

TITLE OF THE INVENTION:

WET CLEAN COMPOSITIONS FOR CoWP AND POROUS DIELECTRICS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of US Provisional Patent Application Serial Number 61/138,244 filed 12/17/2008.

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BACKGROUND OF THE INVENTION

[0002] One of the many challenges faced during continuous scaling of integrated circuits (ICs) is to achieve acceptable electromigration (EM) reliability for Cu interconnects. One way to address this challenge is the deposit of a metallic capping layer on Cu upper interface. The electroless deposition of cobalt tungsten phosphide (CoWP) appears to be the most promising candidate as a capping layer for Cu metallization.

[0003] The successful implementation of CoWP depends, not only on an optimized deposition, but also on a complete CoWP compatible integration processing, which includes wet clean processing. However, the common semi-aqueous fluoride strippers and diluted hydrofluoric acid (DHF) strippers are incompatible with CoWP, which completely remove the CoWP layer during the wet clean process.

[0004] See J. Lauerhaas, Reduced Oxygen Cleaning Process for Advanced Cu/Low-k Integration, SEMATECH Surface Preparation and Cleaning Conference, March 23-25, 2009.

20 The present invention discloses wet clean formulations which demonstrate proficient cleaning on CoWP exposed patterned wafers, while maintaining CoWP integrity, as will be disclosed more fully below.

BRIEF SUMMARY OF THE INVENTION

[0005] The present invention is a wet clean formulation for removal of post etch and ash residue from a semiconductor substrate having a CoWP feature, comprising:

5 Deionized water;

 Organic acid;

 Amine and/or quaternary ammonium hydroxide;

wherein the formulation is compatible with the CoWP feature and either (a) the molar ratio of amine and/or quaternary ammonium hydroxide to organic acid provides a pH in
10 the range of 7-14; or (b) the formulation includes a corrosion inhibitor.

[0006] The present invention is also a process for wet clean removal of post etch and ash residue from a semiconductor substrate having a CoWP feature, comprising:

 Providing a semiconductor substrate having a CoWP feature;

 Contacting the substrate with a formulation comprising

15 Deionized water;

 Organic acid;

 Amine and/or quaternary ammonium hydroxide;

wherein the formulation is compatible with the CoWP feature and either (a) the molar ratio of amine and/or quaternary ammonium hydroxide to organic acid provides a pH in
20 the range of 7-14; or (b) the formulation includes a corrosion inhibitor.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0007] FIG 1 is a scanning electron micrograph (SEM) of a patterned wafer having a CoWP capping layer before any cleaning chemicals are contacted. 1 is copper layer, 2 is
25 CoWP capping layer, 3 is ILD layer, 4 is via hole and 5 indicates post etch/ash residues.

[0008] FIG 2 is a SEM of a patterned wafer having a CoWP capping layer after cleaning with a formulation of the present invention comprising Ex. 2 AW21028-85G at 25°C and 2 minutes of contact. 1 is copper layer, 2 is CoWP capping layer, 3 is ILD layer, 4 is via hole and 5 indicates post etch/ash residues.

[0009] FIG 3 is a SEM of a patterned wafer having a CoWP capping layer after cleaning with a formulation of the present invention comprising Ex. 3 AW21028-85H at 25°C and 2 minutes of contact. 1 is copper layer, 2 is CoWP capping layer, 3 is ILD layer, 4 is via hole and 5 indicates post etch/ash residues.

5 **[0010]** FIG 4 is a SEM of a patterned wafer having a CoWP capping layer after cleaning with a formulation of the present invention comprising Ex. 6 AW21028-67E at 25°C and 2 minutes of contact. 1 is copper layer, 2 is CoWP capping layer, 3 is ILD layer, 4 is via hole and 5 indicates post etch/ash residues.

10 **[0011]** FIG 5 is a SEM of a patterned wafer having a CoWP capping layer after cleaning with a formulation of the comparative art comprising Comp. Ex. 2 DHF (800:1) at 25°C and 30 seconds of contact. 1 is copper layer, 2 is CoWP capping layer, 3 is ILD layer, 4 is via hole and 5 indicates post etch/ash residues.

DETAILED DESCRIPTION OF THE INVENTION

15 **[0012]** The common semi-aqueous fluoride strippers and DHF strippers have high CoWP etch rate and severe CoWP/Cu galvanic corrosion. In contrast, the present invention discloses wet clean formulations, which effectively minimize CoWP etch and CoWP/Cu galvanic corrosion (collectively CoWP compatible), demonstrate proficient cleaning on Cu/low-k patterned wafer with and without CoWP feature and have minimal
20 impact to porous low-k dielectrics. Preferably, the CoWP compatibility represents a CoWP etch rate no greater than 2.5 Å/min.

[0013] This invention discloses non-fluoride wet cleaning formulations suitable for post etch and ash residue cleaning in IC integration processes, especially for CoWP integrated processes. The formulations comprise deionized water (DIW), organic acid
25 and/or the salt thereof, amine and/or quaternary ammonium hydroxide and solvent. The pH of the composition is 7-14, preferably 7-11. Alternately, lower pH can be used if a corrosion inhibitor is present.

[0014] By controlling the formulation pH, solvent and solvent/water ratio, the CoWP etch rate and CoWP/Cu galvanic corrosion can be minimized.

30 **[0015]** The compositions can be mixed by adding sequentially: DIW, organic acid, amine and/or quaternary ammonium hydroxide, and solvent at room temperature. The salt of organic acid and amine and/or quaternary ammonium hydroxide can be formed in-

situ. The molar ratio of amine and/or quaternary ammonium hydroxide to organic acid is equal or greater than 1 or sufficient to maintain a pH of 7-14.

[0016] Examples of the compositions are:

5 Ex. 1: AW21028-83H

DI water	46.36 wt%
Acetic acid	0.84 wt%
TEA	2.8 wt%
Glycerol	50 wt%

(TEA = triethanolamine)

Ex. 2: AW21028-85G

DI water	55.45 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%

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Ex. 3: AW21028-85H

DI water	57.27 wt%
Acetic acid	0.63 wt%
TEA	2.1 wt%
Glycerol	40 wt%

Ex. 4: AW21028-90A

DI water	47.86 wt%
Acetic acid	0.84 wt%
NMEA	1.3 wt%
Glycerol	50 wt%

15 (NMEA = N-methyl monoethanol amine)

Ex. 5: AW21028-66F

DI water	96.69 wt%
Acetic acid	0.42 wt%
TMAH (25%)	3.16 wt%

(TMAH (25%) = tetramethylammonium hydroxide, 25% aqueous solution)

5 Ex. 6: AW21028-67E

DI water	65.41 wt%
Octanoic acid	2 wt%
TEA	2.59 wt%
Glycerol	30 wt%

Ex. 7: AW21656-29G

DI water	55.93 wt%
Ascorbic acid	2.52 wt%
TEA	1.55 wt%
Glycerol	40 wt%

Ex. 8: AW21656-29H

DI water	54.89 wt%
Ascorbic acid	2.52 wt%
TEA	2.59 wt%
Glycerol	40 wt%

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Ex. 9: AW21656-29F

DI water	53.98 wt%
Ascorbic acid	2.52 wt%
TEA	3.50 wt%
Glycerol	40 wt%

Preferred ranges:

DI water	7 – 99.7 wt%
Organic acid	0.2 – 5 wt%
Amine/ quaternary ammonium hydroxide	0.5 – 20 wt%
Solvent	0 – 70 wt%

Most Preferred ranges:

DI water	7 – 99.7 wt%
Organic acid	0.5 – 3 wt%
Amine/ quaternary ammonium hydroxide	1.5 – 10 wt%
Solvent	25 – 55 wt%

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Exemplary organic acids:

[0017] Examples of organic acids may be aliphatic/aromatic carboxylic acids, amino carboxylic acid, sulfonic acids and aminosulfonic acid. Exemplary carboxylic acids include, but are not limited to, acetic acid, propionic acid, butyric acid, pentanoic acid, 3-methylbutanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, dodecanedioic acid, 2-methylheptanoic acid, 2-hexyldecanoic acid, oxalic acid, malonic acid, maleic acid, fumaric acid, succinic acid, itaconic acid, glutaric acid, adipic acid, malic acid, tartaric acid, acrylic acid, methacrylic acid, citric acid, lactic acid, glycolic acid, ascorbic acid, anthranilic acid, gallic acid, benzoic acid, isophthalic acid, phthalic acid, trimellitic acid, pyromellitic acid, salicylic acid, 2,4-dihydroxy benzoic acid and others. Exemplary amino carboxylic acids include, but are not limited to, glycine, dihydroxy ethyl glycine, alanine, valine, leucine, asparagine, glutamine, aspartic acid, glutaric acid, lysine, arginine, imino diacetic acid, nitrilo triacetic acid, ethylenediamine tetraacetic acid, 1,2-cyclohexadiamine tetraacetic acid, diethylene triamine pentaacetic acid, and others. Exemplary sulfonic/aminosulfonic acids include, but are not limited to, benzyl sulfonic acid, p-toluene sulfonic acid, 2-(N-morpholino)ethanesulfonic acid, N-(2-hydroxyethyl)piperazine-N'-(ethanesulfonic acid), 3-[N,N-bis(2-hydroxyethyl)amino]-2-hydroxypropanesulfonic acid, 4-(N-morpholino)butanesulfonic acid, N-(2-hydroxyethyl)piperazine-N'-(2-hydroxypropanesulfonic acid), N-(2-

hydroxyethyl)piperazine-N'-(3-propanesulfonic acid), 2-(N-cyclohexylamino)ethanesulfonic acid, and others.

Exemplary amines:

- [0018]** Examples of amines may be aliphatic/aromatic primary, secondary, tertiary amines, diamines and triamines, alkanolamines, alicyclic amines, heterocyclic amines and hydroxylamines. Examples of amines includes methylamine, ethylamine, propylamine, butylamine, monoethanolamine, monoisopropanolamine, 2-(2-aminoethoxy) ethanol, dimethylamine, diethylamine, dipropylamine, dibutylamine, diethanolamine, N-methyl ethanolamine, N-ethyl ethanolamine, trimethylamine, triethylamine, tripropylamine, tributylamine, N,N-dimethylethanolamine, N,N-diethyl ethanolamine, N-methyl diethanolamine, N-ethyl diethanolamine, triethanolamine, cyclohexylamine, dicyclohexylamine, pyrrole, pyrrolidine, pyridine, morpholine, pyrazine, piperidine, benzylamine, dibenzylamine, N-methyl benzylamine, N-ethyl benzylamine and others. Examples of hydroxylamines that may be used in the cleaning composition described herein include; hydroxylamine or alkyl-substituted derivatives of hydroxylamine, such as, without limitation, hydroxylamine, N-methyl hydroxylamine, N,N-dimethyl hydroxylamine, N,N-diethyl hydroxylamine and others.

Exemplary quaternary ammonium hydroxides:

- [0019]** Examples of quaternary ammonium hydroxides may be those compounds having the formula: $[N-R_1R_2R_3R_4]^+ OH^-$ wherein R_1 , R_2 , R_3 , and R_4 are each independently an alkyl group, a hydroxyalkyl group, and combinations thereof. The term "alkyl" as used herein refers to straight or branched chain unsubstituted hydrocarbon groups of 1 to 20 carbon atoms, or preferably from 1 to 8 carbon atoms, or more preferably from 1 to 4 carbon atoms.

- [0020]** Examples of suitable alkyl groups include; methyl, ethyl, propyl, isopropyl, butyl, isobutyl and tertbutyl.

- [0021]** The term "hydroxyalkyl" as used herein refers to straight or branched unsubstituted hydroxyalkyl groups containing hydrocarbon groups of from 1 to 20 carbon atoms, or preferably from 1 to 8 carbon atoms, or more preferably from 1 to 4 carbon atoms.

- [0022]** Examples of suitable hydroxyalkyl groups include hydroxyethyl and hydroxypropyl.

[0023] Examples of suitable quaternary ammonium hydroxide compounds include; tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide, tetrabutylammonium hydroxide (TBAH), tetrapropylammonium hydroxide, trimethylethylammonium hydroxide, (2-hydroxyethyl)trimethylammonium hydroxide, (2-hydroxyethyl)triethylammonium hydroxide, (2-hydroxyethyl)tripropylammonium hydroxide, (1-hydroxypropyl)trimethylammonium hydroxide, ethyltrimethylammonium hydroxide, diethyldimethylammonium hydroxide and benzyltrimethylammonium hydroxide.

Exemplary solvents:

[0024] The formulations disclosed herein may contain at least one organic polar solvent, that is preferably water-soluble. Examples of organic polar solvents may be amides and sulfoxides. Examples of organic polar solvents include, but are not limited to, dimethylacetamide (DMAC), N-methyl pyrrolidinone (NMP), dimethylsulfoxide (DMSO), tetramethylene sulfone, dimethylformamide, N-methylformamide, formamide, dimethyl-2-piperidone (DMPD) and other amides, alcohols or sulfoxides, or multifunctional compounds, such as hydroxyamides or amino alcohols.

[0025] Further examples of the organic polar solvent include diols and polyols such as (C_2 – C_{20}) alkanediols and (C_3 – C_{20}) alkanetriols, cyclic alcohols and substituted alcohols. Particular examples of these organic solvents are ethylene glycol, propylene glycol, glycerol, tetrahydrofurfuryl alcohol, diacetone alcohol and 1, 4-cyclohexanedimethanol.

[0026] The non-aqueous solvents enumerated above may be used alone or in combination with two or more solvents.

[0027] In certain embodiments, the organic polar solvent may comprise a glycol ether. Examples of glycol ethers include ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monophenyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monoisopropyl ether, diethylene glycol monobutyl ether, diethylene glycol monoisobutyl ether, diethylene glycol monobenzyl ether, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol monomethyl ether, triethylene glycol dimethyl ether, polyethylene glycol monomethyl ether, diethylene glycol methyl ethyl ether, triethylene glycol monomethyl ether acetate, ethylene glycol monethyl ether acetate, propylene glycol methyl ether acetate, propylene glycol monomethyl ether,

propylene glycol dimethyl ether, propylene glycol monobutyl ether, propylene glycol monopropyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monopropyl ether, dipropylene glycol monoisopropyl ether, dipropylene glycol monobutyl ether, dipropylene glycol diisopropyl ether, tripropylene glycol monomethyl ether, 1-methoxy-2-butanol, 2-methoxy-1-butanol, 2-methoxy-2-methylbutanol and 2-(2-butoxyethoxy) ethanol.

Comparative examples:

[0028] Comparative Ex. 1 DHF (100:1)

DI water 99 wt%

HF(49%) 1 wt%

10 **[0029]** Comparative Ex. 2 DHF (800:1)

DI water 799 wt%

HF(49%) 1 wt%

[0030] The summary of etch rates ("ER") of Co, CoWP and Cu are provided in Table 1 and 2. In determining the Co and Cu etch rate, the wafers had a blanket layer of a known thickness deposited upon it. The initial thickness of the wafer was determined using the CDE ResMap 273 Four Point Probe. After determining the initial thickness, test wafers were immersed in the wet clean formulations. After five minutes, the test wafers were removed from the wet clean formulation, rinsed for three minutes with deionized water and completely dried under nitrogen. The thickness of each wafer was measured. The procedure was repeated at 10, 20, 40, and 60 minutes of exposure. Thickness measurements were determined at each time interval and graphed using a "least squares fit" model on the results for each clean formulation. The calculated slope of the "least squares fit" model of each composition is the resultant etch rate provided in angstroms/minute (Å/min). In determining the CoWP etch rate, the film thickness could not easily be measured by conventional ellipsometric methods, because the CoWP films were very thin and the underlying Cu causes reflection of the incident beam. As an alternative, the open circuit potential (OCP) of the CoWP layer was measured as a function of time of immersion in the wet clean formulation. A blanket CoWP substrate (1 x 4 cm²) was immersed in the 500 ml air-saturated wet clean formulations and the potential was monitored over time. The OCP of CoWP film is significantly different from

underlying Cu. At the point where the CoWP is completely etched, the open circuit potential is similar to Cu. By noting the time it takes to reach the Cu OCP and knowing the starting thickness of CoWP layer, the CoWP etch rate can be determined. In determining the galvanic current of CoWP and Cu couple, the potential polarization was carried out to determine the corrosion current of CoWP in a galvanic couple with Cu when in contact with the various wet clean formulations. The blanket CoWP or Cu substrate (2 x 2 cm²) was immersed in 500 ml of wet clean formulation at ambient temperature under air-saturated conditions with strong agitation (600 RPM). Cathodic current was then applied from -1 V to 0.1 V at a scan rate of 10 mV/s with respect to the Ag/AgCl reference electrode. The polarization curves are plotted as Tafel plots. Extrapolation to zero current density gives the corrosion potential (E_{corr}). The current density at the cross point of CoWP and Cu polarization curves gives galvanic current density of the CoWP and Cu couple.

[0031] Table 1 shows that the wet clean formulations of present invention have lower etch rates on Co, CoWP and Cu and lower galvanic current density compared to Comp. Ex. 1 DHF (100:1). Table 1 and Table 2 show that all wet clean formulations of the present invention have superior low etch rate on CoWP, which is essential for CoWP integration.

Table 1: CoWP Compatibility data on blanket CoWP wafers and Co and Cu etch rates

Clean Formulations	pH	Co etch rate (Å/min)	CoWP etch rate (Å/min)	Cu etch rate (Å/min)	Galvanic current density (A/cm ²)
Comp. Ex. 1 DHF (100:1)	NA	109	14	7	2.2E-04
Ex. 1 AW21028-83H	7.33	13	1.5	2	3.25E-05
Ex. 2 AW21028-85G	7.40	13	2	2	4.5E-05
Ex. 3 AW21028-85H	7.32	13	2	1	6E-05
Ex. 4 AW21-28-90A	9.25	2	<1	4	4.5E-07
Ex. 5 AW21028-66F	10.93	3	1.5	1	2.2E-05
Ex. 6 AW21028-67E	7.23	9	<1	1	3.25E-06

NA: not available

pH determinations were made using 5% aqueous solutions at ambient temperature.

Table 2: Etch rate data on blanket Co, CoWP and Cu wafers

Clean Formulations	pH	Co etch rate (Å/min)	CoWP etch rate (Å/min)	Cu etch rate (Å/min)
Ex. 7 AW21656-29G	4.96	10	1.7	2
Ex. 8 AW21656-29H	7.13	5	1	1
Ex. 9 AW21656-29F	7.66	33	<1	<1

[0032] The summary of cleaning data, along with the exposure temperature and time, are provided in Table 3. The test wafers are post etch and ash patterned wafers featuring trenches and vias in a Cu/CoWP/ILD stack. In this procedure, one or more test wafers were placed in a 600 milliliter (ml) beaker that contained 400 ml of each wet clean formulation. The 600 ml beaker further included a 1" stir bar that rotated at 400 revolutions per minute. The wet clean formulations having the wafer(s) contained therein were then heated at the time and temperature provided in Table 3. After exposure to the wet clean formulation, the wafer(s) were rinsed with deionized water and dried with nitrogen gas. The wafers were cleaved to provide an edge, then examined using scanning electron microscopy (SEM) on a variety of pre-determined locations on the wafer and the results were visually interpreted for cleaning performance and CoWP compatibility. Table 3 shows Comp. Ex. 2 DHF (800:1) completely cleans the residue and removes the CoWP layer at 25°C/30 second. This clearly demonstrates that DHF is incompatible to CoWP capping layer. The wet clean formulations of the present invention, comprising, in this instance: Ex.2 AW21028-85G and Ex. 6 AW21028-67E completely clean residues without undercutting the CoWP layer at 25°C/2 min. These results demonstrate good cleaning efficiency and CoWP compatibility of the wet clean formulations of the present invention.

Table 3: Cleaning performance of patterned CoWP wafers

Clean Formulations	Temp. (°C)	Time (min)	CoWP patterned wafer	
			Cleaning performance	CoWP compatibility
Comp. Ex. 2 DHF (800:1)	25	0.5	no residue	CoWP removed
Ex. 1 AW21028-83H	25	2	slight residue	slight undercut
Ex. 2 AW21028-85G	25	2	no residue	no undercut
Ex. 3 AW21028-85H	25	2	no residue	slight undercut
Ex. 4 AW21028-90A	25	2	some residue	no undercut
Ex. 5 AW21028-66F	25	2	slight residue	slight undercut
Ex. 6 AW21028-67E	25	2	no residue	no undercut

[0033] The summary of blanket porous ILD compatibility data are provided in Table 4 and 5. Diethoxymethylsilane (DEMS) based porous organosilicate glass (OSG) films were deposited using a Precision 5000 integrated deposition platform. DEMS and a porogen were used as the chemical precursors to deposit the composite film onto <100> Si 8-12 ohm/cm 200 mm wafers. The films were UV-cured to prepare the final porous film having a dielectric constant of 2.5. The thickness and refractive index of the dielectrics film were determined using SCI FilmTek™ 2000 Reflectometer. The k value and FTIR (Fourier Transform Infrared Spectroscopy) spectra were obtained using MSI electronics Mercury probe (Model Hg-401) and NEXUS 470 FT-IR spectroscopy, respectively.

[0034] Table 4 summarizes dielectric compatibility of wet clean formulations of the present invention with DEMS-based porous OSG (k=2.5). The pristine ILD wafer with a k value of 2.5 was processed in wet clean formulations: Ex.1 AW21028-83H, Ex. 2 AW21028-85G and Ex. 3 AW21028-85H at 25°C for 2 minutes. There were no changes in film thickness, refractive index or k value after processing. FTIR data in Table 5 show that the bond retention of C-H/SiO₂ and Si-CH₃/SiO₂ are almost constant, indicating no damage to surface Si-CH₃ bond and SiO₂ network. These results indicate the wet clean formulations of the present invention have no negative impact on blanket porous ILD dielectrics.

Table 4: Blanket porous ILD PDEMS 2.5 compatibility

Clean Formulations	Temp. (°C)	Time (min)	etch rate (Å/min)	Change of refractive index	Change of k
Ex. 1 AW21028-83H	25	2	<1	0	0.02
Ex. 2 AW21028-85G	25	2	<1	0.001	0
Ex. 3 AW21028-85H	25	2	<1	0.001	0

Table 5: Blanket porous ILD PDEMS 2.5 compatibility: FTIR

Clean Formulations	Temp. (°C)	Time (min)	Before		After	
			Si-CH ₃ /SiO	C-H/SiO	Si-CH ₃ /SiO	C-H/SiO
Ex. 2 AW21028-85G	25	2	0.020	0.015	0.021	0.014
	30	2	0.020	0.015	0.021	0.013
	35	2	0.020	0.014	0.020	0.013
Ex. 3 AW21028-85H	25	2	0.021	0.014	0.021	0.014

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[0035] Patterned trench features on porous OSG dielectrics were used to determine the effect of the wet clean formulations on etch-damaged dielectric sidewall. The patterned wafers were prepared based upon 90 nm design rules. During the patterned wafer process, a photoresist layer is coated on the substrate with porous OSG dielectrics. Using a photolithographic process, a pattern is defined on the photoresist layer. The patterned photoresist layer is then subjected to plasma etch, by which the pattern is transferred to the substrate. The patterned substrate is subsequently etched and ashed to form the desired trench features. The CD (critical dimension) changes of dielectrics trench (M1 trench), after treatment with the wet clean formulations, were measured by SEM and provided in Table 6.

[0036] Table 6 demonstrates minimal change of CD (0.03 μm , 3%) after processing in the wet clean formulation of the present invention, comprising: Ex. 2 AW21028-8G at 25°C for 2 minutes. By contrast, a severe CD shift was observed (0.21 μm , 21%) after processing in Comp. Ex. 1 DHF (100:1) at 25°C for 20 seconds. These results indicate that the wet clean formulations of the present invention is compatible with etch-damaged porous low-k dielectrics.

Table 6: Patterned porous ILD PDEMS 2.5 compatibility

Clean Formulations	Temp. (°C)	Time (second)	CD change (μm)	CD change (%)
Comp. Ex. 1 DHF (100:1)	25	20	0.21	21
Ex. 2 AW21028-85G	25	120	0.03	3

[0037] As can be seen from the above data, this invention discloses wet clean formulations which effectively prevent CoWP etch and CoWP/Cu galvanic corrosion, demonstrate proficient cleaning on Cu/low-k patterned with and without CoWP wafers and have minimal impact to porous low-k dielectrics.

[0038] The wet clean formulations may also include one or more of the following additives: corrosion inhibitors, O₂ scavengers, and other additives. The additive(s) may be added to the extent that they do and/or do not adversely affect the pH range of the composition. With corrosion inhibitor and/or O₂ scavenger additives, the molar ratio of amine and/or quaternary ammonium hydroxide to organic acid can be: (a) equal to, (b) greater, or (c) less than 1.

[0039] Examples of the compositions are:

Ex. 10: AW21656-16D

DI water	53.45 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Benzotriazole	2 wt%

Ex. 11: AW21656-16E

DI water	54.45 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Benzotriazole	1 wt%

Ex. 12: AW21656-16F

DI water	54.95 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Benzotriazole	0.5 wt%

Ex. 13: AW21656-19A

DI water	55.35 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Benzotriazole	0.1 wt%

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Ex. 14: AW21656-18A

DI water	54.95 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Tolyltriazole	0.5 wt%

Ex. 15: AW21656-19B

DI water	55.35 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Tolyltriazole	0.1 wt%

10 Ex. 16: AW21656-18G

DI water	53.45 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%

1,2,4-triazole 2 wt%

Ex .17: AW21656-18C

DI water 54.95 wt%

Acetic acid 1.05 wt%

TEA 3.5 wt%

Glycerol 40 wt%

1,2,4-triazole 0.5 wt%

Ex. 18: AW21656-19C

DI water 55.35 wt%

Acetic acid 1.05 wt%

TEA 3.5 wt%

Glycerol 40 wt%

1,2,4-triazole 0.1 wt%

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Ex. 19: AW21656-19D

DI Water 50.45 wt%

Acetic acid 1.05 wt%

TEA 3.5 wt%

Glycerol 40 wt%

Ascorbic acid 5 wt%

Ex. 20: AW21656-18H

DI water 53.45 wt%

Acetic acid 1.05 wt%

TEA 3.5 wt%

Glycerol 40 wt%

Ascorbic acid 2 wt%

Ex. 21: AW21656-18D

DI water	54.95 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Ascorbic acid	0.5 wt%

Ex. 22: AW21656-18F

DI water	53.45 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Carbohydrazide	2 wt%

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Ex. 23: AW21656-18B

DI water	54.95 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Carbohydrazide	0.5 wt%

Ex. 24: AW21656-16A

DI water	50.45 wt%
Acetic acid	1.05 wt%
TEA	3.5 wt%
Glycerol	40 wt%
Catechol	5 wt%

Ex. 25: AW21656-29A

DI water	64.91wt%
Octanoic acid	2 wt%
TEA	2.59 wt%
Glycerol	30 wt%
Ascorbic acid	0.5 wt%

Ex. 26: AW21656-30D

DI water	56.9 wt%
Acetic acid	1.05 wt%
TEA	1.55 wt%
Glycerol	40 wt%
Benzotriazole	0.5 wt%

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Ex. 27: AW21656-30E

DI water	55.86 wt%
Acetic acid	1.05 wt%
TEA	2.59 wt%
Glycerol	40 wt%
Benzotriazole	0.5 wt%

Ex. 28: AW21656-30H

DI water	56.9 wt%
Acetic acid	1.05 wt%
TEA	1.55 wt%
Glycerol	40 wt%
Tolyltriazole	0.5 wt%

Ex. 29: AW21656-30I

DI water	55.86 wt%
Acetic acid	1.05 wt%
TEA	2.59 wt%
Glycerol	40 wt%
Tolyltriazole	0.5 wt%

Ex. 30: AW21656-30F

DI water	56.9 wt%
Acetic acid	1.05 wt%
TEA	1.55 wt%
Glycerol	40 wt%
1,2,4-triazole	0.5 wt%

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Ex. 31: AW21656-30G

DI water	55.86 wt%
Acetic acid	1.05 wt%
TEA	2.59 wt%
Glycerol	40 wt%
1,2,4-triazole	0.5 wt%

Preferred ranges:

DI water	7 – 99.7 wt%
Organic acid	0.2 – 5 wt%
Amine/ quaternary ammonium hydroxide	0.5 – 20 wt%
Solvent	0 – 70 wt%
Corrosion inhibitor and /or O ₂ scavenger	0.01 – 10 wt%
Contact Time Interval	0.1 – 5 min.

Most Preferred ranges:

DI water	7 – 99.7 wt%
Organic acid	0.5 – 3 wt%
Amine/ quaternary ammonium hydroxide	1.5 – 10 wt%
Solvent	25 – 55 wt%
Corrosion inhibitor and /or O ₂ scavenger	0.1 – 5 wt%
Contact Time Interval	0.5 – 2 min.

5 Exemplary organic corrosion inhibitors and O₂ scavengers:

[0040] The compositions of the present disclosure can also optionally contain up to about 10 wt%, or about 0.1 to about 5 wt% of a corrosion inhibitor and/or oxygen scavenger to further reduce the attack on the Cu, Co and CoWP. Examples of corrosion inhibitors may be a triazole, such as 1,2,4-triazole, or triazoles substituted with substituents such as C1-C8 alkyl, amino, thiol, mercapto, imino, carboxy and nitro groups, such as benzotriazole, 5-carboxylic acid benzotriazole, tolyltriazole, 5-phenyl-benzotriazole, 5-nitro-benzotriazole, 3-amino-5-mercapto-1,2,4-triazole, 1-amino-1,2,4-triazole, hydroxybenzotriazole, 2-(5-amino-pentyl)-benzotriazole, 1-amino-1,2,3-triazole, 1-amino-5-methyl-1,2,3-triazole, 3-amino-1,2,4-triazole, 3-mercapto-1,2,4-triazole, 3-isopropyl-1,2,4-triazole, 5-phenylthiolbenzotriazole, naphthotriazole, and thiazoles, tetrazoles, imidazoles, phosphates, thiols and azines such as 2-mercaptobenzoimidazole, 2-mercapto-benzothiazole, 4-methyl-2-phenylimidazole, 2-mercaptothiazoline, 5-aminotetrazole, 5-amino-1,3,4-thiadiazole-2-thiol, 2,4-diamino-6-methyl-1,3,5-triazine, thiazole, triazine, methyltetrazole, 1,3-dimethyl-2-imidazolidinone, 1,5-pentamethylenetetrazole, 1-phenyl-5-mercaptotetrazole, diaminomethyltriazine, mercaptobenzothiazole, imidazoline thione, mercaptobenzoimidazole, 4-methyl-4H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiadiazole-2-thiol, benzothiazole, tritoyl phosphate, indiazole, etc. Suitable corrosion inhibitors further include an organic acid, an organic acid salt, a phenol, a hydroxylamine or acid salt thereof. Examples of particular corrosion inhibitors include citric acid, anthranilic acid, salicylic acid, lactic acid, iminodiacetic acid, benzoic acid, isophthalic acid, maleic acid, fumaric acid, D,L-malic acid, malonic acid, phthalic acid, maleic anhydride, phthalic anhydride, resorcinol, diethyl hydroxylamine and the lactic acid and citric acid salts thereof, and the like. Yet other

examples of suitable corrosion inhibitors include fructose, ammonium thiosulfate, glycine, tetramethylguanidine, benzoguanamine, melamine, guanine, adenine, thioglycerol, salicylamide, and dimethylacetoacetamide. In embodiments wherein the corrosion inhibitor is an organic acid, the organic acid may be the same as that used in the solution.

[0041] Exemplary oxygen scavengers include ascorbic acid, catechol, carbonylhydrazide, gallic acid, hydroquinone, pyrogallol, cyclohexanedione, hydrazine, a sulfite, a bisulfate, and/or a nitrile.

[0042] The composition may also include one or more of the following additives:
surfactants, chelating agents, chemical modifiers, dyes, biocides, and other additives. The additive(s) may be added to the extent that they do not adversely affect the pH range of the composition. Some examples of representative additives include acetylenic alcohols and derivatives thereof, acetylenic diols (non-ionic alkoxylated and/or self-emulsifiable acetylenic diol surfactants) and derivatives thereof, alcohols, quaternary amines and di-amines, amides (including aprotic solvents such as dimethyl formamide and dimethyl acetamide), alkyl alkanolamines (such as diethanolamine), and chelating agents such as beta-diketones, beta-ketoimines, carboxylic acids, malic acid and tartaric acid based esters and diesters and derivatives thereof, and tertiary amines, diamines and triamines. Specific acetylenic diols include Surfynol 465 surfactant available from Air Products and Chemicals, Inc., Allentown, Pennsylvania, USA. Surfynol 465 is 2,4,7,9-tetramethyl-5-decyn-4,7-diol, which is ethoxylated with 10 ethylene oxide units. See US Patent 6,717,019 at column 9, line 46.

Comparative examples:

[0043] Comparative Ex. 3 AW21656-30B

DI water	57.40 wt%
Acetic acid	1.05 wt%
TEA	1.55 wt%
Glycerol	40 wt%

[0044] Comparative Ex. 4 AW21656-30C

DI water	56.36 wt%
Acetic acid	1.05 wt%
TEA	2.59 wt%
Glycerol	40 wt%

5 Table 7 and 8 summarize the metal etch rate data of wet clean formulations with additional corrosion inhibitors and/or O₂ scavengers. The corrosion inhibitor and/or O₂ scavenger, and/or combination of two or more corrosion inhibitor and/or O₂ scavenger are useful to improve the compatibility of the composition with the metals at pH >7 or pH<7.

Table 7: Etch rate data on blanket Co, CoWP and Cu wafers

Clean Formulations	Corrosion inhibitors /O ₂ scavengers (wt%)	pH	Co etch rate (Å/min)	CoWP etch rate (Å/min)	Cu etch rate (Å/min)
Ex. 10 AW21656-16D	Benzotriazole (2)	7.13	2	<1	<1
Ex. 11 AW21656-16E	Benzotriazole (1)	7.26	3	<1	<1
Ex. 12 AW21656-16F	Benzotriazole (0.5)	7.24	2	<1	<1
Ex. 13 AW21656-19A	Benzotriazole (0.1)	7.33	2	<1	<1
Ex. 14 AW21656-18A	Tolyltriazole (0.5)	7.33	2	<1	<1
Ex. 15 AW21656-19B	Tolyltriazole 0.1	7.35	4	<1	1
Ex. 16 AW21656-18G	1,2,4-triazole (2)	7.36	4	<1	1
Ex. 17 AW21656-18C	1,2,4-triazole (0.5)	7.43	4	<1	<1
Ex. 18 AW21656-19C	1,2,4-triazole (0.1)	7.50	8	<1	1
Ex. 19 AW21656-19D	Ascorbic acid (5)	4.47	10	<1	3
Ex. 20 AW21656-18H	Ascorbic acid (2)	5.22	12	1.1	2
Ex. 21 AW21656-18D	Ascorbic acid (0.5)	7.15	5	1.2	1
Ex. 22 AW21656-18F	Carbohydrazide (2)	7.42	11	2.2	7
Ex. 23 AW21656-18B	Carbohydrazide (0.5)	7.45	14	1.5	6
Ex. 24 AW21656-16A	Catechol (5)	7.42	2	1.8	5
Ex. 25 AW21028-29A	Ascorbic acid (0.5)	6.44	8	1.3	3

Table 8: Etch rate data on blanket Co, CoWP and Cu wafers

Clean Formulations	Corrosion inhibitors /O ₂ scavenger (wt%)	pH	Co etch rate (Å/min)	CoWP etch rate (Å/min)	Cu etch rate (Å/min)
Comp.Ex. 3 AW21028-30B	none	4.89	199	4.3	6
Comp. Ex. 4 AW21656-30C	none	6.19	>1011	3.2	5
Ex. 26 AW21656-30D	Benzotriazole (0.5)	4.88	33	<1	<1
Ex. 27 AW21656-30E	Benzotriazole (0.5)	6.15	3	<1	<1
Ex. 28 AW21656-30H	Tolyltriazole (0.5)	4.93	10	<1	1
Ex. 29 AW21656-30I	Tolyltriazole (0.5)	6.15	2	<1	<1
Ex. 30 AW21656-30F	1,2,4-triazole (0.5)	4.84	16	1.6	14
Ex. 31 AW21656-30G	1,2,4-triazole (0.5)	6.12	7	1.3	<1

CLAIMS

1. A non-fluoride wet clean formulation for removal of post etch and ash residue from a semiconductor substrate having a CoWP feature, consisting of:
 - deionized water;
 - an acid selected from the group consisting of Acetic acid, Octanoic acid and mixtures thereof;
 - amine selected from the group consisting of triethanol amine and N-methyl monoethanol amine;
 - glycerol;
 - optionally a corrosion inhibitor;wherein the formulation is compatible with the CoWP feature and (a) the molar ratio of amine to organic acid provides an 7-11 pH and (b) the formulation has an acid content greater than 0.84wt% and equal to or less than 2.0wt%.
2. The formulation of Claim 1 wherein the corrosion inhibitor is included and is selected from the group consisting of benzotriazole, tolyltriazole and mixtures thereof.