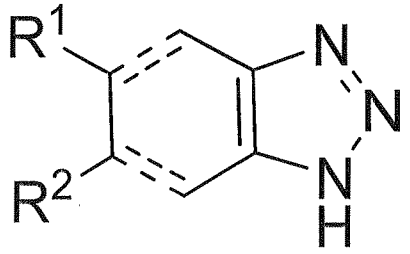
A related object of the embodiments disclosed herein is to provide a process for the manufacture of a semiconductor device comprising chemical mechanical polishing of a substrate, particularly of a substrate comprising a tantalum layer and/or a copper layer.

A further object of the embodiments disclosed herein is to provide corrosion inhibitors, especially for increasing the selectivity of a chemical mechanical polishing (CMP) composition for the removal of tantalum from a substrate for the manufacture of a semiconductor device in the presence of copper on said substrate.

Summary

There is provided a chemical-mechanical polishing (CMP) composition is provided comprising

(A) one or more compounds of formula (1)



(1)

wherein the pairs of dashed lines in formula (1) either each represent a double bond or each represent a single bond

wherein

(i) when each pair of dashed lines in formula (1) represents a double bond

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and – $COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of $-(CH_2-CH_2-O)_n-H$ and $-(CH_2-CH_2-O)_n-CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

and

(ii) when each pair of dashed lines in formula (1) represents a single bond

R^1 and R^2 are hydrogen

or one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and – $COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ and $\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$ wherein n in each case is an integer in the range of from 1 to 15

or

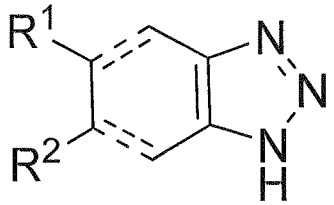
R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

(B) inorganic particles, organic particles, or a composite or mixture thereof,

wherein the total amount of cations selected from the group consisting of magnesium and calcium is less than 1 ppm based on the total weight of the respective CMP composition.

In an aspect, there is provided a chemical-mechanical polishing (CMP) composition comprising

(A) one or more compounds of formula (1)



(1)

wherein the pairs of dashed lines in formula (1) either each represent a double bond or each represent a single bond

wherein

(i) when each pair of dashed lines in formula (1) represents a double bond

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and – $COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ and $\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

and

(ii) when each pair of dashed lines in formula (1) represents a single bond

R^1 and R^2 are hydrogen

or

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and – $COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ and $\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

(B) inorganic particles, organic particles, or a composite or mixture thereof, and

(I) one or more buffers

wherein the one or at least one of the more than one buffers of constituent (I) is preferably selected from the group consisting of potassium carbonate or potassium hydrogen carbonate, and

wherein the total amount of cations selected from the group consisting of magnesium and calcium is less than 1 ppm based on the total weight of the respective CMP composition.

When each pair of dashed lines in formula (1) represents a double bond, the six membered ring in formula (1) is in the aromatic state.

When R^1 is alkyl it is preferred that said alkyl is selected from the group consisting of tert-butyl and sec-butyl.

When none of R^1 and R^2 is hydrogen it is preferred that both R^1 and R^2 are bromine.

When R^1 or R^2 is – $COOR^3$ wherein R^3 is a substituent comprising a structural unit selected from the group consisting of – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ and $\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$, wherein n in each case is an integer in the range of from 1 to

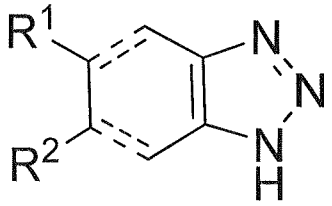
R^3 preferably is an ethoxylate residue or a methyl-terminated ethoxylate residue. An ethoxylate residue is a substituent of the structure – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$. A methyl-terminated ethoxylate residue is a substituent of the structure – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$. In each case n is an integer selected in the range of from 1 to 15.

It is known that benzotriazole irrespective of the presence of substituents on the benzene ring is subject to tautomerism, i.e., chemical equilibrium between molecular forms differing with regard to the position of the hydrogen atom on the

Claims

1. Chemical-mechanical polishing (CMP) composition comprising

(A) one or more compounds of formula (1)



(1)

wherein the pairs of dashed lines in formula (1) either each represent a double bond or each represent a single bond

wherein

(i) when each pair of dashed lines in formula (1) represents a double bond

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and $-COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of $-(CH_2-CH_2-O)_n-H$ and $-(CH_2-CH_2-O)_n-CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

and

(ii) when each pair of dashed lines in formula (1) represents a single bond

R^1 and R^2 are hydrogen

or

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and $-COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of $-(CH_2-CH_2-O)_n-H$ and $-(CH_2-CH_2-O)_n-CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

(B) inorganic particles, organic particles, or a composite or mixture thereof, and

(I) one or more buffers

wherein the one or at least one of the more than one buffers of constituent (I) is preferably selected from the group consisting of potassium carbonate or potassium hydrogen carbonate, and

wherein the total amount of cations selected from the group consisting of magnesium and calcium is less than 1 ppm based on the total weight of the respective CMP composition.

2. Chemical-mechanical composition according to claim 1, wherein (A) the one or at least one of the more than one compounds of formula (1) is selected from the group consisting of

5-bromo-1H-benzotriazole,

5-tert-butyl-1H-benzotriazole,

5-(benzoyl)-1H-benzotriazole,

5,6-dibromo-1H-benzotriazole,

5-chloro-1H-benzotriazole,

5-sec-butyl-1H-benzotriazole,

4,5,6,7-tetrahydro-1H-benzotriazole.

3. Chemical-mechanical polishing (CMP) composition according to claim 1 or 2, wherein the particles of constituent (B) are particles selected from the group consisting of alumina, ceria, copper oxide, iron oxide, nickel oxide, manganese oxide, silica, silicon nitride, silicon carbide, tin oxide, titania, titanium carbide, tungsten oxide, yttrium oxide, zirconia and mixtures and composites thereof.

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

(C) one or more complexing agents selected from the group consisting of inorganic acids and their salts and organic acids and their salts.

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

(D) one or more non-ionic surfactants

wherein the one or at least one of the more than one non-ionic surfactants of constituent (D) is preferably selected from the group consisting of amphiphilic non-ionic surfactants.

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

(E) one or more alcohols

wherein the one or at least one of the more than one alcohols of constituent (E) is preferably selected from the group consisting of ethanediol (ethylene glycol), propanediol (propylene glycol) and butanediol (butylene glycol).

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

(F) one or more oxidizing agents

wherein the one or at least one of the more than one oxidizing agents of constituent (F) is preferably selected from the group consisting of peroxides, persulfates, perchlorates, perbromates, periodates and permanganates.

8. Chemical mechanical polishing (CMP) composition according to any preceding claim having a pH value in the range of from 6 to 14, more preferably from 7 to 13, most preferably from 8 to 12.

9. Chemical-mechanical polishing (CMP) composition according to claim 8,

comprising

(H) one or more pH adjusting agents mixed

with the constituents (A), (B) and optionally one, more or all of constituents (C), (D), (E), (F) and (I) of the chemical-mechanical polishing composition

wherein the one or at least one of the more than one pH adjusting agents (H) is preferably selected from the group consisting of nitric acid, sulfuric acid, ammonia, tetramethylammonium hydroxide, sodium hydroxide and potassium hydroxide.

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

(A) a total amount of one or more compounds of formula (1) in a range of from 0.0001% to 1 wt.-% based on the total weight of the respective CMP composition,

and/or

(B) a total amount of inorganic particles, organic particles, or a composite or mixture thereof in a range of from 0.002 to 10 wt.-% based on the total weight of the respective CMP composition,

and/or

(C) a total amount of one or more complexing agents selected from the group of organic acids and salts thereof in a range of from 0.001 to 10 wt.-% based on the total weight of the respective CMP composition,

and/or

(D) a total amount of one or more non-ionic surfactants in a range of from 0.00001 to 10 wt.-% based on the total weight of the respective CMP composition,

and/or

(E) a total amount of one or more alcohols in a range of from 0.001 to 10 wt.-% based on the total weight of the respective CMP composition,

and/or

(F) a total amount of one or more oxidizing agents in a range of from 0.01 to 20 wt.-% based on the total weight of the respective CMP composition,

and/or

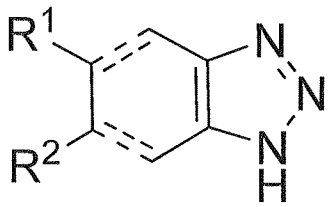
(I) a total amount of one or more buffers in a range of from 0.001 to 10 wt.-% based on the total weight of the respective CMP composition.

11. Chemical mechanical polishing (CMP) composition according to any preceding claim, wherein the CMP composition contains cations selected from the group consisting of magnesium and calcium in a total amount of less than 0.9 ppm based on the total weight of the respective CMP composition, preferably in an amount of less than 0.5 ppm based on the total weight of the respective CMP composition, and most preferably does not contain any cations selected from the group consisting of magnesium and calcium.

12. 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 11.

13. The process according to claim 12, wherein the substrate comprises a surface region consisting of tantalum or tantalum nitride or of a tantalum alloy and/or a surface region consisting of copper or of a copper alloy.

14. Use of a compound of formula (1)



(1)

wherein the pairs of dashed lines in formula (1) either each represent a double bond or each represent a single bond

wherein

(i) when each pair of dashed lines in formula (1) represents a double bond

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of bromine, alkyl with three to six carbon atoms, benzoyl and $-COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of $-(CH_2-CH_2-O)_n-H$ and $-(CH_2-CH_2-O)_n-CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

and

(ii) when each pair of dashed lines in formula (1) represents a single bond

R^1 and R^2 are hydrogen

or

one of R^1 and R^2 is hydrogen and the other of R^1 and R^2 is selected from the group consisting of chlorine, bromine, alkyl with three to six carbon atoms, benzoyl and $-COOR^3$ wherein R^3 is selected from the group consisting of alkyls with three to six carbon atoms or R^3 is a substituent comprising a structural unit selected from the group consisting of $-(CH_2-CH_2-O)_n-H$ and $-(CH_2-CH_2-O)_n-CH_3$, wherein n in each case is an integer in the range of from 1 to 15

or

R^1 and R^2 are both independently selected from the group consisting of bromine and chlorine

as corrosion inhibitor.

15. Use of a compound of formula (1) as defined in claim 14

for increasing the selectivity of a chemical mechanical polishing (CMP) composition for the removal of tantalum or tantalum nitride from a substrate for the manufacture of a semi-conductor device in the presence of copper on said substrate.