FLUORIDE-CONTAINING PHOTORESIST STRIPPER OR RESIDUE REMOVING CLEANING COMPOSITIONS CONTAINING CONJUGATE OLIGOMERIC OR POLYMERIC MATERIAL OF ALPHA-HYDROXYCARBONYL COMPOUND/AMINE OR AMMONIA REACTION

FIELD OF THE INVENTION

[0001] This invention relates to compositions useful for removing photoresist, contaminants, or plasma or etch residue from microelectronic devices, which compositions provide good corrosion copper corrosion inhibition or resistance while maintaining cleaning efficiency. In particular the invention provides aqueous or semi-aqueous, highly alkaline, fluoride-containing cleaning compositions having present in the composition 'browned" oligomeric or polymeric conjugate material of alpha-hydroxycarbonyl compounds, especially 'browned" oligomeric or polymeric conjugate material of monosaccharides. The invention also provides method for cleaning microelectronic substrates and devices employing such compositions.

BACKGROUND TO THE INVENTION

[0002] Semiconductor devices have been produced by the steps of coating an inorganic substrate with a photoresist; patterning the photoresist film by exposure to light and subsequent development; etching exposed region of the inorganic substrate using the patterned photoresist film as a mask to form minute circuits; and removing the patterned photoresist film from the inorganic substrate. Alternatively, after forming minute circuits in the same manner as above, the patterned photoresist film is ashed, and then the remaining resist residues are removed from the inorganic substrate.

[0003] Many alkaline based cleaning compositions have been proposed for the cleaning of photoresist and residue from such microelectronic devices. However, one significant problem encountered in the cleaning of such microelectronic devices has been the propensity of the cleaning compositions to permit corrosion of the metal, particularly copper, in such microelectronic devices. However, the stripper solutions currently available, usually alkaline stripper solutions, produce various types of metal corrosion, such as corrosion whiskers, galvanic corrosion, pitting, notching of metal lines, have been observed due, at least in part, to reaction of the metals with alkaline strippers

[0004] Prior methods used to avoid this corrosion problem employed intermediate rinses with non-alkaline organic solvents such as isopropyl alcohol. However, such methods are expensive and have unwanted safety, chemical hygiene, and environmental consequences.

[0005] In US Patent 6,465,403 there is disclosed aqueous alkaline compositions useful in the microelectronics industry for stripping or cleaning semiconductor wafer substrates by removing photoresist residues and other unwanted contaminants. The aqueous compositions typically contain (a) one or more metal ion-free bases at sufficient amounts to produce a pH of about 10-13; (b) about 0.01% to about 5% by weight (expressed as % SiO_2) of a water-soluble metal ion-free silicate; (c) about 0.01% to about 10% by weight of one or more metal chelating agents and (d) optionally other ingredients.

[0006] However, none of the compositions disclosed in the prior art effectively remove all organic contamination and metal-containing residues remaining after a typical etching process. Silicon containing residues are particularly difficult to remove using these formulations. There is, therefore, a need for stripping compositions that clean semiconductor wafer substrates by removing inorganic and organic contamination from such substrates without damaging the integrated circuits. Such compositions must not corrode the metal features that partially comprise the integrated circuit and should avoid the expense and adverse consequences caused by intermediate rinses. Fluoride is good for Si rich residue, but it corrodes many metal (Al, Cu, etc) and damages many ILDs (e.g., TEOS, CDO, and the like). There is, therefore, a need for a fluoride-containing microelectronic cleaning composition that: (1) Is compatible with essentially all metals used in semiconductor devices (Al, Cu, Mo, and the like), i.e., that produces essentially no corrosion of such metals;

(2) requires no need for intermediate rinse;

(3) is good for Si rich residue cleaning; and

(4) produces essentially no damage for ILDs.

SUMMARY OF THE INVENTION

[0007] In accordance with this invention there are provided aqueous or semi-aqueous fluoride-containing microelectronics cleaning composition or formulations comprising (a) at least one fluoride compound providing fluoride ions, (b) at least one "browned" alpha-hydroxycarbonyl conjugate that is a oligomeric or polymeric conjugate of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound, and (c) water. The alpha-hydroxy carbonyl compound is of the general formula $R^1CH(OH)COR^2$, where R^1 and R^2 are independently selected from H, an aliphatic group, or a cyclic group, which aliphatic or cyclic groups may contain one or more substituents . Such substituents include, but are not limited to, a group selected from an aromatic group, a heteroaromatic group, an hydroxyl group (-OH group, an ether group (-C-O-C), an amide group (-C(O)NH), a sulfoxide group (-C-S(O)-C), an amine ($-NR^3R^4$) where R^3 and R^4 are H or alkyl of from 1 to 10 carbon atoms, and a ketone group (-C(O)). In the alpha-hydroxy carbonyl compound of the general formula $R^1CH(OH)COR^2$, R^1 and R^2 are preferably an group selected from H and an alkyl group, more preferably from H, CH_3, and $(CH_2)_nCH_3$ where n is an integer of from 0 to 20, preferably 1 to 10 and more preferably 1 to 6. Some examples of suitable alpha-hydroxycarbonyl compounds include, but are not limited to, 1-hydroxy-2-propanone (CH_3COCH_2OH) CAS#119-09-6, 1,3-dihydroxyacetone ($HOCH_2COCH_2OH$) CAS#62147-49-3, and monosaccharides, including particularly glucose, fructose or galactose, fit the above generic structure. The reaction of an amine and an alpha-hydroxy carbonyl compound is known to proceed first by nucleophilic addition of the amine at the carbonyl carbon then continue via the Maillard reaction (Yaylayan, V. A.; Harty-Majors, S.; Ismail, A. A.; J. Agric. Food Chem. 1999, 47, 2335-2340). The Maillard reaction is actually a complex series of and details can be found in (Dills, W. L; Am. J. Clin. Nutr. 1993, 58, 779S-787S.

[0008] The cleaning compositions of the invention may optionally contain other ingredients such as (d) at least one polar, water miscible organic solvent. The pH of the composition can be of any suitable pH, from acidic to basic pH. In one embodiment of the compositions of this invention the composition may also contain (e) at least one metal ion-free base at sufficient amounts to produce a final composition of pH, 7 or above, preferably a pH of about 9.5 to about

10.8. The compositions of this invention may also include and one or more of (f) a polyhydric alcohol and (g) a surfactant. The browned oligomeric or polymeric conjugate of a alpha-hydroxycarbonyl compound employed in the compositions of this invention are those oligomeric or polymeric conjugates having an absorbance peak at about 300 to 330 nm with the absorbance peak beginning at a wavelength of from about 600 to 800 nm. These browned ologomeric or polymeric conjugates can be formed by the known "Maillard Reaction"-L.C. Maillard, *Compt. Rend.* 154, 66 (1912); *Ann. Chim.* 9, 5, 258 (1916). The "browned" conjugates that are oligomeric or polymeric conjugates of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound that are employed in the compositions of this invention are distinguished from merely "yellowed" conjugates of alpha-hydroxycarbonyl compounds that are the reaction product oligomeric or polymeric conjugates of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound as the "yellowed" alpha-hydroxycarbonyl conjugates do not work in the formulations of this invention since such formulations containing the "yellowed" alpha-hydroxycarbonyl conjugates do not provide adequate Cu etch rate protection. The "yellowed" alpha-hydroxycarbonyl conjugates are those reaction products of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound that have an absorbance peak at about 300 to 330 nm, however the absorbance peak begins at about 500 to 580 nm.

[0009] The cleaning compositions of this invention are placed in contact with a semiconductor device for a time and at a temperature sufficient to clean unwanted contaminants and/or residues from the substrate surface. The compositions of this invention provide enhanced corrosion resistance, especially copper corrosion resistance, and improved cleaning efficiency.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

[0010] The cleaning compositions of this invention comprise neutral to alkaline, aqueous or semi-aqueous cleaning formulations comprising: (a) at least one fluoride compound providing fluoride ions, (b) at least one "browned" alpha-hydroxycarbonyl conjugate that is a oligomeric or polymeric conjugate of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound, and (c) water. Such formulations may also comprise other optional components, including, but not limited to, (d) at least one polar, water miscible organic solvent, (e) at least one metal ion-free base at sufficient amounts to produce a final composition of pH, 7 or above, preferably a pH of about 9.5 to about 10.8 when an alkaline cleaning composition is desired, and one or more of (f) a polyhydric alcohol and (g) a surfactant.

[0011] The "browned" alpha-hydroxycarbonyl conjugates used in the compositions of this invention are those oligomeric or polymeric conjugates of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound and having an absorbance peak at about 300 to 330 nm with the absorbance peak beginning at a wavelength of from about 600 to 800 nm. Such browned oligomeric or polymeric conjugates are prepared according to know procedures such as by the previously mentioned "Maillard Reaction". However, any suitable means of obtaining the "browned" alpha-hydroxycarbonyl conjugates may be employed. Additionally, such "browned" alpha-hydroxycarbonyl conjugates may be employed in the form of dark molasses, for example. The reaction of the alpha-hydroxycarbonyl compound and amine or ammonia containing compound may be carried out with the stoichiometric ratio of alpha-hydroxycarbonyl compound to amine or ammonia compound being from about 1:1 to about 16:1 on the basis of

reaction of 1 molecule of alpha-hydroxycarbonyl compound and 1 mol of amine or ammonia compound. However, it is preferred that the ratio be 1:1 as the presence of less amine or ammonia compound to react with the alpha-hydroxycarbonyl compound results in a diminution of the copper corrosion inhibition capability of the reaction product. Excess amine or ammonia containing compound does not appear to have any significant effect on the copper corrosion inhibition property of the cleaning composition. Although the reaction can be conducted over a wide range of times and temperatures, it is preferred that the reaction be conducted by heating the alpha-hydroxycarbonyl compound with the amine or ammonia compound to about 70° C or higher for a period of about 3 hours or longer. Any suitable time and temperature may be employed so long as the resulting oligomeric or polymeric conjugate reaction product is a "browned" product, i.e., one having an absorbance peak at about 300 to 330 nm and with that peak beginning at about 600 to 800 nm. In general, the browned alpha-hydroxycarbonyl conjugates preferably employed in this invention are characterized by having a low bandgap of about 0.5eV or less.

[0012] The browned alpha-hydroxycarbonyl conjugates may be obtained from the reaction of any suitable alpha-hydroxycarbonyl compound with and amine or ammonia compound. Suitable alpha-hydroxycarbonyl compounds include, but are not limited to, 1-hydroxy-2-propanone, CH_3COCH_2OH and 1,3-dihydroxyacetone, $HOCH_2COCH_2OH$, and all of monosaccharides including arabinose, lyxose, ribose, deoxyribose, xylose, ribulose, xylulose, allose, altrose, galactose, glucose, gulose, idose, mannose, fructose, psicose, sorbose, tagatose, mannoheptulose, seldoheptulose, octolose, 2-keto-3-deoxy-manno-octonate and sialose. Particularly preferred is fructose. Disaccharides are not usable in this invention.

[0013] Any suitable amine or ammonia containing compound may be reacted with the alpha-hydroxycarbonyl compounds of this invention to produce the browned oligomeric or polymeric conjugate of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound. Among the suitable amines are amines, diamines, triaamines, alkanolamines, amino acids particularly primary and secondary amines and alkanolamines. Especially useful are alkanolamines of the formula $NH_2(CH_2)_nOH$ wheren n is an integer of from 1 to about 10, preferably t to about 4, and especially 2. Ammonia is suitable just like amines described above. Suitable amine compounds include, but are not limited to monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diethylenetriamine, aminoacetic acid. Especially preferred is monoethnolamine. The preferred browned alpha-hydroxycarbonyl compound is obtained from reaction of fructose with monoethanolamine.

[0014] Any suitable fluoride compound providing fluoride ions may be employed in the compositions of this invention. Suitable fluoride compounds include HF, ammonium fluoride, tetraalkylammonium fluorides, especially those wherein the alkyl groups contain from 1 to 4 carbon atoms, fluoride salts such as ammonium fluoride. Among those fluoride compounds that are especially useful there may be mentioned tetramethylammonium fluoride, tetrabutylammonium fluoride, and ammonium fluoride, preferably ammonium fluoride.

[0015] The amount of fluoride compound in the cleaning compositions of this invention will generally range from about 0.0001 to about 10 wt.%, preferably from about 0.01 to about 5 wt.%, and more preferably from about 0.5 to about 1 wt.%. The "browned" oligomeric or polymeric alpha-hydroxycarbonyl compound will generally be present in the cleaning composition of this invention in an amount of from about 0.1 to about 20 wt.%, preferably from

about 1 to about 10 wt.%, and more preferably from about 3 to about 7 wt.%. Water will be present in the compositions of this invention in an amount of from about 10 to about 99.9 wt.%, preferably from about 60 to about 99 wt.%, and more preferably from about 85 to about 96.5 wt.%. All percentages are based on the total weight of the cleaning composition.

[0016] The pH of the cleaning compositions will acidic or alkaline, but preferably will be 7 or above, preferably from about pH 7 to about 10.8, more preferably from pH of about 9.5 to about 10.8. If necessary to adjust the pH of the composition a metal ion-free base may optionally be added to the cleaning composition. Any suitable metal ion-free base may be employed. Among the suitable metal ion-free bases that may be employed in the cleaning compositions there may be quaternary ammonium hydroxides, such as tetraalkyl ammonium hydroxides (including hydroxy- and alkoxy-containing alkyl groups generally of from 1 to 4 carbon atoms in the alkyl or alkoxy group). The most preferable of these alkaline materials are tetramethyl ammonium hydroxide and trimethyl-2-hydroxyethyl ammonium hydroxide (choline). Examples of other usable quaternary ammonium hydroxides include: trimethyl-3-hydroxypropyl ammonium hydroxide, trimethyl-3-hydroxybutyl ammonium hydroxide, trimethyl-4-hydroxybutyl ammonium hydroxide, triethyl-2-hydroxyethyl ammonium hydroxide, tripropyl-2-hydroxyethyl ammonium hydroxide, tributyl-2-hydroxyethyl ammonium hydroxide, dimethylethyl-2-hydroxyethyl ammonium hydroxide, dimethyldi(2-hydroxyethyl) ammonium hydroxide, monomethyltri(2-hydroxyethyl) ammonium hydroxide, tetraethyl ammonium hydroxide, tetrapropyl ammonium hydroxide, tetrabutyl ammonium hydroxide, monomethyl-triethyl ammonium hydroxide, monomethyltripropyl ammonium hydroxide, monomethyltributyl ammonium hydroxide, monoethyltrimethyl ammonium hydroxide, monoethyltributyl ammonium hydroxide, dimethyldiethyl ammonium hydroxide, dimethyldibutyl ammonium hydroxide, and the like and mixtures thereof.. Other bases that will function in the present invention include ammonium hydroxide, organic amines particularly alkanolamines such as 2-aminoethanol, 1-amino-2-propanol, 1-amino-3-propanol, 2-(2-aminoethoxy)ethanol, 2-(2-aminoethylamino)ethanol, 2-(2-aminoethylamino)ethylamine and the like, and other strong organic bases such as guanidine, 1,3-pentanediamine, 4-aminomethyl-1,8-octanediamine, aminoethylpiperazine, 4-(3-aminopropyl)morpholine, 1,2-diaminocyclohexane, tris(2-aminoethyl)amine, 2-methyl-1,5-pentanediamine and hydroxylamine. The amount of such bases employed in the composition will be an amount to give a desired pH to the composition and will generally be an amount of from about 0 to about 15 wt.%, preferably from about 0.5 to about 5 wt.%, and more preferably an amount of from about 1 to about 2 wt.%.

[0017] The formulations of this invention may be aqueous based but may also be semi-aqueous. That is, the formulations may optionally contain at least one polar, water miscible organic solvent. Any suitable polar, water miscible organic solvent may be employed in the formulation. Such suitable polar, water miscible organic solvent, include, but are not limited to amides, sulfones, sulfoxides, saturated alcohols and the like. Such organic polar solvents include, but are not limited to, organic polar solvents such as sulfolane (tetrahydrothiopene-1,1-dioxide), 3-methylsulfolane, n-propyl sulfone, dimethyl sulfoxide (DMSO), methyl sulfone, n-butyl sulfone, 3-methylsulfolane, amides such as 1-(2-hydroxyethyl) –2-pyrrolidone (HEP), dimethylpiperidone (DMPD), N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), and dimethylformamide (DMF) and mixtures thereof. Especially preferred as the organic

polar solvent are N-methylpyrrolidone, sulfolane, and DMSO. If present the polar, water miscible organic solvent will generally be employed in an amount of from about more than 0 to about 50 wt %, preferably from about 5 to about 30 wt %, and more preferably from about 10 to about 20 wt %.

[0018] The formulation of this invention may also optionally contain any suitable polyhydric alcohol component. Such suitable polyhydric alcohols include, but are not limited to sorbitol, xylitol, glycerol, ethylene glycol, butane-1,4-diol. Preferably the polyhydric alcohol employed is, preferably D-sorbitol. The amount of polyhydric alcohol present in the composition, if present, can range from about more than 0 to about 10 wt%, preferably from about more than 0 to about 7 wt %, and more preferably from about more than 0 to about 5 wt %.

[0019] The formulations of this invention may also contain optional ingredients that are not harmful to the effectiveness of the cleaning composition, such as for example, surfactants. The compositions of the present invention may also contain any suitable water-soluble amphoteric, non-ionic, cationic or anionic surfactant. The addition of a surfactant will reduce the surface tension of the formulation and improve the wetting of the surface to be cleaned and therefore improve the cleaning action of the composition. Amphoteric surfactants useful in the compositions of the present invention include betaines and sulfobetaines such as alkyl betaines, amidoalkyl betaines, alkyl sulfobetaines and amidoalkyl sulfobetaines; aminocarboxylic acid derivatives such as amphoglycinates, amphopropionates, amphodiglycinates, and amphodipropionates; iminodiacids such as alkoxyalkyl iminodiacids or alkoxyalkyl iminodiacids; amine oxides such as alkyl amine oxides and alkylamido alkylamine oxides; fluoroalkyl sulfonates and fluorinated alkyl amphoterics; and mixtures thereof. Preferably, the amphoteric surfactants are cocoamidopropyl betaine, cocoamidopropyl dimethyl betaine, cocoamidopropyl hydroxy sultaine, capryloamphodipropionate, cocoamidodipropionate, cocoamphopropionate, cocoamphohydroxyethyl propionate, isodecyloxypropylimino dipropionic acid, laurylimino dipropionate, cocoamidopropylamine oxide and cocoamine oxide and fluorinated alkyl amphoterics. Non-ionic surfactants useful in the compositions of the present invention include acetylenic diols, ethoxylated acetylenic diols, fluorinated alkyl alkoxylates, fluorinated alkylesters, fluorinated polyoxyethylene alkanols, aliphatic acid esters of polyhydric alcohols, polyoxyethylene monoalkyl ethers, polyoxyethylene diols, siloxane type surfactants, and alkylene glycol monoalkyl ethers. Preferably, the non-ionic surfactants are acetylenic diols or ethoxylated acetylenic diols. Anionic surfactants useful in the compositions of the present invention include carboxylates, N-acylsarcosinates, sulfonates, sulfates, and mono and diesters of orthophosphoric acid such as decyl phosphate. Preferably, the anionic surfactants are metal-free surfactants. Cationic surfactants useful in the compositions of the present invention include amine ethoxylates, dialkyldimethylammonium salts, dialkylmorpholinum salts, alkylbenzyldimethylammonium salts, alkyltrimethylammonium salts, and alkylpyridinium salts. Preferably, the cationic surfactants are halogen-free surfactants. The surfactants, if employed in the compositions of this invention will generally be present in an amount of from about more than 0 to about 1 wt.%, preferably from about 0.05 to about 0.2 wt.%.

[0020] The formulations of the present invention may also be formulated with one or more metal suitable

chelating agents to increase the capacity of the formulation to retain metals in solution and to enhance the dissolution of metallic residues on the wafer substrate. Typical examples of metal chelating agents useful for this purpose are the following organic acids and their isomers and salts: (ethylenedinitrilo)tetraacetic acid (EDTA), butylenediaminetetraacetic acid, cyclohexane-1,2-diaminetetraacetic acid (CyDTA), diethylenetriaminepentaacetic acid (DETPA), ethylenediaminetetrapropionic acid, (hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), N,N,N',N'-ethylenediaminetetra(methylenephosphonic) acid (EDTMP), triethylenetetraminehexaacetic acid (TTHA), 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (DHPTA), methyliminodiacetic acid, propylenediaminetetraacetic acid, nitrolotriacetic acid (NTA), citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, oxalic acid, phthalic acid, maleic acid, mandelic acid, malonic acid,lactic acid, salicylic acid, catechol, gallic acid, propyl gallate, pyrogallol, 8-hydroxyquinoline, and cysteine. Preferred as the metal chelating agents are aminocarboxylic acids such as cyclohexane-1,2-diaminetetraacetic acid (CyDTA). The at least one metal chelating agent may be present in the formulation in an amount from about more than 0 to about 1 wt. % by weight, preferably in an amount from about 0.05 to about 0.2wt. %.

[0021] The cleaning compositions of this invention are used to clean photoresist or plasma or ethch residue from microelctronic devices by contacting the microelectronic devise with the cleaning compositions of this invention for a suitable time and at a suitable temperature to remove the photoresist or plasma or etch residue from the microelectronic device.

[0022} The invention is illustrated by, but limited to, the following illustrative examples.

[0023] The following are examples of "browned" alpha-hydroxycarbonyl conjugated oligomers or polymers useful in the compositions of this invention.

Browned Component A: 100g of a 50:50 wt. mixture of fructose and water was reacted with 50g monoethanolamine at a temperature of 70° C for about 3 hr.

Browned Component B: 100g of a 50:50 wt. mixture of fructose and water was reacted with 16g monoethanolamine at a temperature of 70° C for about 3 hr.

Browned Component C: 100g of a 50:50 wt. mixture of fructose and water was reacted with 5g monoethanolamine at a temperature of 70° C for about 3 hr.

Browned Component D: 100g of a 50:50 wt. mixture of fructose and water was reacted with 1g monoethanolamine at a temperature of 70° C for about 3 hr.

Browned Component E: 50g of fructose was dissolved in 10g water and the mixture heated to 80° C and then 20.8g monoisopropanolamine was added, the solution heated up by itself and released water under boiling action.

Browned Component F: 50g of fructose was dissolved in 10g water and the mixture heated to 80° C and then 29.2 diethanolamine was added, the solution heated up by itself and released water under boiling action.

Browned Component G: 50g of fructose was dissolved in 10g water and the mixture heated to 80° C and then 41.9 triethanolamine was added, the solution heated up by itself and

released water under boiling action.

Browned Component H: 50g of fructose was dissolved in 10g water and the mixture heated to 80° C and then 26.5 g diethylenetriamine was added, the solution heated up by itself and released water under boiling action.

Browned Component J: 50g of fructose was dissolved in 10g water and the mixture heated to 80° C and then 20.8g aminoacetic acid (glycine) was addded, the solution heated up by itself and released water under boiling action.

Browned Component K: 50g of glucose was dissolved in 10g water and the mixture heated to 80° C and then 17.0g monoethanolamine was added, the solution heated up by itself and released water under boiling action.

Browned Component L: 50g of galactose was dissolved in 10g water and the mixture heated to 80° C and then 20.8g monoethanolamine was added, the solution heated up by itself and released water under boiling action.

Browned Component M: 50 g of a 50:50 mixture of 1-hydroxy-2-propanone and water was reacted with 8 g monoethanolamine at 70° c for about 1 hour.

Browned Component N: 50 g of a 50:50 mixture of dihydroxyacetone and water was reacted with 8 g monoethanolamine at 70° c for about 1 hour.

[0024] Comparative "yellowed" reaction products of a alpha-hydroxycarbonyl compound and an amine were prepared for comparison purposes. These yellowed reaction products are the following.

Yellowed Component 1: 100g of a 50:50 wt. mixture of fructose and water was left overnight at room temperature of about 20° C with 16g monoethanolamine at a temperature of 70° C for about 3 hr

Yellowed Component 2: 100g of a 50:50 wt. mixture of fructose and water was left overnight at room temperature of about 20° C with 50g monoethanolamine at a temperature of 70° C for one week

[0025] An additional comparative composition was prepared wherein fructose was employed alone, i.e., without being reacted with an amine or ammonia-containing compound so as to provide a baseline measurement of Cu etch rate.

[0026} Copper corrosion inhibition for the compositions of this invention and for comparative compositions were tested in the following manner. Copper blanket wafers were placed in a 150 ml beaker containing the test compositions at about 20° C. The compositions were stirred at about 200rpm for 15 minutes, Cu surface away from the stirbar. The test composition were prepared by adding the above described "browned" components, or the above-described "yellowed" comparative components, or just fructose alone to one of the following two Base Solutions. Base Solution # 1:consisted of 3.25 g 40% aqueous NH_4F solution (1.3g NH_4F and 1.95 g water), 4.33g 30% aqueous NH_4OH solution (1.3g NH_4OH and 3.03g water), 466.82g deionized water; total solution weight 474.4g. Base Solution # 2 consisted of 1.75g 40% aqueous solution of NH_4F (0.7g NH_4F and 1.05g water) and

deionized water sufficient to make the composition of the invention 100g total weight..

[0027] The compositions and the test results are presented in Table 1.

TABLE 1

Browned or Yellowed Component Amount	**Base Solution Amount**	**Composition pH**	**Cu etch rate Å/min.**
Browned Component A 5.15 g	Base Solution #1 94.85g	10.003	3.39
Browned Component B 5.15g	Base Solution #1 94.85g	9.57	4.64
Browned Component B 1.7g	Base Solution #1 98.3g	9.58	4.64
Browned Component C 5.15g	Base Solution #1 94.85g	9.57	8.90
Browned Component D 5.15g	Base Solution #1 94.85g	9.59	17.08
Browned Component E 51g	Base Solution #2 49g	5.52 (diluted 20X for using)	3.04 (diluted 20X for using)
Browned Component F 51g	Base Solution #2 49g	5.85 (diluted 20X for using)	0.83 (diluted 20X for using)
Browned Component G 51g	Base Solution #2 49g	7.94 (diluted 20X for using)	9.04 (diluted 20X for using)
Browned Component H 51g	Base Solution #2 49g	9.17 (diluted 20X for using)	14.47 (diluted 20X for using)
Browned Component J 51g	Base Solution #2 49g	9.19 (diluted 20X for using)	1.16 (diluted 20X for using)
Browned Component K 51g	Base Solution #2 49g	5.67 (diluted 20X for using)	2.24 (diluted 20X for using)
Browned Component L 51g	Base Solution #2 49g	5.18 (diluted 20X for using)	1.35 (diluted 20X for using)
Browned Component M 2.58g	Base Solution #1 47.42g	8.24	0.84
Browned Component 0.85 g	Base Solution #1 49.15g	8.07	5.4
Browned Component N	Base Solution #1	7.54	4.38

2.58g	47.42g		
Browned Component N 0.85g	Base Solution #1 49.15g	7.11	9.51
Yellowed component 1 1.7g	98.3g	9.840	49.05
Yellowed Component 2 5.1g	94.9g	10.213	35.26
Fructose alone 1.7g	94.85g	9.59	47

[0028] Several compounds were tested to confirm the necessity of the alpha-hydroxycarbonyl compound in the reaction with an amine to provide adequate copper corrosion inhibition. Different types of carbonyl compounds were tested; a ketone (acetone, H_3CCOCH_3), a diketone (2,3-pentanedione, $H_3CCOCOCH_2CH_3$), an aldehyde (formaldehyde, HCOH), and two different alpha-hydroxy carbonyl compounds (1-hydroxy-2-propanone, CH_3COCH_2OH and 1,3-dihydroxyacetone, $HOCH_2COCH_2OH$). It can be see from Table 2 that both acetone and formaldehyde exhibit no benefit when used in conjunction with monoethanol amine. In contrast, when the alpha-hydroxycarbonyl compounds 1-hydroxy-2-propanone and 1,3-dihydroxyacetone are used, the Cu etch rates are on the order of 20 times lower than the etch of monoethanol amine. It has also been shown that by using a diketone, 2,3-pentanedione, reasonable corrosion inhibition can be obtained. This is rationalized by the phenomenon keto-enol tautomerism, well known in organic chemistry, which will provide some chemical equilibrium concentration of an alpha-hydroxy carbonyl compound (Jones, M; Organic Chemistry 1997, W.W. Norton & Company, Inc., 500 Fifth Avenue, New York, N. Y. 10110). Other data to clearly indicate the necessity of alpha-hydroxycarbonyl compounds is the result with 4-Hydroxy-4-methyl 2-pentanone, a beta-hydroxycarbonyl compound. This compound showed no improvement in copper compatibility, strongly indicating the need of alpha-hydroxycarbonyl compound.

[0029] Copper etch rates (Å/min) in DMSO, NMP or mixtures thereof for tested compositions at 70 °C are set forth in Table 2. All compositions utilized monoethanol amine as the amine reacted with the listed compound at 70 °C for about three hours.

TABLE 2.

Reaction Product	Cu etch rates (Å/min) in DMSO	Cu etch rates (Å/min)in NMP
Blank: monoethanolamine (MEA)_	> 100	> 100
Monoethanolamine + Acetone		192.3
Monoethanolamine + Formaldehyde	19.3 (2:1 mixture of NMP:DMSO was used)	
Monoethanolamine + Glyoxal	33.3 (2:1 mixture of NMP:DMSO was used)	
Monoethanolamine + 1-hydroxy-2-propanone	1.1	1.5
Monoethanolamine + 1,2-dihydroxyacetone	4.7	1.0
Monoethanolamine + 2,3-pentanedione	10.4	5.1
Monoethanolamine + 4-Hydroxy-4-		267.1

methyl 2-pentanone		

{0030} The compositions of this invention provide cleaning of photoresist or plasma or etch residue from microelectronic devices similar to known fluoride containing microelectronic cleaning compositions but without the significant copper corrosion encountered with the use of those known fluoride containing cleaning compositions. A preferred cleaning composition of this invention comprises about 1.74 pars by weight oligomeric or polymeric conjugate of fructose and monoethanolamine, about 0.06 parts by weight ammonium fluoride, and about 98.2 parts by weight water.

[0031] While the invention has been described herein with reference to the specific embodiments thereof, it will be appreciated that changes, modification and variations can be made without departing from the spirit and scope of the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modification and variations that fall with the spirit and scope of the appended claims.

Claims:

1. An aqueous or semi-aqueous fluoride-containing microelectronics cleaning composition comprising: (a) at least one fluoride compound providing fluoride ions, (b) at least one "browned" oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound, and (c) water.

2. The composition according to claim 1 wherein the alpha-hydroxycarbonyl compound is a compound of the formula $R^1CH(OH)COR^2$, where R^1 and R^2 are independently selected from the group consisting of H, an aliphatic group, and a cyclic group.

3. The composition according to claim 2 wherein in the alpha-hydroxycarbonyl compound R^1 and R^2 are independently selected from the group consisting of H, CH_3, and $(CH_2)_nCH_3$ where n is an integer of from 0 to 20, and the oligomeric or polymeric conjugate of the alpha-hydroxycarbonyl compound with an amine or an ammonium compound has an absorbance peak at about 300 to 330 nm and said absorbance peak begins at about 600 to 800 nm.

4. The composition according to claim 1 wherein the alpha-hydroxycarbonyl compound is a monosaccharide selected from the group consisting of arabinose, lyxose, ribose, deoxyribose, xylose, ribulose, xylulose, allose, altrose, galactose, glucose, gulose, idose, mannose, fructose, psicose, sorbose, tagatose, mannoheptulose, seldoheptulose, octolose, 2-keto-3-deoxy-manno-octonate and sialose and the oligomeric or polymeric conjugate of the alpha-hydroxycarbonyl compound with an amine or an ammonium compound has an absorbance peak at about 300 to 330 nm and said absorbance peak begins at about 600 to 800 nm.

5. The composition according to claim 1 wherein the oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound is a conjugate of fructose and monoethnolamine.

6. The composition according to claim 5 wherein the oligomeric or polymeric conjugate of fructose and monoethanolamine has an absorbance peak at about 300 to 330 nm and said absorbance peak begins at about 600 to 800 nm.

7. The composition according to claim 6 wherein the conjugate has been prepared by heating fructose and monoethanolamine together at a temperature of at least 70° C for at least 3 hours.

8. A composition according to claim 1 comprising ammonium fluoride as the fluorine compound.

9. A composition according to claim 5 comprising ammonium fluoride as the fluorine compound

10. The composition according to claim 9 wherein the composition additionally comprises ammonium hydroxide.

11. The composition according to claim 1 wherein the pH of the composition is from about pH 7 to about pH 10.8.

12. The composition according to claim 5 wherein the pH of the composition is from about pH 7 to about pH 10.8.

13. A composition according to claim 1 comprising from about 0.0001 to about 10 wt. % fluoride component; from about 0.1 to about 20 wt. % oligomeric or polymeric conjugate component, and from about 10 to about 99.9 wt. % water.

14. A composition according to claim 5 comprising from about 0.5 to about 1 wt. % fluoride component; from about 3 to about 7 wt. % oligomeric or polymeric conjugate component of fructose and monoethanolamine, and from about 85 to about 96.5 wt. % water.

15 A composition according to claim 1 additionally comprising one or more components selected from the group consisting of surfactants, metal ion-free bases, polar water miscible organic solvents, polyhydric alcohols, and metal chelating agents.

16. A composition according to claim 5 additionally comprising one or more components selected from the group consisting of surfactants, metal ion-free bases, polar water miscible organic solvents, polyhydric alcohols, and metal chelating agents.

17. A composition according to claim 5 comprising about 1.74 pars by weight oligomeric or polymeric conjugate of fructose and monoethanolamine, about 0.06 parts by weight ammonium fluoride, and about 98.2 parts by weight water.

18. A composition according to claim, 1 wherein the browned conjugate has a bandgap of about 0.5eV or less.

19. A composition according to claim, 5 wherein the browned conjugate has a bandgap of about 0.5eV or less.

20. A process for cleaning photoresist, contaminants or etch or ash residue from a microelectronic substrate comprising contacting the microelectronic substrate with a cleaning composition for a time and at a temperature sufficient to remove the photoresist, contaminants or etch or ash residue, wherein the cleaning composition comprises: (a) at least one fluoride compound providing fluoride ions, (b) at least one "browned" oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound, and (c) water..

21. A process according to claim 20 wherein the alpha-hydroxycarbonyl compound is a compound of the formula $R^1CH(OH)COR^2$, where R^1 and R^2 are independently selected from the group consisting of H, an aliphatic group, and a cyclic group.

22. A process according to claim 20 wherein the alpha-hydroxycarbonyl compound is a monosaccharide selected from the group consisting of arabinose, lyxose, ribose, deoxyribose, xylose, ribulose, xylulose, allose, altrose, galactose, glucose, gulose, idose, mannose, fructose, psicose, sorbose, tagatose, mannoheptulose, seldoheptulose, octolose, 2-keto-3-deoxy-manno-octonate and sialose and the oligomeric or polymeric conjugate of the alpha-hydroxycarbonyl compound with an amine or an ammonium compound has an absorbance peak at about 300 to 330 nm and said absorbance peak begins at about 600 to 800 nm.

23. A process according to claim 20 wherein the oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound is a conjugate of fructose and monoethnolamine and has an absorbance peak at about 300 to 330 nm and said absorbance peak begins at about 600 to 800 nm.

24. A process according to claim 23 wherein the conjugate has been prepared by heating fructose and monoethanolamine together at a temperature of at least 70° C for at least 3 hours.

25. A process according to claim 24 wherein the composition comprises ammonium fluoride as the fluorine compound and the composition has a pH of about pH 7 to about pH 10.8. and the conjugate has a bandgap of about 0.5 eV or less.