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(57) **Abrégé/Abstract:**

Aqueous cleaning compositions and method of using the cleaning compositions for cleaning microelectronic substrates, which compositions are able to essentially completely clean such substrates and produce essentially no metal corrosion of the metal elements of such substrates. The aqueous cleaning compositions of this invention have (a) water, (b) at least one of ammonium and quaternary ammonium ions and (c) at least one of hypophosphite ( $\text{H}_2\text{PO}_2^-$ ) and/or phosphite ( $\text{HPO}_3^{2-}$ ) ions. The cleaning compositions also may contain fluoride ions. Optionally, the composition may contain other components such as organic solvents, oxidizing agent, surfactants, corrosion inhibitors and metal complexing agents.



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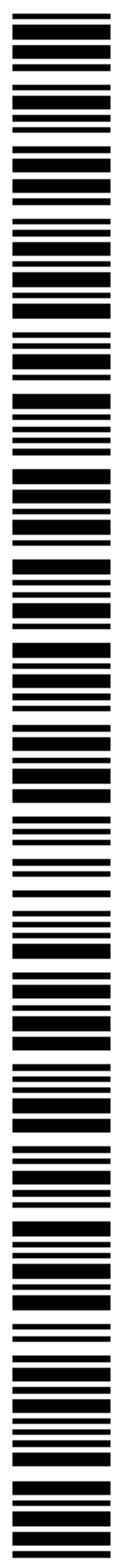
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(54) Title: STRIPPING AND CLEANING COMPOSITIONS FOR MICROELECTRONICS

(57) Abstract: Aqueous cleaning compositions and method of using the cleaning compositions for cleaning microelectronic substrates, which compositions are able to essentially completely clean such substrates and produce essentially no metal corrosion of the metal elements of such substrates. The aqueous cleaning compositions of this invention have (a) water, (b) at least one of ammonium and quaternary ammonium ions and (c) at least one of hypophosphite ( $\text{H}_2\text{PO}_2^-$ ) and/or phosphite ( $\text{HPO}_3^{2-}$ ) ions. The cleaning compositions also may contain fluoride ions. Optionally, the composition may contain other components such as organic solvents, oxidizing agent, surfactants, corrosion inhibitors and metal complexing agents.



**WO 2005/019939 A1**

## STRIPPING AND CLEANING COMPOSITIONS FOR MICROELECTRONICS

### FIELD OF THE INVENTION

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**[0001]** This invention relates to methods and aqueous post-etch and/or photoresist ash residue cleaning compositions for cleaning microelectronics substrates. The compositions of this invention provide enhanced protection of metal, i.e., inhibition of corrosion, when such microelectronic substrates are  
10 subjected to cleaning and a subsequent aqueous rinse.

### BACKGROUND TO THE INVENTION

**[0002]** Many photoresist strippers and residue removers have been proposed  
15 for use in the microelectronics field as downstream or back end of the manufacturing line cleaners. In the manufacturing process a thin film of photoresist is deposited on a substrate material, and then circuit design is imaged on the thin film. Following baking, the exposed resist is removed with a photoresist developer. The resulting image is then transferred to the underlying material, which is generally a dielectric or  
20 metal, by way of plasma etch gases or chemical etchant solutions. The etchant gases or chemical etchant solutions selectively attack the photoresist-unprotected area of the substrate. As a result of the plasma etching process, photoresist and etched material by-products are deposited as residues around or on the sidewall of the etched openings on the substrate and the photoresist.

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**[0003]** Additionally, following the termination of the etching step, the resist mask must be removed from the protected area of the substrate so that the next process operation can take place. This can be accomplished in a plasma ashing step by the use of suitable plasma ashing gases or wet chemical strippers. Finding  
30 a suitable cleaning composition for removal of this resist mask material without



adversely affecting, e.g., corroding, etching or dulling, the metal circuitry has also proven problematic.

**[0004]** As microelectronic fabrication integration levels have increased and  
5 patterned microelectronic device dimensions have decreased, it has become  
increasingly difficult to provide suitable photoresist stripping and cleaning  
compositions that provide suitable stripping and cleaning properties without  
producing other detrimental effects. In the area of semiconductors and flat panel  
displays (FPD), the problem of metal corrosion during photoresist stripping, residue  
10 removal and the water rinse is a severe drawback, particularly with the use of select  
metals such as aluminum, titanium, and tungsten and alloys.

**[0005]** A typical residue remover for microelectronic applications might be an  
alkaline-containing composition that includes polar organic solvents blended with  
15 organic amines or hydroxylamines and other solvating agents in an attempt to  
lessen metal and dielectric attack or corrosion. Amines and hydroxylamines have  
been shown to increase the effectiveness of photoresist and residue removal in  
solvent blends. However, such alkaline ash residue removal formulations  
experience carbon dioxide uptake from the air, which in most cases shortens the  
20 cleaner solution's effective bath life. Moreover, these alkaline cleaner compositions  
are relatively slow acting and require the substrates to be kept in the cleaner  
solutions for extended times at elevated temperatures. Moreover, the water rinse  
following this type of remover can create a strongly alkaline aqueous solution that  
can lead to considerable loss of metal from the patterned lines. This necessitates  
25 an intermediate rinse between the cleaning/stripping step and the aqueous rinse.  
Such an intermediate rinse, typically with isopropyl alcohol, adds undesirable time,  
safety concerns, environmental consequences, and cost to the manufacturing  
process.

30 **[0006]** There is, therefore, a need for stripping and cleaning compositions for

photoresists and residues that enable one to completely remove etch and/or ash residue from the microelectronic substrate, especially a need for such cleaner and residue removing compositions that do not produce any significant metal corrosion.

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## SUMMARY OF THE INVENTION

**[0007]** The invention provides aqueous cleaning compositions for cleaning microelectronic substrates that are able to essentially completely clean such substrates and produce essentially no metal corrosion of the metal elements of such substrates, and to do so at relatively short cleaning times and relatively low temperatures compared to the cleaning times required for prior art alkaline-containing cleaning compositions. The invention also provides method of using such aqueous cleaning compositions to clean microelectronic substrates, particularly FPD microelectronic substrates, without producing any significant metal corrosion of the metal elements of the microelectronic substrate. The aqueous cleaning compositions of this invention comprise (a) water, (b) at least one of ammonium or quaternary ammonium ions and (c) at least one of hypophosphite ( $\text{H}_2\text{PO}_2^-$ ) or phosphite ( $\text{HPO}_3^{2-}$ ) ions. It will be appreciated that both ammonium and quaternary ammonium ions may be present in a composition of this invention, and both hypophosphite and phosphite ions also may both be present in a composition of this invention. In a further embodiment of the invention the cleaning compositions of this invention also preferably contain fluoride ions. The cleaning compositions of this invention optionally can have present in the compositions other components, such as for example surfactants, metal complexing or chelating agents, organic solvents and the like. The cleaning and residue removal compositions of this invention are especially suitable for cleaning microelectronic substrates.

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## DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

**[0008]** The aqueous cleaning compositions of this invention contain water generally in an amount of from about 60% to about 99.5%, preferably from about 75% to about 99%, more preferably from about 80% to about 98%, and most preferably from about 83% to about 98%, by weight of the composition.

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**[0009]** The aqueous cleaning compositions of this invention contain hypophosphite and/or phosphite ions and ammonium ions. The hypophosphite/phosphite and ammonium/quaternary ammonium ions are preferably provided by ammonium salts of the phosphites employed in an amount of from  
10 about 0.5% to about 40%, generally from about 1% to about 25%, preferably from about 2% to about 20%, more preferably from about 2% to about 17%, and in some instances 1.8% to 2.0%, by weight of the composition. The hypophosphite/phosphite and ammonium ions can also be provided by other components suitable for providing such ions, e.g., by providing in the compositions  
15 hypophosphorous and or phosphorous acid or their salts, preferably sodium salts, in combination with ammonium or quaternary ammonium, preferably tetraalkylammonium salts. In any event the combination of components will be sufficient to provide in the cleaning compositions of this invention hypophosphite/phosphite ions and ammonium/quaternary ammonium ions in an  
20 amount equivalent to that which would be contributed by the ammonium salts as stated hereinbefore. That is, the components contributing the hypophosphite/phosphite ions and ammonium/quaternary ammonium ions constitute, in total from about 0.5% to about 40%, preferably from about 1% to about 25%, more preferably from about 2% to about 20%, and most preferably from about  
25 2% to about 17%, by weight of the composition.

**[0010]** The aqueous cleaning compositions of this invention will, in a preferred embodiment, also contain fluoride ions from any suitable fluoride compound, such as for example, from hydrogen fluoride, a tetraalkylammonium fluoride such as  
30 tetramethylammonium fluoride and tetrabutylammonium fluoride, and ammonium

fluoride. Other suitable fluorides include, for example fluoroborates, tetrabutylammonium fluoroborates, aluminum hexafluorides, antimony fluoride and the like. The fluoride components will generally be present in the composition an amount of 0 ppm up to about 10,000 ppm or 0% up to about 1% by weight of the composition, preferably in an amount of from about 10 to about 5,000 ppm or 0.001% to about 0.5% by weight of the composition, and more preferably from about 10 ppm to about 2000 ppm. or 0.001% to about 0.2% weight of the composition.

**[0011]** The aqueous cleaning compositions of this invention may, and preferably do, also contain one or more suitable water-soluble organic solvents. Among the various organic solvents suitable are alcohols, polyhydroxy alcohols, such as glycerol, glycols, glycol ethers, alkyl-pyrrolidinones such as N-methylpyrrolidinone (NMP), 1-hydroxyalkyl-2-pyrrolidinones such as, 1-(2-hydroxyethyl)-2-pyrrolidinone (HEP), dimethylformamide (DMF), dimethylacetamide (DMAc), sulfolane or dimethylsulfoxide (DMSO). These solvents may be added to limit the aggressiveness of the cleaning compositions and to reduce metal, especially aluminum or aluminum alloy corrosion rates if further aluminum and/or aluminum- alloy corrosion inhibition is desired. Preferred water-soluble organic solvents are polyhydroxy alcohols such as glycerol, N-methylpyrrolidinone and/or 1-hydroxyalkyl-2-pyrrolidinones such as 1-(2-hydroxyethyl)-2-pyrrolidinone (HEP). Such organic solvents may be employed in an amount of up from 0% to about 50% by weight based on the weight of the composition, preferably in an amount of about 5% to about 50% by weight and more preferably in an amount of from about 10% to about 50% by weight.

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**[0012]** The cleaning compositions of this invention also will preferably contain an oxidizing agent to provide further protection against metal, especially aluminum, corrosion. Any suitable oxidizing agent, including, but not limited to, hydrogen peroxide, persulfates, perphosphates, hyposulfites, hypochlorites and the like may



be employed in the cleaning compositions of this invention. The preferred oxidizing agent is hydrogen peroxide. The amount of oxidizing agent employed will generally be in an amount of from 0% up to about 5%, preferably from about 0.25% to about 5%, more preferably from about 0.5% to 3%, and most preferably from about 0.6%  
5 to about 1.5%, by weight of the composition.

**[0013]** 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  
10 improve the wetting of the surface to be cleaned and therefore improve the cleaning action of the composition. The surfactant may also be added to reduce aluminum corrosion rates if further aluminum corrosion inhibition is desired. Amphoteric surfactants useful in the compositions of the present invention include betaines and sulfobetaines such as alkyl betaines, amidoalkyl betaines, alkyl sulfobetaines and  
15 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 amphoteric; and mixtures thereof. Preferably, the  
20 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  
25 amphoteric. Non-ionic surfactants useful in the compositions of the present invention include acetylenic diols, ethoxylated acetylenic diols, fluorinated alkyl alkoxyates, fluorinated alkylesters, fluorinated polyoxyethylene alkanols, aliphatic acid esters of polyhydric alcohols, polyoxyethylene monoalkyl ethers, polyoxyethylene diols, siloxane type surfactants, and alkylene glycol monoalkyl  
30 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, dialkylmorpholinium salts, alkylbenzyltrimethylammonium salts, alkyltrimethylammonium salts, and alkylpyridinium salts. Preferably, the cationic surfactants are halogen-free surfactants. Example of especially suitable surfactants include, but are not limited to 3,5-dimethyl-1-hexyn-3-ol (Surfynol-61), ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol (Surfynol-465), polytetrafluoroethylene cetoxypolybetaine (Zonyl FSK), Zonyl FSH, Triton X-100, namely octylphenoxypolyethoxyethanol, and the like. The surfactant will generally be present in an amount of from 0 to about 5 wt%, preferably 0.001 to about 3 wt% based on the weight of the composition.

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**[0014]** The aqueous cleaning compositions of this invention can also optionally contain other components, including but not limited to, corrosion inhibitors and similar non-corrosive components employed in microelectronic cleaner compositions. The compounds may include catechol, resorcinol, gallic acid, propyl gallate, pyrogallol, hydroquinone, derivatives of benzotriazole, and polyfunctional carboxylic acids such as citric acid, tartaric acid, gluconic acid, saccharic acid, glyceric acid, oxalic acid, phthalic acid, maleic acid, mandelic acid, malonic acid, lactic acid, and salicylic acid.

25 **[0015]** Organic or inorganic chelating or metal complexing agents are not required, but offer substantial benefits, such as for example, improved product stability when incorporated into the aqueous cleaning compositions of this invention. Examples of suitable chelating or complexing agents include but are not limited to trans-1,2-cyclohexanediamine tetraacetic acid (CyDTA), ethylenediamine tetraacetic acid (EDTA), stannates, pyrophosphates, alkylidene-diphosphonic acid derivatives

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(e.g. ethane-1-hydroxy-1,1-diphosphonate), phosphonates containing ethylenediamine, diethylenetriamine or triethylenetetramine functional moieties [e.g. ethylenediamine tetra(methylene phosphonic acid) (EDTMP), diethylenetriamine penta(methylene phosphonic acid), triethylenetetramine hexa(methylene phosphonic acid)]. The chelating agent will be present in the composition in an amount of from 0 to about 5 wt%, preferably from about 0.1 to about 2 wt% based on the weight of the composition. Metal chelating or complexing agents of various phosphonates, such as ethylenediamine tetra(methylene phosphonic acid) (EDTMP) offer much improved stabilization of the cleaning compositions of the cleaning compositions of this invention when they are combined with oxidizing agents at acidic and alkaline conditions and thus are generally preferred.

**[0016]** In one preferred embodiment of the invention the cleaning composition comprises water and ammonium hypophosphite, especially 2 wt% ammonium hypophosphite in 98 wt% water. Another preferred cleaning composition of this invention comprises a composition of water, ammonium hypophosphite and hydrofluoric acid. A still further preferred embodiment of a cleaning composition of this invention comprises water, ammonium hypophosphite, hydrofluoric acid, glycerol and hydrogen peroxide. An additional preferred composition comprises hypophosphorous and/or phosphorous acid, ammonium hydroxide, and water.

**[0017]** The compositions on this invention, their use to clean microelectronic substrates and their non-metal corroding properties is illustrated by, but not limited to, the following examples.

25

**[0018] Example 1-5**

Ammonium hypophosphite, DI water and 50:1 HF were mixed to give a solution of 2 weight % ammonium hypophosphite, 98 weight % water and 100 ppm fluoride ion to provide a cleaning composition of this invention. The pH of the solution was 4.3. A given quantity of this solution was placed in a beaker and

30

brought to 45° C. Patterned silicon wafer samples having TiN/Al/TiN/PTEOS layers were placed in the heated solution for a prescribed time after which they were removed, rinsed in DI water and blown dry with nitrogen. A Scanning Electron Micrograph (SEM) was taken of the cleaned wafer samples and evaluated as to the degree of ash removal and aluminum metal corrosion. The results in Table 1 demonstrate the cleaning and relatively non-corrosive nature of the composition of this invention.

**Table 1**

Example No.	Immersion Time (min)	% Ash removed	Aluminum corrosion Å/min
1	1.0	100	1058
2	1.5	100	-
3	2.0	100	-
4	2.5	100	1084
5	3.0	100	1033

10

**[0019]****Examples 6-10**

The solution employed in Examples 1-5 was also employed in the following Examples 6-10. The wafer employed in Examples 6-10 were wafers of the type employed in Examples 1-5 with vias patterned through the PTEOS stopping on top of the underlying TiN layer. The cleaning solution was the same as that of Examples 1-5. The wafers were placed in the heated (45° C) solution for a prescribed time after which they were removed, rinsed in DI water and blown dry with nitrogen. A Scanning Electron Micrograph (SEM) was taken of the cleaned wafer samples and evaluated as to the degree of ash removal and aluminum metal corrosion. The results are reported in Table 2 showing the increasing aggressive nature of the compositions of this invention when employed for longer cleaning periods.

°



**Table 2**

Example No.	Immersion Time (min)	% Ash removed	% Aluminum corrosion
6	2.0	3	0
7	2.5	40	0
8	3.0	50	0
9	3.5	90	20
10	40	100	80

**[0020]****Examples 11-12**

5 Patterned wafers of the same type as employed in Example 1-5 were employed in Examples 11 and 12. The cleaning solution employed was that employed in Examples 1-5 but with the addition of glycerol thereto in an amount that the glycerol constituted approximately 10 weight % of the composition. The solution still had a pH of 4.3. The wafers were placed in the heated (45° C) solution for a

10 prescribed time after which they were removed, rinsed in DI water and blown dry with nitrogen. A Scanning Electron Micrograph (SEM) was taken of the cleaned wafer samples and evaluated as to the degree of ash removal and aluminum metal corrosion. The results are reported in Table 3 and show a further approximately 10% reduction in aluminum corrosion.

15

**Table 3**

Example No.	Immersion Time (min)	% Ash removed	Aluminum corrosion Å/min
11	2.5	100	952
12	3.0	100	903

**[0021]****Example 13-14**

Wafers with vias of the same type as employed in Example 6-10 were employed in Examples 13 and 14. The cleaning solution employed was that employed in Examples 11 and 12. The wafers were placed in the heated (45° C) solution for a prescribed time after which they were removed, rinsed in DI water and blown dry with nitrogen. A Scanning Electron Micrograph (SEM) was taken of the cleaned wafer samples and evaluated as to the degree of ash removal and aluminum metal corrosion. The results are reported in Table 4 and show a further significant reduction in aluminum corrosion even at the extended cleaning periods when the composition is a more aggressive cleaner, as had been indicated by the previous results in Table 2.

**Table 4**

Example No.	Immersion Time (min)	% Ash removed	% Aluminum corrosion
13	3.5	100	20
14	4.0	100	20

15

**[0022]****Examples 15-16**

In Example 15 the wafer employed was the same as the wafer described in Example 1-5 and in Example 16 the wafer with vias employed was the same as the wafer described in Example 6-10. The cleaning composition employed was that of the type described in the previous Examples but with the addition of hydrogen peroxide. The cleaning solution comprised 1.8 weight % ammonium hypophosphite, 88.4 weight % water, 8.8 weight % glycerol, 0.6 weight % hydrogen peroxide and slightly less than 100 ppm fluoride ion and had a pH of 4.3. The wafers were placed in the heated (45° C) solution for a prescribed time after which they were removed, rinsed in DI water and blown dry with nitrogen. A Scanning Electron Micrograph (SEM) was taken of the cleaned wafer samples and evaluated as to the degree of

20  
25

ash removal and aluminum metal corrosion. The results are reported in Table 5 and show a further significant reduction in aluminum corrosion for both types of wafers

**Table 5**

Example No.	Immersion Time (min)	% Ash removed	Aluminum corrosion Å/min	% Aluminum corrosion
15	1.5	100	840	-
16	3.0	100	-	0

5

**[0023]**

**Example 17**

A composition of this invention was prepared having the following composition: 100 g DI water, 25.0g 1.0% hydrofluoric acid, 4.27g 24.96 %  
 10 tetramethylammonium hydroxide solution in water, 20.0g glycerol, 2.0g sodium hypophosphite monohydrate (from Alfa Aesar) and 0.08 weight 5 Triton X-100 surfactant. The composition had a pH of approximately 6.0 at room temperature. A wafer sample having PTEOS/TiN/Al-0.5%Cu layers with via patterned through the PTEOS stopping on top of the underlying TiN layer was plasma ashed to remove  
 15 bulk photoresist after the via etching. The wafer was treated for 20 minutes at 25° C in the cleaning solution. SEM cross-sectional inspection of 0.18 micron wide vias with a 5:1 aspect (height:width) ratio showed the vias were completely clean and contained no residue.

20 **[0024]**

**Example 18**

A cleaning composition of this invention was prepared having the following composition: 100.00g DI water, 25.54g 1% hydrofluoric acid solution in water, 5.96g  
 25 25.08% tetramethylammonium hydroxide solution in water, 60.00g glycerol, and 2.00g ammonium hypophosphite (97% from Fluka). The composition had a pH of 8.36 at 25° C. Patterned metal-line wafer samples with 1 micron wide features with



TiN/Al-0.5%Cu/TiN/Ti/sog layers were plasma ashed to remove bulk photoresist after metal etching. The wafer was treated in the cleaning composition for 2 minutes at 30° C. SEM inspection showed 99.5% residue removal with no observable metal corrosion.

5

**[0025]****Examples 19-21**

Cleaning compositions of this invention were prepared by mixing ammonium hypophosphite and DI water to provide a solution comprising just ammonium hypophosphite and water. Patterned silicon wafer samples having  
 10 TiN/Al/TiN/PTEOS layers were placed in the heated solutions of the cleaning composition for 15 minutes after which they were removed, rinsed in DI water and blown dry with nitrogen. The cleaned wafers were then evaluated for ash residue removal (0= no removal to 10+ 100% removal) and aluminum corrosion (0=no corrosion to 10=severe corrosion). The percent ammonium hypophosphite, the pH  
 15 of the solutions, the temperature of the heated solution in which the wafer were placed and the aluminum corrosion and ash removal results are set forth in Table 6.

**Table 6**

Example No.	% Ammonium hypophosphite	pH	Temp ° C	Aluminum corrosion	Ash residue removal
19	1.6	3	45	0	10
20	3.2	3	25	1	10
21	2.4	4	35	0	10

20

**[0026]****Examples 22-27**

Cleaning compositions of this invention were prepared by mixing hypophosphorous and phosphorous acid, ammonium hydroxide, and DI water. Patterned silicon wafer samples having TiN/Al/TiN/PTEOS layers were placed in  
 25 solutions of the cleaning composition heated to 45° C for 15 minutes after which

they were removed, rinsed in DI water and blown dry with nitrogen. The cleaned wafers were then evaluated for ash residue removal (0= no removal to 10= 100% removal) and aluminum corrosion (0=no corrosion to 10=severe corrosion). The percent of each phosphite, the pH of the solutions, and the aluminum corrosion and  
 5 ash removal results are shown in Table 7.

**Table 7**

Example No.	% hypophosphite	% phosphite	% NH <sub>4</sub> OH	pH	Aluminum corrosion	Ash residue removal
22	15	1	0.3	4.50	1	10
23	15	2	0.6	4.49	2	10
24	15	6	2.3	4.47	2	10
25	30	1	0.2	4.75	0	9
26	30	2	0.6	4.54	1	10
27	30	6	2.5	4.48	2	10

10 **[0027]**

**Examples 28-34**

Cleaning compositions of this invention were prepared by mixing only phosphorous acid, ammonium hydroxide, and DI water. Patterned silicon wafer samples having TiN/Al/TiN/PTEOS layers were placed in solutions of the cleaning composition heated to 45° C for 15 minutes after which they were removed, rinsed in  
 15 DI water and blown dry with nitrogen. The cleaned wafers were then evaluated for ash residue removal (0= no removal to 10= 100% removal) and aluminum corrosion (0=no corrosion to 10=severe corrosion). The percent phosphorous acid, the pH of the solutions, and the aluminum corrosion and ash removal results are shown in Table 8.

20

**Table 8**

Example No.	% phosphorous acid	% NH <sub>4</sub> OH	PH	Aluminum corrosion	Ash residue removal
28	1	0.1	1.3	6	10
29	1	0.5	5.6	0	10
30	2	0.4	3.4	4	10
31	2	0.9	4.5	1	10
32	2	1.4	6.0	0	10
33	6	2.7	3.4	6	10
34	6	4.3	6.0	2	10

**[0028]****Examples 35-40**

5           Cleaning compositions of this invention were prepared by mixing phosphorous acid (final concentration 2%), DI water, and select strong bases to achieve approximately pH=4.5. These bases were: tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrapropylammonium hydroxide (TPAH), tetrabutylammonium hydroxide (TBAH), cetyltrimethylammonium hydroxide (CTMAH), and tetraethanolammonium hydroxide (TEtOHAAH). Patterned silicon wafer samples having TiN/Al/TiN/PTEOS layers were placed in solutions of the cleaning composition heated to 45° C for 15 minutes after which they were removed, rinsed in DI water and blown dry with nitrogen. The cleaned wafers were then evaluated for ash residue removal (0= no removal to 10= 100% removal) and

10 aluminum corrosion (0=no corrosion to 10=severe corrosion). The above abbreviation for the base, the pH of the solutions, and the aluminum corrosion and ash removal results are shown in Table 9.



**Table 9**

Example No.	Strong Base	PH	Aluminum corrosion	Ash residue removal
35	TMAH	4.5	0	10
36	TEAH	4.5	1	10
37	TPAH	4.5	0	9
38	TBAH	4.6	0	8
39	CTMAH	4.5	0	8
40	TEtOHAH	5.0	0	7

**[0029]****Examples 41-44**

Cleaning compositions of this invention were prepared by mixing phosphorous acid, ammonium hydroxide, with and without catechol, and DI water. Patterned silicon wafer samples having TiN/Al/TiN/PTEOS layers were placed in solutions of the cleaning composition heated to 35° C for 10 minutes after which they were removed, rinsed in DI water and blown dry with nitrogen. The cleaned wafers were then evaluated for ash residue removal (0= no removal to 10= 100% removal) and aluminum corrosion (0=no corrosion to 10= severe corrosion). The percent phosphorous acid, ammonium hydroxide, and catechol, the pH of the solutions, and the aluminum corrosion and ash removal results are shown in Table 9 showing the additional beneficial results obtained by the use of a corrosion inhibiting compound, such as catechol, in the compositions of this invention.

**Table 10**

Example No.	% phosphite	% NH <sub>4</sub> OH	% catechol	pH	Aluminum corrosion	Ash residue removal
41	2.5	0.7	0	3.2	1	10
42	2.5	0.7	3	3.2	0	10
43	2.5	0.3	0	2.2	3	10
44	2.5	0.3	3	2.1	1	10

**[0030]** 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,  
5 modification and variations that fall with the spirit and scope of the appended claims.

We claim:

1. An aqueous composition for cleaning microelectronic substrates comprising the following components:
  - 5 (a) water,
  - (b) at least one of ammonium and quaternary ammonium ions, and
  - (c) at least one of hypophosphite ( $\text{H}_2\text{PO}_2^-$ ) and phosphite ( $\text{HPO}_3^{2-}$ ) ions.
- 10 2. An aqueous composition according to claim 1 comprising water and at least one of ammonium hypophosphite and ammonium phosphite.
3. An aqueous composition of claim 1 additionally comprising fluoride ions.
- 15 4. An aqueous composition according to claim 2 additionally comprising fluoride ions.
5. An aqueous composition according to claim 2 additionally comprising hydrogen fluoride.
- 20 6. An aqueous composition according to claim 1 additionally comprising at least one further component selected from the group consisting of an organic solvent and an oxidizing agent.
- 25 7. An aqueous composition according to claim 3 additionally comprising at least one further component selected from the group consisting of an organic solvent and an oxidizing agent.
- 30 8. An aqueous composition according to claim 5 additionally comprising at least one further component selected from the group consisting of an organic solvent and an oxidizing agent



9. An aqueous composition according to claim 8 wherein the organic solvent is selected from the group consisting of glycerol, 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, 1-ethyl-2-pyrrolidinone, 1-propyl-2-pyrrolidinone, 1-hydroxyethyl-2-pyrrolidinone, a dialkyl sulfone, dimethyl sulfoxide, a tetrahydrothiophene-1,1-dioxide, dimethylacetamide and dimethylformamide and the oxidizing agent is selected from the group consisting of hydrogen peroxide, persulfates, perphosphates, hyposulfites, hypochlorites.
10. An aqueous composition according to claim 9 wherein the composition comprises both an organic solvent and an oxidizing agent.
11. An aqueous composition according to claim 10 wherein the organic solvent is glycerol and the oxidizing agent is hydrogen peroxide.
12. An aqueous composition according to claim 8 wherein the organic solvent comprises glycerol.
13. An aqueous composition according to claim 8 wherein the oxidizing agent comprises hydrogen peroxide.
14. An aqueous composition according to claim 1 additionally comprising at least one further component selected from the group consisting of surfactants and corrosion inhibitors.
15. An aqueous composition according to claim 14 wherein the corrosion inhibitor comprises catechol.
16. An aqueous composition according to claim 3 additionally comprising at least one further component selected from the group consisting of surfactants and

corrosion inhibitors.

- 5 17. An aqueous composition according to claim 11 additionally comprising at least one further component selected from the group consisting of surfactants, corrosion inhibitors and metal complexing agents.
- 10 18. An aqueous composition according to claim 2 comprising from about 1.8 to about 6.0 wt% ammonium hypophosphite, ammonium phosphite, or a combination of both, and about 89 to about 98 wt% water based on the weight of the composition.
19. An aqueous composition according to claim 18 additionally comprising about 100 ppm fluoride ions.
- 15 20. An aqueous composition according to claim 19 additionally comprising glycerol.
21. An aqueous composition according to claim 20 additionally comprising hydrogen peroxide.
- 20 22. An aqueous composition according to claim 21 wherein the glycerol is present in the composition in an amount of about 10 wt% of the composition and the hydrogen peroxide is present in the composition in an amount of about 0.6 wt% of the composition.
- 25 23. An aqueous composition according to claim 1 wherein the composition comprises hypophosphorus and phosphorous acid and ammonium hydroxide.
- 30 24. An aqueous composition according to claim 1 comprising phosphorous acid and ammonium hydroxide.

25. An aqueous composition according to claim 24 additionally comprising at least one further component selected from the group consisting of surfactants and corrosion inhibitors.
- 5 26. An aqueous composition according to claim 25 wherein the corrosion inhibitor comprises catechol.
- 10 27. An aqueous composition according to claim 1 wherein the composition comprises quaternary ammonium ions.
28. An aqueous composition according to claim 27 wherein the composition comprises tetraalkylammonium ions.
- 15 29. An aqueous composition according to claim 1 comprising phosphorous acid and a compound selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, tetrabutylammonium hydroxide, cetyltrimethylammonium hydroxide, and tetraethanolammonium hydroxide.
- 20 30. A process for cleaning a microelectronic substrate without producing any substantial metal corrosion, the substrate containing photoresist polymeric material and/or residues and a metal, the process comprising contacting the substrate with a cleaning composition for a time sufficient to clean the
- 25 substrate, wherein the cleaning composition comprises:
- (a) water,
  - (b) at least one of ammonium and quaternary ammonium ions, and
  - (c) at least one of hypophosphite ( $\text{H}_2\text{PO}_2^-$ ) and/or phosphite ( $\text{HPO}_3^{2-}$ ) ions.
- 30 31. A method according to claim 30 wherein the cleaning composition comprises

water and at least one of ammonium hypophosphite and ammonium phosphite.

- 5 32. A method according to claim 30 wherein the cleaning composition additionally comprises fluoride ions.
33. A method according to claim 31 wherein the cleaning composition additionally comprises fluoride ions.
- 10 34. A method according to claim 31 wherein the cleaning composition additionally comprises hydrogen fluoride.
- 15 35. A method according to claim 30 wherein the cleaning composition additionally comprises at least one further component selected from the group consisting of an organic solvent and an oxidizing agent.
- 20 36. A method according to claim 32 wherein the cleaning composition additionally comprises at least one further component selected from the group consisting of an organic solvent and an oxidizing agent.
37. A method according to 34 wherein the cleaning composition additionally comprises at least one further component selected from the group consisting of an organic solvent and an oxidizing agent
- 25 38. A method according to claim 37 wherein the organic solvent is selected from the group consisting of glycerol, 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, 1-ethyl-2-pyrrolidinone, 1-propyl-2-pyrrolidinone, 1-hydroxyethyl-2-pyrrolidinone, a dialkyl sulfone, dimethyl sulfoxide, a tetrahydrothiophene-1,1-dioxide, dimethylacetamide and dimethylformamide and the oxidizing agent is
- 30 selected from the group consisting of hydrogen peroxide, persulfates,



perphosphates, hyposulfites, hypochlorites.

39. A method according to claim 38 wherein the composition comprises both an organic solvent and an oxidizing agent.
- 5 40. A method according to claim 39 wherein the organic solvent is glycerol and the oxidizing agent is hydrogen peroxide.
- 10 41. A method according to claim 37 wherein the organic solvent comprises glycerol.
42. A method according to claim 37 wherein the oxidizing agent comprises hydrogen peroxide.
- 15 43. A method according to claim 30 wherein the cleaning composition additionally comprises at least one further component selected from the group consisting of surfactants and corrosion inhibitors.
- 20 44. A method according to claim 43 wherein the corrosion inhibitor comprises catechol.
45. A method according to claim 32 wherein the cleaning composition additionally comprises at least one further component selected from the group consisting of surfactants and corrosion inhibitors.
- 25 46. A method according to 40 wherein the cleaning composition additionally comprises at least one further component selected from the group consisting of surfactants, corrosion inhibitors and metal complexing agents.
- 30 47. A method according to claim 31 wherein the cleaning composition comprises

about 1.8 to about 6 wt% ammonium hypophosphite, ammonium phosphite or a combination of both, and about 89 to about 98 wt% water based on the weight of the composition.

5 48. A method according to claim 47 wherein the cleaning composition additionally comprises about 100 ppm fluoride ions.

49. A method according to claim 48 wherein the cleaning composition additionally comprises glycerol.

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50. A method according to claim 49 wherein the cleaning composition additionally comprises hydrogen peroxide.

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51. A method according to claim 50 wherein the glycerol is present in the composition in an amount of about 10 wt% of the composition and the hydrogen peroxide is present in the composition in an amount of about 0.6 wt% of the composition.

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52. A method according to according to claim 30 wherein the composition comprises hypophosphorus and phosphorous acid and ammonium hydroxide.

53. A method according to according to claim 30 comprising phosphorous acid and ammonium hydroxide.

25

54. A method according to claim 53 additionally comprising at least one further component selected from the group consisting of surfactants and corrosion inhibitors.

30

55. A method according to claim 54 wherein the corrosion inhibitor comprises catechol.

56. A method according to according to claim 30 wherein the composition comprises quaternary ammonium ions.
- 5 57. A method according to claim 56 wherein the composition comprises tetraalkylammonium ions.
58. A method according to claim 57 comprising phosphorous acid and a compound selected from the group consisting of tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, 10 tetrabutylammonium hydroxide, cetyltrimethylammonium hydroxide, and tetraethanolammonium hydroxide.