thiazole; (xii) mercaptomethylimidazole; (xiii) tannic acid; (xiv) thioglycerol; (xv) thiosalicylic acid; (xvi) triazole; (xvii) vanillin; (xviii) vanillic acid; (xix) and mixtures thereof. For example, the cleaning composition comprises ammonium citrate, ascorbic acid, and cysteine.

WO 2011/000694 A1 discloses an aqueous alkaline cleaning composition comprising (a) at least one thioamino acid having at least one primary amino group and at least one mercapto group, (b) at least one quaternary ammonium hydroxide, (c) at least one specific chelating and/or corrosion inhibiting agent, and (d) at least one organic solvent having wetting properties and a melting point below 0°C. For example, the cleaning composition comprises L-cysteine, tetramethylammonium hydroxide (referred to as TMAH in the following), ethylene diamine, and diethylene glycol monobutyl ether.

WO 2011/000758 A1 discloses an aqueous alkaline cleaning composition comprising (a) at least one thioamino acid having at least one secondary or tertiary amino group and at least one mercapto group and, and (b) at least one quaternary ammonium hydroxide. For example, the cleaning composition comprises N-acetylcysteine, TMAH, ethylene diamine, and diethylene glycol monobutyl ether. In another example, the cleaning composition comprises N-acetylcysteine, TMAH, diethylene triamine, 1,2,4-triazole, citric acid, and a surfactant such as 3,5-dimethyl-1-hexyn-3-ol or polyoxyethylene sorbitan laurate.

Objects

One of the objects of the present disclosure was to provide a post-CMP cleaning composition and a post-CMP cleaning process appropriate for post-CMP cleaning of copper-containing microelectronic substrates and showing an improved cleaning performance, particularly

(i) the effective prevention of undesirable corrosion of copper-containing surfaces, or
(ii) high efficiency of removing residues and contaminants which remained after the CMP step, or
(iii) high efficiency of removing passivation films, especially benzotriazole films, from copper-containing surfaces, or
(iv) applicability in moderate pH range such as from 4 to 8, or
(v) the combination of (i) to (iv).

Furthermore, one of the objects of the present disclosure was to provide a post-CMP cleaning composition containing no or minimal amounts of organic solvents which can cause environmental and safety concerns. Moreover, one of the objects of the present disclosure was to provide a post-CMP cleaning composition which does not cause an increase of surface roughness of the copper-containing surface or an increase of defects thereon. Last but not least, a post-CMP cleaning process was sought that is easy to apply and requires as few steps as possible.

Summary

Accordingly, a post-CMP cleaning composition comprising:

(A) at least one compound comprising at least one thiol (–SH), thioether (–SR^1) or thiocarbonyl (>C=S) group, wherein R^1 is alkyl, aryl, alkylaryl or arylalkyl,

(B) at least one sugar alcohol which contains at least three hydroxyl (–OH) groups and does not comprise any carboxylic acid (–COOH) or carboxylate ($–COO^-$) groups, and

(C) an aqueous medium

was found. This post-CMP cleaning composition of the disclosure is referred to as (Q1) or composition (Q1) in the following.

According to another embodiment of the disclosure, a post-CMP cleaning composition comprising:

(A) at least one compound comprising at least one thiol (–SH), thioether (–SR^1) or thiocarbonyl (>C=S) group, wherein R^1 is alkyl, aryl, alkylaryl or arylalkyl,

(L) at least one oligomeric or polymeric polycarboxylic acid, and

(C) an aqueous medium

was found. This post-CMP cleaning composition of the disclosure is referred to as (Q2) or composition (Q2) in the following.

(Q1) and/or (Q2) are generally referred to as (Q) or composition (Q) in the following.

Moreover, the use of the composition (Q) for removing residues and contaminants from the surface of semiconductor substrates useful for manufacturing microelectronic devices was found.

Furthermore, the process for manufacturing microelectronic devices from semiconductor substrates comprising the step of removing residues and contaminants from the surface of the semiconductor substrates by contacting them at least once with the composition (Q) was found. This process of the disclosure is referred to as the process (P) in the following.

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

(A) is cysteine, glutathione, N-acetylcysteine, or thiourea,

(L) at least one oligomeric or polymeric polycarboxylic acid which is a maleic acid / acrylic acid copolymer, and

(C) an aqueous medium.

In another aspect, there is provided the use of the post-CMP cleaning composition as defined above for removing residues and contaminants from the surface of semiconductor substrates useful for manufacturing microelectronic devices.

In yet another aspect, there is provided a process for manufacturing microelectronic devices from semiconductor substrates comprising the step of removing residues and contaminants

Claims:

1. A post chemical-mechanical-polishing (post-CMP) cleaning composition comprising:
   (A) is cysteine, glutathione, N-acetylcysteine, or thiourea,
   (L) at least one oligomeric or polymeric polycarboxylic acid which is a maleic acid / acrylic acid copolymer, and
   (C) an aqueous medium.

2. A composition according to claim 1, wherein (L) is an oligomeric or polymeric polycarboxylic acid having at least 20 carboxylic acid groups.

3. A composition according to claim 1, wherein the weight average molecular weight of the oligomeric or polymeric polycarboxylic acid (L) is more than 2,000 Dalton as determined by gel permeation chromatography.

4. A composition according to anyone of the claims 1 to 3, wherein the composition further comprises (E) at least one surfactant.

5. A composition according to anyone of the claims 1 to 3, wherein the composition further comprises at least one surfactant (E) which is selected from the group consisting of:

(E1) amphiphilic nonionic, water-soluble or water-dispersible surfactants having

(e11) at least one hydrophobic group selected from the group consisting of branched alkyl groups having 5 to 20 carbon atoms; and

(e12) at least one hydrophilic group consisting of oxyethylene monomer units;

(E2) amphiphilic nonionic, water-soluble or water-dispersible surfactants having

(e21) at least one hydrophobic group selected from the group consisting of branched alkyl groups having 5 to 20 carbon atoms; and

(e22) at least one hydrophilic group selected from the group consisting of polyoxyalkylene groups comprising

(e221) oxyethylene monomer units and

(e222) at least one type of substituted oxyalkylene monomer units wherein the substituents are selected from the group consisting of alkyl, cycloalkyl, aryl, alkyl-cycloalkyl, alkyl-aryl, cycloalkyl-aryl and alkyl-cycloalkyl-aryl groups;

the said polyoxyalkylene group of (e22) containing the monomer units (e221) and (e222) in random, alternating, gradient and/or blocklike distribution; and

(E3) amphiphilic nonionic, water-soluble or water-dispersible alkyl polyglucoside surfactants.

6. The use of the post-CMP cleaning composition as defined in anyone of the claims 1 to 5 for removing residues and contaminants from the surface of semiconductor substrates useful for manufacturing microelectronic devices.

7. The use according to claim 6, wherein the residues and contaminants comprise benzotriazole or a derivative thereof and wherein the surface is a copper-containing surface.

8. The use according to claim 6, wherein the cleaning composition is used for removing residues and contaminants from the surface of semiconductor substrates comprising
   - electrically conductive layers containing or consisting of copper,
   - electrically insulating dielectric layers consisting of low-k or ultra-low-k dielectric materials, and
   - barrier layers containing or consisting of tantalum, tantalum nitride, titanium nitride, cobalt, nickel, manganese, ruthenium, ruthenium-nitride, ruthenium-carbide, or ruthenium tungsten nitride

   after chemical mechanical polishing.

9. A process for manufacturing microelectronic devices from semiconductor substrates comprising the step of removing residues and contaminants from the surface of the semiconductor substrates by contacting them at least once with the post-CMP cleaning composition as defined in anyone of the claims 1 to 5.

10. A process according to claim 9, wherein the residues and contaminants comprise benzotriazole or a derivative thereof and wherein the surface is a copper-containing surface.

11. A process according to claim 9, wherein the semiconductor substrates comprise
    - electrically conductive layers containing or consisting of copper,
    - electrically insulating dielectric layers consisting of low-k or ultra-low-k dielectric materials, and
    - barrier layers containing or consisting of tantalum, tantalum nitride, titanium nitride, cobalt, nickel, manganese, ruthenium, ruthenium-nitride, ruthenium-carbide, or ruthenium tungsten nitride.