

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 embodiments disclosed herein is to provide a chemical mechanical polishing (CMP) composition and a CMP process showing an improved polishing performance especially for dielectric substrates. More specifically it is an object of the embodiments disclosed hereinto 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 embodiments disclosed herein 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 embodiments disclosed herein 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 the present disclosure, 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,

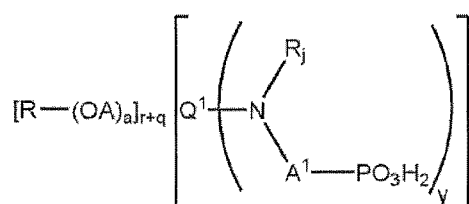
wherein in said polymer (B) the sum of the molar masses of all structure units (ii) is at least 50 % of the molar mass of said polymer (B).

In an aspect, there is provided a 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)

corresponds to formula (10)



wherein

A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other 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

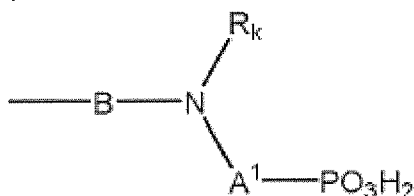
one or more heteroatoms,

- 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

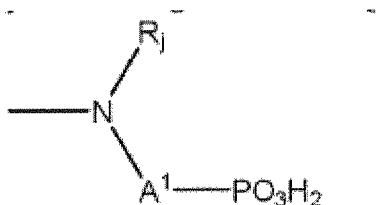
and

- 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.

(OR)

the 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.

In another aspect, there is provided 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 above.

5 In another aspect, there is provided the use of a polymer (B) as defined above for suppressing the agglomeration of ceria containing particles dispersed in aqueous medium and/or for adjusting the zeta potential of ceria containing particles.

10 In another aspect, there is provided 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 above to said aqueous medium wherein the ceria containing particles are dispersed.

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

15 (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.

20 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.

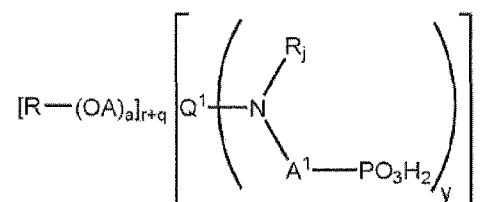
Within the CMP composition of the present invention, the ceria particles are typically dispersed in a colloidal state.

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

Claims

1. Chemical-mechanical polishing (CMP) composition comprising the following constituents:
- (A) abrasive particles containing ceria
- 5 (B) one or more polymers, wherein each macromolecule of said polymers (B)

corresponds to formula (10)



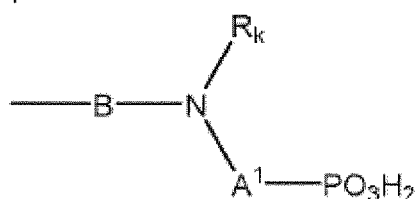
wherein

A is C_xH_{2x} wherein for each A in said structure units $-(AO)_a-R$, x is independently from each other 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

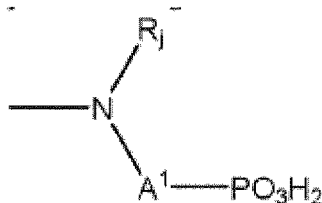
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- one or more heteroatoms,
- A^1 is an alkylene group comprising 1 to 5 carbon atoms,
- the R_j groups are independently from each other selected from the group consisting of:
 - the A^1 - PO_3H_2 group, wherein A^1 has the above-defined meaning,
 - 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.

(OR)

the said polymers (B) is a comb polymer comprising

39b

(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.

2. Chemical-mechanical polishing (CMP) composition according any preceding claim, where-
in 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 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

5 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).

10

4. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 3, wherein said comb polymer comprises

15 - (A) building units each comprising one or more anionic functional groups

and

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

20 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

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

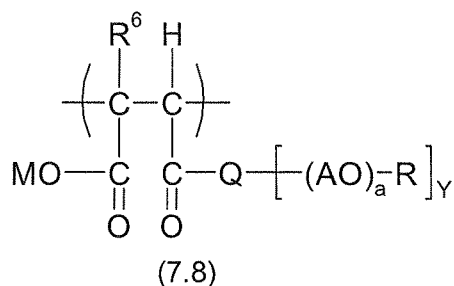
R is hydrogen or a branched or linear alkyl group having 1 to 4 carbon atoms,

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 $W = N$;



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 $Q = N$.

5. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 4, 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.

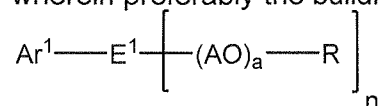
- 5 6. Chemical-mechanical polishing (CMP) composition according to any of claims 1 to 5, wherein said comb polymer (B) is a polycondensate containing

(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) $-(AO)_a-R$
 10 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 $x=2$

15 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)

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

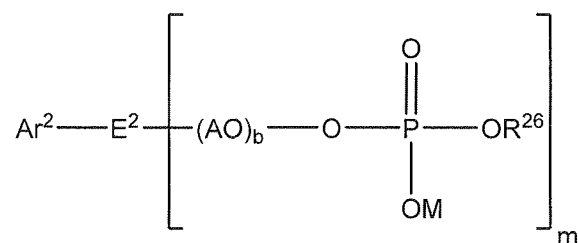
E^1 is selected from the group consisting of N, NH and O, preferably O

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

A, a and R are as defined above

30 (9.2) at least one building unit comprising an aromatic or heteroaromatic system Ar^2 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)

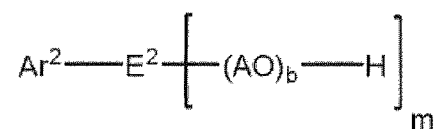
b is an integer selected from the range of from 0 to 300, preferably 1 to 5

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)

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

(C) one or more polyhydroxy compounds.

8. Chemical-mechanical polishing (CMP) composition according to any preceding claim, further comprising

(D) one or more pH adjustors.

9. 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.

10. 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

(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

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

11. 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 10.

12. The process according to claim 11, 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.

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

5 and/or

for adjusting the zeta potential of ceria containing particles.

- 10 14. 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.