FLUORIDE-FREE 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 organic solvent based or semi-aqueous based, fluoride-free cleaning compositions having present in the composition oligomeric or polymeric material of alpha-hydroxycarbonyl compounds, particularly both "browned" or "yellowed" oligomeric or polymeric conjugate material of alpha-hydroxycarbonyl compounds, and especially both "browned" or "yellowed" 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. There is, therefore, a need for a cleaner that:

(1) is compatible with essentially all metals used in semiconductor devices (Al, Cu, Mo, and the like);

(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 neutral to organic solvent based or semi-aqueous based, fluoride-free microelectronics cleaning compositions or formulations comprising (a) at least one "browned" or "yellowed" alpha-hydroxycarbonyl conjugate that is a oligomeric or polymeric conjugate of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound, (b) at least one amine, and (c) an at least one organic solvent or at least one organic solvent and 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 re 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, 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 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 (d) 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 (e) a polyhydric alcohol and , (f) a metal chelating agent, and (g) a surfactant. The browned or yellowed 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 500 to 800 nm. It is to be understood that the term "yellowed" and "browned" is inclusive of colors and shades of color that are a combination of brown and yellow such as light and dark orange. These browned or yellowed oliogomeric or polymeric conjugates are formed by the known "Maillard Reaction"-L.C. Maillard, *Compt. Rend.* 154, 66 (1912); *Ann. Chim.* 9, 5, 258 (1916). The yellowed 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 may be formed in the same Maillard reaction, generally at lower temperatures or shorter reaction times, and may even be formed by the reactants standing together at room temperature for a suitable time period. 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 those 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, whereas the "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 have an absorbance peak at about 300 to 330 nm, however the absorbance peak begins at about 500 to 580 nm. The conjugates may be formed first and then added to the compositions of this invention, or they may be is then heated to a temperature, e.g., 70°C or more for a time sufficient to cause the Maillard type reaction between the alpha-hydroxycarbonyl compound and an amine or an ammonium compound to form the oligomer to occur.

[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 organic solvent based or semi-aqueous based fluoride-free cleaning formulations comprising: (a) at least one "browned" or "yellowed' alpha-hydroxycarbonyl conjugate that is a oligomeric or polymeric conjugate of a alpha-hydroxycarbonyl compound with an amine or an ammonium compound, and (b) at least one amine and (c) at least one organic solvent or at least one organic solvent and water. Such formulations may also comprise other optional components, including, but not limited to: (d) 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 (e) a polyhydric alcohol and, (f) a metal chelating agent, and (g) a surfactant.

[0011] The "browned" and "yellowed" 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 500 to 800 nm. Such browned and yellowed 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. Although the reaction can be conducted over a wide range of times and temperatures, it is preferred that the reaction be conducted at room temperature for several hours or a day or more, or by heating the alpha-hydroxycarbonyl compound with the amine or ammonia compound to about 70° C or higher for a period of about 15 minutes or more, such as 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" or "yellowed" product, i.e., one having an absorbance peak at about 300 to 330 nm and with that peak beginning at about 500 to 800 nm. In general, the browned and yellowed alpha-hydroxycarbonyl conjugates preferably employed in this invention are characterized by having a low bandgap of about 0.5eV or less.

[0012] The browned or yellowed 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 or yellowed oligomeric or polymeric conjugate of an 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] The composition will also contain at least one amine component. The amine component can be either free excess amine left over in the product resulting from the reaction to form the browned or yellowed oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound or can be amine added to the composition in addition to the browned or yellowed oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl 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.

[0015] The formulations of this invention may be organic solvent based or organic solvent plus water based. That is, the formulations will 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, glycol ethers 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), alkylene glycol mono and dialkyl ethers such as ethylene glycol monothyl ether (Carbitol®), and mixtures thereof. Especially preferred as the organic polar solvent are N-methylpyrrolidone, sulfolane, ethylene glycol monothyl ether, DMSO and mixtures therreof. The organic solvent is a water miscible organic solvent and will generally be present in an amount of from about 35 to about 98 wt.%, preferably from about 40 to about 90 wt. %, and still more preferably from about 45 to about 85 wt%. Water may optionally also be present in the composition in addition to the at least one organic solvent. Water, if present with the organic solvent will generally be present in an amount of from will be present in the compositions of this invention in an amount of from about more than 0 to about 20 wt.%, preferably from about 3 to about 15 wt.%, and more preferably from about 5 to about 10 wt.%.

[0016] The "browned" or "yellowed" 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.%. The amine will be present in the composition in an amount of from about 1% to about 15 wt.%, preferably from about 3% to about 12 wt.%, and more preferably from about 5 to about 10 wt.%. The organic solvent is a water miscible organic solvent and will generally be present in an amount of from about 35 to about 98 wt.%, preferably from about 40 to about 90 wt. %, and still more preferably from about 45 to about 85 wt%. Water, if present with the organic solvent will generally be present in an amount of from will be present in the compositions of this invention in an amount of from more than 0 to about 20 wt.%, preferably from about 3 to about 15 wt.%, and more preferably from about 5 to about 10

wt.%. All percentages are based on the total weight of the cleaning composition.

[0017] The pH of the cleaning compositions will be alkaline or acidic, and 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.%.

[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 are also formulated with suitable one or more metal 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" or "yellowed" alpha-hydroxycarbonyl conjugated oligomers or polymers useful in the compositions of this invention.

Browned Component 1: 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 2: 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 3: 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 4: 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 5: 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 6: 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 7: 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 8: 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 9: 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 10. 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 11. 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 12. 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 13. 50 g of a 50:50 mixture of dihydroxyacetone and water was reacted with 8 g monoethanolamine at 70° c for about 1 hour.

Yellowed Component 14. 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 15. 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

[0024] Further oligomeric components of this invention are those set forth in Compositions A through T in Table 1. The oligomeric components of those compositions were each prepared *in situ* by the reaction of the fructose with monoethanol by their being in the components in the cleaning composition as such and heating the cleaning composition having been heated to a temperature of 70° C for 15 minutes so as to form the conjugate.

[0025} 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 70° C. The compositions were stirred at about 200rpm for 15 minutes, Cu surface away from the stirbar.

[0026] The compositions and the test results are presented in Table 1.

TABLE 1

Composition	A	B	C	D	E	F	G
N-methyl pyrrolidinone	10%	105	40%	10%	10%	10%	40%
Fructose	105	10%	10%	10%	10%	1%	10%
Water	105	0%	0%	0%	10&	10%	10%
Monoethanolamine	15%	15%	5%	15%	5%	15%	5%
Sorbitol	5%	5%	5%	0%	0%	0%	5%
Carbitol®	50%	60%	$0%	65%	65%	64%	30%
	Dk. orange	Dk. orange	Lt. brown	Orange	Lt. brown	Yellow	Lt. brown
CU etch rate (Å/min)	0.36	0.50	4.44	1.08	0.28	4.90	0.96

Table 1 (Cont'd)

Composition	H	I	1J	K	L	M	N

N-methyl pyrrolidinone	40%	40%	10%	10%	10%	40%	10%
Fructose	10%	10%	10%	1%	10%	10%	10%
Water	0%	0%	0%	10%	0%	10%	10%
Monoethanolamine	15%	15%	5%	15%	5%	15%	15%
Sorbitol	5%	5%	0%	5%	5%	5%	0%
Carbitol®	30%	30%	75%	59%	70%	20%	55%
	Orange	Dk. Orange	Brown	Yellow	Brown	Orange	Orange
CU etch rate (Å/min)	0.61	0.88	3.63	3.56	0.48	0.41	0.36

Table 1 (Cont'd)

Composition	O	P	Q	R	S	T
N-methyl pyrrolidinone	10%	40%	10%	40%	40%	40%
Fructose	1%	10%	10%	19%	1%	10%
Water	10%	0%	10%	10^	105	10%
Monoethanolamine	5%	5%	5%	15%	5%	55
Sorbitol	5%	05	5%	0%	5%	05
Carbitol®	69%	45%	60%	25%	39%	35%
	Yellow	Orange	Lt. brown	Lt. brown	Yellow	Lt. Brown
CU etch rate (Å/min)	4.34	0.72	0.28	1.50	4.85	1.96

[0027] 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. 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-methyl 2-pentanone		267.1

{0028} 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 a composition of an oligomer of fructose and monoethanolamine, free monoethanolamine, N-methyl pyrrolidinone. water, sorbitol and carbitol, such as in Composition M of Table 1.

[0029] 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. A fluoride-free microelectronics cleaning composition comprising: (a) at least one "browned" or "yellowed" oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound, (b) at least one amine and (b) at least one organic water-miscible organic solvent or at least one water-miscible organic solvent and 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 an aliphatic or cyclic group.

3. The composition according to claim 2 wherein the alpha-hydroxycarbonyl compound is a compound of the formula $R^1CH(OH)COR^2$, where R^1 and R^2 is a group selected from the group consisting of consisting of H, CH_3, $(CH_2)nCH_3$ where n is an integer of from 0 to 20, and the oligomeric or polymeric conjugate of an 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 500 to 800 nm.

4. The composition according to claim 3 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.

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 500 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. The composition according to claim 7 wherein the composition additionally comprises a polyhydric alcohol.

9 The composition according to claim 8 wherein the polyhydric alcohol is sorbitol.

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

11. A composition according to claim 1 comprising from 0.1 to about 20 wt. % oligomeric or polymeric conjugate component from about 1 to about 15 wt% amine component, and from about 35 to about 98 wt% of the organic solvent or organic solvent.

12 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.

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

14. A composition according to claim 1 comprising an oligomer of fructose and monoethanolamine, free monoethanolamine, N-methyl pyrrolidinone, water, sorbitol and carbitol.

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

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

17. 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 is a fluoride-free microelectronics cleaning composition comprising: (a) at least one "browned" or "yellowed" oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound, (b) at least one amine and (b) at least one organic water-miscible organic solvent or at least one water-miscible organic solvent and water.

18. A process according to claim 17 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 an

aliphatic or cyclic group

19. A process according to claim 18 wherein the alpha-hydroxycarbonyl compound is a compound of the formula $R^1CH(OH)COR^2$, where R^1 and R^2 is a group selected from the group consisting of consisting of H, CH_3, $(CH_2)nCH_3$ where n is an integer of from 0 to 20, and the oligomeric or polymeric conjugate of an alpha-hydroxycarbonyl compound with an amine or an ammonium compound has an absorbance

20. A process according to claim 17 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

21. A process according to claim 17 wherein the composition additionally comprises sorbitol.

22. A process according to claim 17 wherein he composition comprises an oligomer of fructose and monoethanolamine, free monoethanolamine, N-methyl pyrrolidinone, water, sorbitol and carbitol.

23. A process according to claim 17 wherein the conjugate has a bandgap of about 0.5eV or less.