refers to an alloy containing at least 80 wt.-% copper) are often used as metal interconnect materials. However, when Cu or Cu-base alloys are used for metallization it is generally necessary to provide a diffusion barrier between the Cu or Cu-base alloy metallization feature and the adjacent thin layers of dielectric insulation material (interlayer dielectric (ILD) or intermetal dielectric (IMD). Currently, tantalum (Ta)-containing layers, e.g. elemental Ta and tantalum nitride (TaN), are most commonly employed for these barrier purposes.

In the production chain of a semiconductor device, barrier chemical-mechanical polishing (Barrier CMP) is employed in order to remove barrier layers (TaN, TiN, Ta, Ti, etc.). This process step is ideally conducted so that the barrier materials are removed without damaging the wafer surface, the conducting wire (Cu or Cu base alloy, see above) or the dielectric insulation material, see above.

During CMP steps, and in particular during Barrier CMP, depending on the wafer stack, attempts have been made to polish different layers at desired rate and selectivity to get the desired defect free surface. See e.g. US2009/0311864A1 and US2005/0076578A1.

CMP compositions are known which comprise a corrosion inhibitor in order to control the corrosion of the surface of metal. Typically, such a corrosion inhibitor adheres to the surface to be polished to form a protective film. Benzotriazole (BTA) and certain BTA derivatives are known as corrosion inhibitors, see US 2009/0311864 A1 as well as " Chemical Mechanical Planarization of Microelectronic Materials (Joseph M. Steigerwald, Shyam P. Murarka, Ronald J. Gutmann), Wiley-VCH, 2008.

The following documents disclose specific benzotriazole derivatives: US 2008/0105652 A1, US 2008/0067077 A1, US 2007/0128872 A1, US 2007/0082456 A1, US 2005/0090104 A1, US 6821309 B2, US 6565619 B1.

Objects of the ~~Invention~~ Embodiments Disclosed

One of the objects of the ~~present invention~~embodiments disclosed herein is to provide a chemical-mechanical polishing (CMP) composition suitable for use in a process for the chemical-mechanical polishing (CMP) of substrates used in the semiconductor industry, particularly for the chemical-mechanical polishing of substrates comprising

(1) copper or a copper alloy, and/or

(2) tantalum, tantalum nitride, titanium, titanium nitride, ruthenium, cobalt, or alloys thereof.

More particularly, the chemical-mechanical polishing (CMP) composition to be provided should have an effect on the ratio of the removal rate of a first metal or alloy to the removal rate of a second metal or alloy, and even more particularly, if copper and tantalum are present in the substrate, on the ratio of the removal rate of tantalum (or tantalum alloy) to the removal rate of copper (or copper alloy) during CMP processing. According to a related ~~aspect~~embodiment, it was an object of the ~~present invention~~embodiments disclosed herein to provide a CMP composition appropriate for the chemical-mechanical polishing of substrates used in the semiconductor industry which provides a high removal rate of tantalum (preferably in combination with a high selectivity for removal of tantalum in relation to copper) during CMP processing of substrates comprising copper and tantalum. The CMP composition to be provided should preferably have a low material removal rate (MRR) of the material not to be removed in the CMP process, for example copper and/or low k material in contrast to tantalum.

Furthermore, the CMP composition should be a stable formulation or dispersion where no phase separation should occur.

As far as barrier layers and low-k or ultra-low-k materials are present in the semiconductor substrate used, the CMP composition of the ~~invention~~ disclosure should preferably remove the barrier layers and maintain the integrity of the low-k and ultra-low-k materials, i.e. it should have a particularly high selectivity for barrier layer over low-k or ultra-low-k materials with regard to the MRRs. Particularly, as far as copper layers, barrier layers and low-k or ultra-low-k materials are present in the substrate to be polished, the CMP composition of the ~~invention~~ disclosure should show the combination of as many as possible of the following properties: (a) high MRR of barrier layer, (b) low MRR of copper layer, (c) low MRR of low-k or ultra-low-k materials, (d) high selectivity for barrier layer over copper layer with regard to MRR, (e) high selectivity for barrier layer over low-k and ultra-low-k materials with regard to MRR. Most particularly, as far as copper layers, tantalum or tantalum nitride layers and low-k or ultra-low-k materials are present in the substrate to be polished, the CMP composition of the ~~invention~~ disclosure should show the combination of as many as possible of the following properties: (a') high MRR of tantalum or tantalum nitride, (b') low MRR of copper layer, (c') low MRR of low-k or ultra-low-k materials, (d') high selectivity for tantalum or tantalum nitride over copper with regard to MRR, and (e') high selectivity for tantalum or tantalum nitride over low-k or ultra-low-k materials with regard to MRR.

Furthermore, the CMP composition of the ~~invention~~ disclosure should show a long shelf life, while high MRR of barrier layer is maintained.

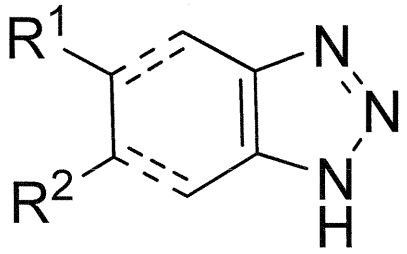
A related object of the ~~invention~~ embodiments disclosed herein is to provide a process for the manufacture of a semiconductor device comprising chemical mechanical polishing of a substrate, particularly of a substrate comprising a tantalum layer and/or a copper layer.

A further object of the ~~invention~~ 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 ~~of the invention~~

According to a first aspect of the present ~~invention~~disclosure, 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 – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ 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

triazole ring (1*H*, 2*H* and 3*H*). In the solid state and in solution, the 1H-tautomer of benzotriazole is the predominant species [Advances in Heterocyclic Chemistry, Volume 76, 2000, 157– 323], while the concentration of the *2H*-tautomeric form is negligible [J. Phys. Chem. A, Vol. 111, No. 28, 2007]. However, especially in aqueous solution, the *1H* and *3H* tautomers are in rapid equilibrium [Tetrahedron. Vol. 25, 1667-4670, 1969; J. Phys. Chem. A, Vol. 111, No. 28, 2007]. These findings also hold true for substituted benzotriazoles where an equilibrium mixture of *1H* and *3H* tautomers is present as well [Magn. Reson. Chem. 2009, 47, 142–148]. Therefore, in the context of the present application, for each compound of formula (1) mentioned hereinbelow, all of the respective tautomeric forms (*1H, 2H, 3H*) are included.

Preferably the one or at least one of the more than one compounds of formula (1) of constituent (A) of the CMP composition of the present ~~invention~~ disclosure 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,

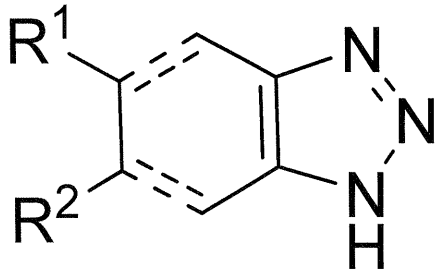
4,5,6,7-tetrahydro-1H-benzotriazole.

For certain applications the use of 5-chloro-1H-benzotriazole in a CMP composition of the present ~~invention~~ disclosure is slightly less preferred than the use of the other compounds of this group.

Typically, due to tautomerism the benzotriazole derivatives which are substituted in the 5-position are present in chemical equilibrium with the corresponding benzotriazole derivative substituted in the 6-position.

According to a further aspect of the ~~invention~~disclosure, a process is provided 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 hereinabove and hereinbelow. With respect to preferred CMP compositions for use in the process of the ~~invention~~ disclosure see below.

In a further aspect, the present ~~invention~~ disclosure relates to the use of a compound of the 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 – $(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$ 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