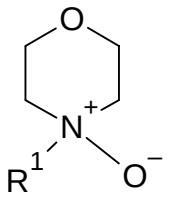
Claims:

1. Use of a cleaning composition comprising at least the following components:

(A) as solubilizer, one or more compounds of formula I:



(I)

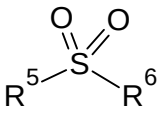
wherein R^1 is selected from the group consisting of branched or unbranched alkyl having 1, 2, 3 or 4 carbon atoms;

(B) one or more corrosion inhibitors, selected from the group consisting of benzotriazoles which are unsubstituted or substituted once or twice independently by branched or unbranched alkyl having 1, 2, 3 or 4 carbon atoms, aminoalkyl wherein the alkyl is branched or unbranched and has 1, 2, 3 or 4 carbon atoms, phenyl, thiophenyl, halogen, hydroxy, nitro and/or thiol, and mixtures thereof;

(C) one or more polar, non-protogenic organic solvents

wherein the one, or at least one of the more, or all of the more, polar, non-protogenic organic solvents (C) are selected from the group consisting of

– an alkyl sulfone compound of formula IV:



(IV)

wherein

R^5 is a branched or unbranched alkyl group having 1 to 5 carbon atoms,

R^6 is a branched or unbranched alkyl group having 1 to 5 carbon atoms,

or

R^5 and R^6 together form a branched or unbranched alkylen group having 3 to 5 carbon atoms, wherein one or two carbon atoms of said alkylen group can independently be substituted by -O-R^7, wherein R^7 is a branched or unbranched alkyl group having 1 to 4 carbon atoms;

~~– dimethyl formamide,~~

~~– dimethyl sulfoxide,~~

~~– dimethyl acetamide,~~

~~– N-methylpyrrolidone,~~

~~– propylene carbonate,~~

~~– tetrahydrofuran,~~

~~– 2-imidazolidinone which is substituted once or twice by a branched or unbranched alkyl group having 1 to 4, preferably 1 to 2, carbon atoms~~

and

– mixtures thereof;

and

(D) water,

in combination with one or more oxidants,

wherein the one or more oxidants are selected from the group consisting of hydrogen peroxide, peroxide urea, peroxydisulfuric acid, ammonium persulfate, peroxymonosulfuric acid, pyrosulfuric acid, ozone and mixtures thereof

– for removing post-etch or post-ash residue from the surface of a semiconductor substrate

and/or

– for etching or partially etching of a layer or mask comprising or consisting of a material selected from the group consisting of Ti, TiN, Ta, TaN, Al and HfO_x and/or a layer or mask comprising or consisting of a material selected from the group consisting of tungsten carbide and tungsten nitride.

2. Use according to claim 1, wherein the one, or at least one of the more, or all of the more, polar, non-protogenic organic solvents (C) is an alkyl sulfone compound of formula IV as defined in claim 1, ~~preferably~~ selected from the group consisting of ethyl methyl sulfone, ethyl isopropyl sulfone, ethyl isobutyl sulfone, isopropyl isobutyl sulfone, sulfolane, 3-methoxy sulfolane and mixtures thereof, ~~more~~ preferably selected from the group consisting of ethyl methyl sulfone, ethyl isopropyl sulfone, sulfolane and mixtures thereof.

3. Use according to any of the preceding claims, wherein the cleaning composition further comprises:

(F) a buffering system which is suitable to buffer the pH of the cleaning composition in the range of from 6 to 9, preferably of from 7 to 8.5;

and/or

(G) one or more chelating agents,

preferably in a total amount in the range of from 0.01 mass-% to 3 mass-%, more preferably in the range of from 0.1 mass-% to 2 mass-% and yet more preferably in the range of from 0.15 mass-% to 1.5 mass-%, relative to the total mass of the cleaning composition;

and/or

(H) one or more surfactants, preferably comprising one or more fluorosurfactants.

4. Use according to any of the preceding claims, wherein in the cleaning composition

– the one or at least one of the more solubilizers (A) is or comprises 4-methylmorpholine-4-oxide,

and/or

– the one or at least one of the more corrosion inhibitors (B) is selected from the group consisting of benzotriazoles which are unsubstituted or substituted once or twice independently by branched or unbranched alkyl having 1, 2, 3 or 4 carbon atoms and/or by halogen, preferably selected from the group consisting of chlorine and bromine, and mixtures thereof;

and/or

– the one or at least one of the more polar, non-protogenic organic solvents (C) is ~~selected from the group consisting of dimethyl formamide, dimethyl sulfoxide, dimethyl acetamide, N-methylpyrrolidone, propylene carbonate,~~ sulfolane~~, tetrahydrofuran and mixtures thereof~~,

~~wherein preferably the one or at least one of the more polar, non-protogenic organic solvents (C) is dimethyl sulfoxide or sulfolane,~~

and/or

– the total amount of etchants comprising fluoride anions is < 0.001 mass-%, relative to the total mass of the cleaning composition, wherein preferably the cleaning composition does not comprise etchants comprising fluoride anions;

5. Use according to any of the preceding claims, wherein in the cleaning composition

– the total amount of the one or more solubilizers (A), preferably of 4-methylmorpholine-4-oxide, is in the range of from 1 mass-% to 15 mass-%, preferably in the range of from 2 mass-% to 12 mass-% and more preferably in the range of from 3 mass-% to 10 mass-%, relative to the total mass of the cleaning composition,

and/or

– the total amount of the one or more corrosion inhibitors (B), preferably selected from the group consisting of benzotriazoles which are unsubstituted or substituted once or twice independently by branched or unbranched alkyl having 1, 2, 3 or 4 carbon atoms and/or by halogen, and mixtures thereof, is in the range of from 0.1 mass-% to 6 mass-%, preferably in the range of from 0.2 mass-% to 6

mass-% and more preferably in the range of from 0.5 mass-% to 5 mass-%, relative to the total mass of the cleaning composition;

and/or

– the total amount of the one or more polar, non-protogenic organic solvents (C) is in the range of from 1 mass-% to 50 mass-%, preferably in the range of from 3 mass-% to 45 mass-% and more preferably in the range of from 5 mass-% to 40 mass-%, relative to the total mass of the cleaning composition;

and/or

– the one, or at least one of the more, or all of the more, polar, non-protogenic organic solvents (C) is an alkyl sulfone compound of formula IV as defined in claim 1 and the total amount of the one or more polar, non-protogenic organic solvents (C) is in the range of from 10 mass-% to 50 mass-%, preferably in the range of from 15 mass-% to 45 mass-% and more preferably in the range of from > 30 mass-% to 45 mass-%, relative to the total mass of the cleaning composition;

and/or

– the cleaning composition comprises at least the components (A), (B), (C), (D) and (F)

and preferably comprises the components (A), (B), (C), (D), (F), (G) and (H);

and/or

– water (D) makes up the balance to 100 mass-% of the cleaning composition.

6. Use according to any of the preceding claims, wherein the use comprises removing post-etch or post-ash residue from the surface of a semiconductor substrate and wherein

– the semiconductor substrate comprises at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

and/or

– the use comprises cleaning a semiconductor substrate comprising at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material;

and/or

– the use comprises removing post-etch or post-ash residue from the surface of a semiconductor substrate in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

wherein the post-etch or post-ash residue comprises one or more residues selected from the group comprising or consisting of

- one or more organic compounds, preferably organic polymers, comprising or not comprising fluorine,
- metal organic complexes and
- metallic materials, preferably titanium and/or an oxide of titanium and/or a nitride of titanium;

and/or

– the use comprises removing residues and contaminants from the surface of a semiconductor substrate comprising at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

- wherein preferably the residues and contaminants comprise or consist of organic compounds, preferably organic polymers, comprising or not comprising fluorine.

7. Use according to any of the preceding claims, wherein the use comprises etching, preferably oxidative etching, or partially etching, preferably partially oxidative etching, of a layer or mask, preferably a hard mask, comprising or consisting of a material selected from the group consisting of Ti, TiN, Ta, TaN, Al and HfO_x and/or a layer or mask, preferably a hard mask, selected from the group comprising or consisting of

a material selected from the group consisting of tungsten carbide (WC_x) and tungsten nitride (WN_x), wherein the etching or partially etching of a layer or mask, preferably a hard mask, comprises

– removing or partially removing a metal-containing hard mask, preferably selected from the group consisting of a Ti hard mask, a TiN hard mask, a Ta hard mask, a TaN hard mask, an Al hard mask and a HfOx hard mask and/or selected from the group consisting of a tungsten carbide hard mask and a tungsten nitride hard mask, more preferably a TiN hard mask, preferably in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

and/or

– etching, preferably oxidative etching, or partially etching, preferably partially oxidative etching, in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material, on the surface of a semiconductor substrate;

and/or

– etching, preferably selectively etching, a layer comprising an aluminium compound in the presence of a layer of a low-k material and/or preferably a layer comprising tungsten and/or a layer comprising copper and/or cobalt;

and/or

– removing, preferably selectively removing, from a semiconductor substrate a layer comprising an aluminium compound in the presence of a layer of a low-k material and/or preferably a layer comprising tungsten and/or a layer comprising copper and/or cobalt,

and/or

– removing, preferably selectively removing, from the surface of a semiconductor substrate a layer comprising an aluminium compound in the presence of a layer of a low-k material and/or preferably a layer comprising tungsten and/or a layer comprising copper and/or cobalt.

8. Use according to any of the preceding claims, wherein

– the cleaning composition is used in combination with the one or more oxidants in a one-step-process of removing

(i) a metal-containing hard mask,

preferably selected from the group consisting of a Ti hard mask, a TiN hard mask, a Ta hard mask, a TaN hard mask, an Al hard mask and a HfO_x hard mask and/or selected from the group consisting of a tungsten carbide hard mask and a tungsten nitride hard mask, more preferably a TiN hard mask

and

(ii) an etch-stop layer of an aluminium compound deposited on a layer comprising copper, preferably a copper layer, and/or on a layer comprising cobalt, preferably a cobalt layer;

preferably in the presence of tungsten which is fully covered by at least one layer of a low-k material;

and/or

– the cleaning composition is used in combination with the one or more oxidants in a separate step or simultaneously in the same step, preferably simultaneously in the same step;

and/or

– the one or more oxidants, preferably hydrogen peroxide, are used in a total amount in the range of from 2 mass-% to 25 mass-%, preferably in the range of from 5 mass-% to 20 mass-%, more preferably in the range of from 7.5 mass-% to 20 mass-% and even more preferably of from 10 mass-% to 17.5 mass-%, relative to the total mass of the cleaning composition;

and/or

– one or more stabilizers are used in combination with the one or more oxidants and/or in combination with the cleaning composition, preferably selected from the group consisting of amine-N-oxides; citric acid; 1-hydroxyethane 1,1-diphosphonic acid; glycolic acid; lactic acid; hydroxybutyric acid; glyceric acid; malic acid; tartaric acid; malonic acid; succinic acid; glutaric acid; maleic acid and mixtures thereof.

9. Cleaning composition, as defined in any of claims 1 to 5, wherein the cleaning composition comprises

(F) a buffering system which is suitable to buffer the pH of the cleaning composition in the range of from 6 to 9,

and wherein the total amount of etchants comprising fluoride anions is < 0.001 mass-%, relative to the total mass of the cleaning composition, wherein preferably the cleaning composition does not comprise etchants comprising fluoride anions.

10. Use of a cleaning composition according to claim 9, for removing post-etch or post-ash residue from the surface of a semiconductor substrate, preferably as defined in claim 1 and/or 6.

11. Wet-etch composition comprising

(W1) a cleaning composition as defined in any of claims 1 to 5, preferably as defined in any of claims 2 to 5

and

(W2) one or more oxidants selected from the group consisting of hydrogen peroxide, peroxide urea, peroxydisulfuric acid, ammonium persulfate, peroxymonosulfuric acid, pyrosulfuric acid and ozone;

preferably in a total amount in the range of from 2 mass-% to 25 mass-%, preferably in the range of from 5 mass-% to 20 mass-%, more preferably in the range of from 7.5 mass-% to 20 mass-% and even more preferably of from 10 mass-% to 17.5 mass-%, relative to the total mass of the cleaning composition

12. Use of a wet-etch composition according to claim 11, for

– removing or partially removing a metal-containing hard mask, preferably selected from the group consisting of a Ti hard mask, a TiN hard mask, a Ta hard mask, a TaN hard mask, an Al hard mask and a HfO_x hard mask and/or selected from the group consisting of a tungsten carbide hard mask and a tungsten nitride hard mask, more preferably a TiN hard mask, preferably in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

and/or

– etching, preferably oxidative etching, or partially etching, preferably partially oxidative etching, of a layer or mask, comprising or consisting of a material selected from the group consisting of Ti, TiN, Ta, TaN, Al and HfO_x and/or a layer or mask comprising or consisting of a material selected from the group consisting of tungsten carbide (WC_x) and tungsten nitride (WN_x), preferably comprising or consisting of TiN,

preferably in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material, on the surface of a semiconductor substrate;

and/or

– etching, preferably selectively etching, a layer comprising an aluminium compound in the presence of a layer of a low-k material and/or a layer comprising copper and/or cobalt and/or preferably a layer comprising tungsten;

and/or

– removing, preferably selectively removing, from a semiconductor substrate a layer comprising an aluminium compound in the presence of a layer of a low-k material and/or a layer comprising copper and/or cobalt and/or preferably a layer comprising tungsten;

and/or

– removing, preferably selectively removing, from the surface of a semiconductor substrate a layer comprising an aluminium compound in the presence of a layer of a low-k material and/or a layer comprising copper and/or cobalt and/or preferably a layer comprising tungsten;

and/or

– removing post-etch or post-ash residue from the surface of a semiconductor substrate, preferably in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

wherein the post-etch or post-ash residue preferably comprises one or more residues selected from the group comprising or consisting of:

– one or more organic compounds, preferably organic polymers, comprising or not comprising fluorine,

– metal organic complexes and

– metallic materials, preferably titanium and/or an oxide of titanium and/or a nitride of titanium.

13. Process for the manufacture of a semiconductor device from a semiconductor substrate, comprising the following steps

P1) preparing a wet-etch composition by mixing a cleaning composition according to any of claims 1 to 5, preferably according to any of claims 2 to 5, with one or more oxidants selected from the group consisting of hydrogen peroxide, peroxide urea, peroxydisulfuric acid, ammonium persulfate, peroxymonosulfuric acid, pyrosulfuric acid, ozone and mixtures thereof,

or

providing a wet-etch composition according to claim 11,

and

P2) contacting at least once with the wet-etch composition received or provided in step P1), preferably in the presence of at least one material selected from the group consisting of copper, cobalt, preferably tungsten, and a low-k material,

- a layer or hard mask, preferably selected from the group consisting of a Ti layer or mask, a TiN layer or mask, a Ta layer or mask, a TaN layer or mask, an Al layer or mask and a HfO_x layer or mask and/or selected from the group consisting of a tungsten carbide hard mask and a tungsten nitride hard mask; more preferably a TiN layer or mask, on the surface of a semiconductor substrate,

and/or

- an etch-stop layer comprising or consisting of one or more aluminium compounds deposited on a layer comprising copper, preferably a copper layer, and/or on a layer comprising cobalt, preferably a cobalt layer, on the surface of a semiconductor substrate,

preferably so as to

- etch, preferably selectively oxidatively etch, or partially etch, preferably selectively partially oxidatively etch, said layer or mask

and/or

- remove, preferably selectively remove, from the surface of the semiconductor substrate the etch-stop layer comprising or consisting of one or more aluminium compounds,

and/or

- remove post-etch or post-ash residue from the surface of said semiconductor substrate,

preferably in a one-step process.

14. Kit,

preferably for post-etch or post-ash residue removal from the surface of a semiconductor substrate and/or for etching, preferably for oxidative etching, or partially etching, preferably partially oxidative etching, of a layer or mask comprising or consisting of a material selected from the group consisting of Ti, TiN, Ta, TaN, Al and HfO_x and/or a layer or mask comprising or consisting of a material selected from the group consisting of tungsten carbide and tungsten nitride, preferably comprising or consisting of TiN, on the surface of a semiconductor substrate and/or for etching, preferably selectively etching, a layer comprising or consisting of one or more aluminium compounds in the presence of a layer of a low-k material and/or preferably a layer comprising tungsten, more preferably subjacent tungsten, and/or a layer comprising copper and/or cobalt on the surface of a semiconductor substrate,

comprising as separate components:

(K1) a cleaning composition according to any of claims 1 to 5;

and

(K2) one or more oxidants selected from the group consisting of hydrogen peroxide, peroxide urea, peroxydisulfuric acid, ammonium persulfate, peroxymonosulfuric acid, pyrosulfuric acid, ozone and mixtures thereof; more preferably the one or one of the more oxidants is hydrogen peroxide;

and further optionally comprising, as separate component or combined with component (K1) and/or with component (K2):

(K3) one or more stabilizers, preferably selected from the group consisting of amine-N-oxides; citric acid; 1-hydroxyethane 1,1-diphosphonic acid; glycolic acid; lactic acid; hydroxybutyric acid; glyceric acid; malic acid; tartaric acid; malonic acid; succinic acid; glutaric acid; maleic acid and mixtures thereof.