 [wt.-%]	pH	polyhydroxy compound (C)	concentration of (C) [wt.-%]	MRR SiO_2 [A/min]	Selectivity SiO_2/Si_3N_4	Selectivity SiO_2/poly-Si
0.01	8	galactose	0.25	2103	100	96
0.01	8	sucralose	0.25	1882	125	118

Combination of Stab0557 as polymer (B) with a polyhydroxy compound (C) as listed in table 8 at pH =8 results in improved selectivities SiO_2/Si_3N_4 and SiO_2/poly-Si, compared to CMP compositions comprising no polymer (B) or Stab 100 as polymer (B) but no polyhydroxy compound (C).

Measurement of the zeta potential

For several CMP compositions according to the invention as well as for comparison CMP compositions not according to the invention, the zeta potential is measured as a function of the pH value in the pH range from 4 to 10 using a Zetasizer Nano (supplier: Malvern). The measurements start at the pH value which the respective CMP composition has after dilution to a ceria content of 0.1 wt.-% in the presence of 10 mmol/l KCl. For further measurements, the pH of the respective CMP compositions is adjusted by automatic titration with NaOH or HCl.

The concentration of polymers in the tested compositions are as follows:

1. no polymer (comparison composition)
2. 0.002 wt.-% Polyaspartic acid (comparison composition)
3. 0.002 wt.-% Melpers 0045
4. 0.002 wt.-% EPPR312
5. 0.001 wt.- % EPPR312
6. 0.002 wt.-% Stab 100.

The results (see figure 1) show that polymers (B) used according to the present invention are capable of screening the charge of the ceria containing abrasive particles against electrophoretic excitation. Accordingly, the absolute value of the zeta potential calculated from the electrophoretic mobility is significantly lower than in a CMP composition not comprising any polymer or comprising polyanions without a significant amount of structure units having such screening effect (as it is the case with polyaspartic acid). In the presence of polyaspartic acid, due to the large amount of negative charges of the polyanion, the sign of the zeta potential is negative, and the absolute value of the zeta potential is high.

Despite the low zeta potential of the ceria containing particles in the CMP compositions according to the invention at a pH in the range of from 6 to 10, no coagulation of ceria occurs in this pH range of or at least in a significant subrange of this pH range, due to steric stabilization of the ceria particles.

Stability test

CMP compositions comprising (A) ceria containing particles were prepared as follows: To 100 ml ultra pure water ceria containing particles (Rhodia HC 60) is added under stirring. The final concentration of ceria containing particles (A) is 0.5 wt.-% The pH is adjusted to with ammonia to the values given in table 9 below.

CMP compositions comprising (A) ceria containing particles and (B) the polymer Stab 100 (see above) were prepared as follows: To 100 ml ultra pure water Stab 100 is added that a concentration of 0.01 wt.-% is reached. Ceria containing particles (Rhodia HC 60) s added under stirring. The final concentration of ceria containing particles (A) is 0.5 wt.-% The pH is adjusted to with ammonia to the values given in table 9 below.

The CMP compositions are stored for three days. Each day, the particle size distribution is measured with Horiba LB 550 V (dynamic light scattering DLS) at different times of storage. The results are given in table 9.

For the CMP composition adjusted to pH 10 without polymer (B), the particle size distribution could not be measured any more after 1 day because the ceria was completely coagulated. In contrast, the CMP composition adjusted to pH 10 containing 0.01 wt.-% of polymer (B) remained stable over three days. The same applies to a CMP composition adjusted to pH 10.8 containing 0.01 wt.-% of polymer (B)

For the CMP composition adjusted to pH 9 without polymer (B), the particle size distribution could not be measured any more at the third day because the ceria was completely coagulated. In contrast, the CMP composition adjusted to pH 9 containing 0.01 wt.-% of polymer (B) remained stable over three days.

Table 9: D50 values of ceria in CMP compositions with and without polymer (B) at different pH values and storage times

	0,5 wt.-% ceria			0,5 wt.-% ceria + 0,01% Stab 100		
pH	Day 1	Day 2	Day 3	Day 1	Day 2	day 3
9	126	151	settled	135	136	128
10	settled			133	131	123
10.8				124	119	122

Long term stability test

CMP compositions comprising (A) ceria containing particles were prepared as follows: To 100 ml ultra pure water ceria containing particles (Rhodia HC 60) is added under stirring. The final concentration of ceria containing particles (A) is 0.5 wt.-% The pH is adjusted with ammonia to the values given in table 10 below or the pH is adjusted with KOH to the values given in table 12 below.

CMP compositions comprising (A) ceria containing particles and (B) the polymer Stab 100 (see above) were prepared as follows: To 100 ml ultra pure water Stab 100 is added that a concentration of 0.01 wt.-% is reached. Ceria containing particles (Rhodia HC 60) s added under stirring. The final concentration of ceria containing particles (A) is 0.5 wt.-% The pH is adjusted with ammonia to the values given in table 11 below or the pH is adjusted with KOH to the values given in table 13 below.

The CMP compositions are stored for forty (40) days. After five (5) days, twelve (12) days, twenty six (26) days and forty (40) days, the particle size distribution is measured with Horiba LB 550 V (dynamic light scattering DLS) at different times of storage. The results are given in tables 10, 11, 12 and 13.

Table 10: D50 values [nm] of 0.5 wt.-% ceria in CMP compositions at different pH values and storage times, the pH value is adjusted by ammonia. X: The dispersion has settled and no PSD measurement could be performed any more.

	Time [days]				
pH	Day 0	Day 5	Day 12	Day 26	Day 40
5.0	130	120	116	142	151
7.0	116	124	107	241	X
9.0	230	X			
10.8	X				

Table 11: D50 values [nm] of 0.5 wt.-% ceria in CMP compositions with 0.01 wt.-% polymer (B) Stab100 at different pH values and storage times, the pH value is adjusted by ammonia. X: The dispersion has settled and no PSD measurement could be performed any more.

	Time [days]				
pH	Day 0	Day 5	Day 12	Day 26	Day 40
5.0	125	123	127	129	130
7.0	119	113	138	167	136
9.0	124	117	118	114	121
10.8	124	124	122	118	118

Table 12: D50 values [nm] of 0.5 wt.-% ceria in CMP compositions at different pH values and storage times, the pH value is adjusted by KOH. X: The dispersion has settled and no PSD measurement could be performed any more.

	Time [days]				
pH	Day 0	Day 5	Day 12	Day 26	Day 40
5.0	143	138	141	123	162
7.0	140	147	293	X	
9.0	X				
10.8	X				

Table 13: D50 values [nm] of 0.5 wt.-% ceria in CMP compositions with 0.01 wt.-% polymer (B) Stab100 at different pH values and storage times, the pH value is adjusted by KOH. X: The dispersion has settled and no PSD measurement could be performed any more.

	Time [days]				
pH	Day 0	Day 5	Day 12	Day 26	Day 40
5.0	135	129	134	115	117
7.0	139	138	167	127	125
9.0	130	114	117	128	134
10.8	132	119	117	130	122

The CMP compositions according to the invention comprising (A) ceria containing particles and (B) one or more polymers are leading to long term stable dispersions combined with high polishing performance in terms of SiO_2 over Si_3N_4- and SiO_2 over poly-Si-selectivity and material removal rate as can be seen in the examples and tables above

Claims

1. Chemical-mechanical polishing (CMP) composition comprising the following constituents:
(A) abrasive particles containing ceria
(B) one or more polymers, wherein each macromolecule of said polymers (B) comprises
(i) one or more anionic functional groups
(ii)
and

(iii) one or more structure units $-(AO)_a-R$
wherein in each structure unit $-(AO)_a-R$ independently from each other structure unit $-(AO)_a-R$
A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other x selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2
wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different
a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135,
R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,
wherein in said polymer (B) the sum of the molar masses of all structure units (ii) is at least 50 % of the molar mass of said polymer (B).

2. Chemical-mechanical polishing (CMP) composition according any preceding claim, wherein the concentration of said one or more polymers (B) is selected so that
- no flocculation of ceria containing particles (A) occurs in the pH range of from 6 to 10
-
and/or

- at a pH in the range of from 6 to 10 the zeta potential of the particles containing ceria is in a range between + 30 mV and – 30 mV.

3. Chemical-mechanical polishing (CMP) composition according to any preceding claim, wherein in the macromolecules of said polymer (B) or of at least one of said polymers (B) said one or more anionic functional groups are selected from the group consisting of the carboxylic group, the sulfonic group, the sulfate group, the phosphoric group and the phosphonic group.

4. Chemical-mechanical polishing (CMP) composition according to any preceding claim, wherein in said polymer (B) or in at least one of said polymers (B)

the molar mass of each of said one or more structure units (ii) $-(AO)_a-R$ is 500 g/mol or more, preferably 1000 g/mol or more, more preferably 2000 g/mol or more, most preferably 3000 g/mol or more

and/or

the sum of the molar masses of all of said structure units (ii) $-(AO)_a-R$ is 60 % or more, preferably 70 % or more, most preferably 80 % or more of the molar mass of said polymer (B).

5. Chemical-mechanical polishing (CMP) composition according to any preceding claim, wherein said polymer (B) or at least one of said polymers (B) is selected from the group consisting of comb polymers and block copolymers.

6. Chemical-mechanical polishing (CMP) composition according to any preceding claim, wherein said polymer (B) or at least one of said polymers (B) is a comb polymer comprising

(i) a backbone to which one or more anionic functional groups are linked
and

(ii) one or more side chains each comprising a structure unit $-(AO)_a-R$
wherein in said comb polymer the sum of the molar masses of all said structure units (ii) $-(AO)_a-R$ is at least 50 % of the molar mass of said comb polymer.

7. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 6, wherein said comb polymer comprises

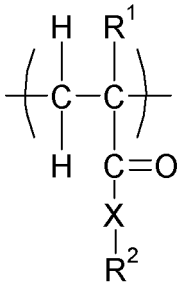
- building units each comprising one or more anionic functional groups

and

- side chains each comprising a structure unit (ii) $-(AO)_a-R$ wherein
A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other x selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2
wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different
a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135

R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein one or more of the building units comprising an anionic functional group are selected from general formulae (7.1), (7.2), (7.3) and (7.4):



(7.1)

in which

R^1 is H or an unbranched or branched C_1-C_4 alkyl group, CH_2COOH or CH_2CO-X-R^2;

R^2 is PO_3M_2, O-PO_3M_2, (C_6H_4)-PO_3M_2 or (C_6H_4)-OPO_3M_2;

X is NR^7-(C_nH_{2n}) or O-(C_nH_{2n}) with n = 1, 2, 3 or 4, the nitrogen atom or the oxygen atom, respectively, being attached to the CO group;

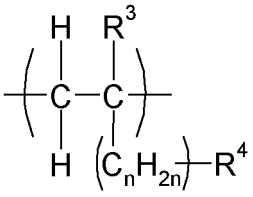
R^7 is H, C_1-C_6 alkyl, (C_nH_{2n})-OH, (C_nH_{2n})-PO_3M_2, (C_nH_{2n})-OPO_3M_2, (C_6H_4)-PO_3M_2, (C_6H_4)-OPO_3M_2 or (C_nH_{2n})-O-(A^2O)$_\alpha$ -R^9; with n = 1, 2, 3 or 4

A^2 is C_zH_{2z} with z = 2, 3, 4 or 5 or is $CH_2CH(C_6H_5)$;

α is an integer from 1 to 350; and

R^9 is H or an unbranched or branched C_1-C_4 alkyl group;

or X is a chemical bond and R^2 is OM;



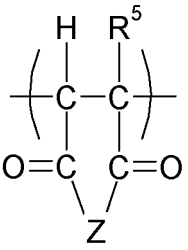
(7.2)

in which

R^3 is H or an unbranched or branched C_1-C_4 alkyl group;

n is 0, 1, 2, 3 or 4;

R^4 is PO_3M_2, or O-PO_3M_2;



(7.3)

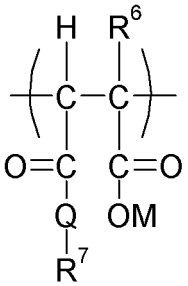
in which

R^5 is H or an unbranched or branched C_1-C_4 alkyl group;

Z is O or NR^7; and

R^7 is H, (C_nH_{2n})-OH, (C_nH_{2n})-PO_3M_2, (C_nH_{2n})-OPO_3M_2, (C_6H_4)-PO_3M_2, or (C_6H_4)-OPO_3M_2, wherein

n is 1, 2, 3 or 4;



(7.4)

in which

R^6 is H or an unbranched or branched C_1-C_4 alkyl group;

Q is NR^7 or O;

R^7 is H, (C_nH_{2n})-OH, (C_nH_{2n})-PO_3M_2, (C_nH_{2n})-OPO_3M_2, (C_6H_4)-PO_3M_2, (C_6H_4)-OPO_3M_2 or (C_nH_{2n})-O-$(A^2O)_\alpha$ -R^9,

n is 1, 2, 3 or 4;

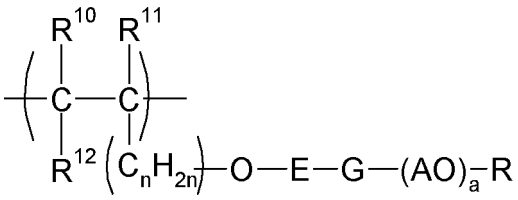
A^2 is CzH_{2z} with z = 2, 3, 4 or 5 or is $CH_2CH(C_6H_5)$;

α is an integer from 1 to 350;

R^9 is H or an unbranched or branched C_1-C_4 alkyl group;

wherein in formulae (7.1), (7.2), (7.3) and (7.4) each M independently of any other M is H or one cation equivalent

and/or wherein one or more of the side chains comprising a structure unit (ii) $-(AO)_a$-R are selected from general formulae (7.5), (7.6), (7.7) and (7.8):



(7.5)

in which

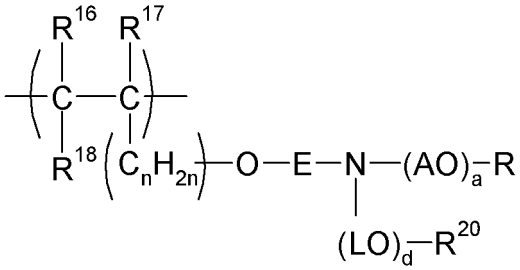
R^{10}, R^{11} and R^{12} independently of one another are H or an unbranched or branched C_1-C_4 alkyl group;

n is 0, 1, 2, 3, 4 and/or 5;

E is an unbranched or branched C_1-C_6 alkylene group, a cyclohexylene group, CH_2-C_6H_{10}, 1,2-phenylene, 1,3-phenylene or 1,4-phenylene;

G is O, NH or CO-NH; or

E and G together are a chemical bond;



(7.6)

in which

R^{16}, R^{17} and R^{18} independently of one another are H or an unbranched or branched C_1-C_4 alkyl group;

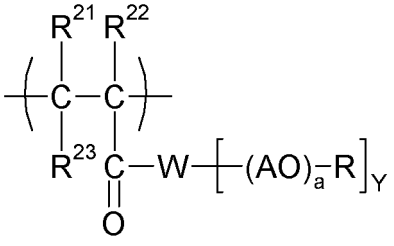
n is 0, 1, 2, 3, 4 or 5;

E is an unbranched or branched C_1-C_6 alkylene group, a cyclohexylene group, CH_2-C_6H_{10}, 1,2-phenylene, 1,3-phenylene or 1,4-phenylene or is a chemical bond;

L is C_zH_{2z} with z = 2, 3, 4 or 5 or is CH_2-$CH(C_6H_5)$;

d is an integer from 1 to 350;

R^{20} is H or an unbranched C_1-C_4 alkyl group;



(7.7)

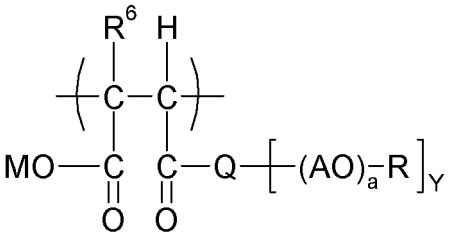
in which

R^{21}, R^{22} and R^{23} independently of one another are H or an unbranched or branched C_1-C_4 alkyl group;

W is O, NR^{25} or N

R^{25} is H or an unbranched or branched C_1-C_4 alkyl group;

Y is 1, if W = O or NR^{25}, and is 2 if W = N;



(7.8)

in which

R^6 is H or an unbranched or branched C_1-C_4 alkyl group;

Q is NR^{10}, N or O;

R^{10} is H or an unbranched or branched C_1-C_4 alkyl group;

Y is 1 if Q = O or NR^{10} , and is 2 if Q = N.

8. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 6, wherein said comb polymer (B) is obtainable by copolymerisation of the monomers

(8.1) acrylic acid and

(8.2) one or more macromers each comprising a polymerizable double bond, preferably a double bond of a vinyl group, an allyl group, an isoprenyl group, an acrylate group, a methacrylate group or a maleinic ester group,

and a structure unit (ii) $-(AO)_a-R$ wherein

A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other x selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2

wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different
a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135

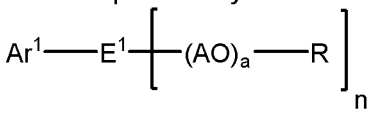
R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

wherein the amounts of the monomers (8.1) and (8.2) are selected so that a comb polymer is obtained wherein in said comb polymer the sum of the molar masses of all said structure units (ii) $-(AO)_a-R$ is at least 70 % of the molar mass of said comb polymer.

9. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 6, wherein said comb polymer (B) is a polycondensate containing

(9.1) at least one building unit comprising an aromatic or heteroaromatic system Ar^1 and a side chain comprising or consisting of a structure unit (ii) – $(AO)_a-R$
wherein in each building unit (9.1) independently from each other building unit (9.1)

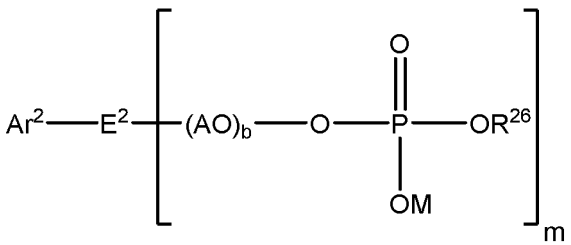
A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other x selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2
wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different
a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135
R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,
wherein preferably the building units (9.1) are represented by general formula (9.1)



(9.1)

wherein for each building unit of formula (9.1) independently from each other building unit of formula (9.1)
Ar^1 is selected from the group consisting of unsubstituted aromatic or heteroaromatic systems having 5 to 10 carbon atoms in each case
E^1 is selected from the group consisting of N, NH and O, preferably O
n = 2 if E^1 = N and n = 1 if E^1 = NH or O
A, a and R are as defined above

(9.2) at least one building unit comprising an aromatic or heteroaromatic system Ar^1 and a phosphoric group
wherein preferably one or more of the building units (9.2) are represented by general formula (9.2)



(9.2)

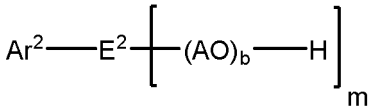
wherein for each building unit of formula (9.2) independently from each other building unit of formula (9.2)

Ar^2 is selected from the group consisting of unsubstituted aromatic or heteroaromatic system having 5 to 10 carbon atoms in each case
E^2 is selected from the group consisting of N, NH and O, preferably O
m = 2 if E^2 = N and m = 1 if E^2 = NH or O

A is as defined above for building unit (9.1)
b is an integer selected from the range of from 0 to 300, preferably 1 to 5
M independently of any other M is H or one cation equivalent,
R^{26} is M or Ar^1-O-$(AO)_a$-.

(9.3) at least one building unit comprising an aromatic or heteroaromatic system $Ar^{2,}$ wherein building unit (9.3) differs from building unit (9.2) exclusively in that the phosphonic group of the building unit (9.2) is replaced by H in building unit (9.3), and building unit (9.3) is not the same as building unit (9.1)

wherein preferably the building unit (9.3) is represented by general formula (9.3)

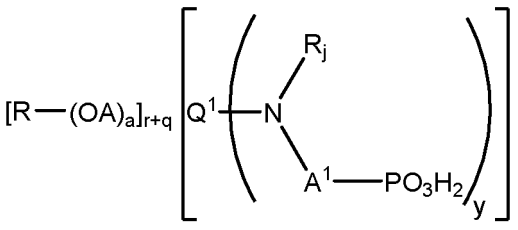


(9.3)

wherein for each building unit of formula (9.3) independently from each other building unit of formula (9.3)

Ar^2, E^2, m, A and b are as defined for building unit (9.2)

10. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 4, wherein said polymer (B) or at least one of said polymers (B) corresponds to the formula (10)



(10)

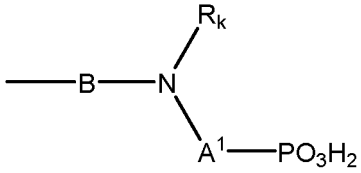
wherein

A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other x selected from the range of integers from 2 to 4, wherein x is preferably 2 or 3, further preferably x =2; wherein within each structure unit $-(AO)_a-R$ the groups A are the same or different

- a is an integer selected from the range of from 5 to 200, preferably 8 to 150, most preferably 20 to 135
- R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,
- Q^1 is a hydrocarbon group comprising 2 to 18 carbon atoms and possibly one or more heteroatoms,
- A^1 is an alkylene group comprising 1 to 5 carbon atoms,
- the R_j groups are independently from each other selected from the group consisting of:
  - the A^1-PO_3H_2 group, wherein A^1 has the above-defined meaning,
  - the alkyl group comprising 1 to 18 carbon atoms and able to carry $-(AO)_a-R$ groups

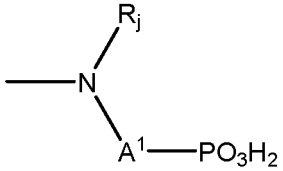
and

- the group



wherein B designates an alkylene group having 2 to 18 carbon atoms,

- r is the number of structure units $-(AO)_a-R$ carried by all the R_j groups,
- q is the number of structure units $-(AO)_a-R$ carried by Q,
- the sum "r+q" is selected so that in said polymer (B) the sum of the molar masses of all said structure units (ii) $-(AO)_a-R$ is at least 50 % of molar mass of said polymer (B) preferably 90 % or more, based on the molar mass of said polymer
- y is an integer in the range of from 1 to 3, wherein when y > 1, the groups



are the same or different

- Q^1, N, and the R_j groups can form together one or more rings, this ring or these rings moreover able to contain one or more other heteroatoms.

11. Chemical mechanical polishing (CMP) composition according to any preceding claim, further comprising
(C) one or more polyhydroxy compounds.

12. Chemical-mechanical polishing (CMP) composition according to any preceding claim, further comprising
(D) one or more pH adjustors.

13. Chemical-mechanical polishing (CMP) composition according to any preceding claim, wherein said composition has a pH in the range of from 5 to 10.8, preferably 6 to 10.

14. Chemical mechanical polishing (CMP) composition according to any preceding claim, comprising

(A) a total amount of abrasive particles containing ceria in a range of from 0.01 wt.-% to 5 wt.-% based on the total weight of the respective CMP composition,

and/or

(B) a total amount of polymers (B) as defined in claims 1 to 10 in a range of from 0.0002 wt.-% to 1 wt.-%; based on the total weight of the respective CMP composition.

and/or

(C) a total amount of poylyhdroxy compounds in a range of from 0.001 wt.-% to 2 wt.-% based on the total weight of the respective CMP composition.

15. A process for the manufacture of a semiconductor device comprising chemical mechanical polishing of a substrate in the presence of a chemical mechanical polishing (CMP) composition as defined in any of claims 1 to 14.

16. The process according to claim 15, wherein the substrate comprises
- a surface region or a layer consisting of silicon dioxide

and

- a surface region or a layer consisting of silicon nitride or polycrystalline silicon.

17. Use of a polymer (B) as defined in claims 1 to 10
for suppressing the agglomeration of ceria containing particles dispersed in aqueous medium

and/or

for adjusting the zeta potential of ceria containing particles.

18. Process for suppressing the agglomeration and/or adjusting the zeta potential of ceria containing particles dispersed in aqueous medium, said process comprising the step of adding an effective amount of one or more polymers (B) as defined in claims 1 to 10 to said aqueous medium wherein the ceria containing particles are dispersed.