

**ACIDIC SEMI-AQUEOUS FLUORIDE ACTIVATED ANTI-REFLECTIVE COATING
CLEANERS WITH SUPERIOR SUBSTRATE COMPATIBILITIES AND
EXCEPTIONAL BATH STABILITY**

FIELD OF THE INVENTION

This invention relates to a microelectronic cleaning composition and to the use of such a cleaning composition in a method of cleaning microelectronic devices, particularly for Anti-reflective coating (ARC) removal and residual cleaning compositions with greater substrate and metallization compatibilities.

BACKGROUND

The recent advances in production of micro- and nano-electronic devices has resulted in the need for new stripping and cleaning compositions with both front end of the line (FEOL) and back end of the line (BEOL) stripping or cleaning capabilities. The cleaning compositions typically employed heretofore have been found to be unsuitable for new materials employed in production of microelectronic or nanoelectronic platforms. The previously employed stripping or cleaning compositions are either too aggressive and/or are not selective enough. Among the newly utilized materials employed to produce these newer microelectronic or nanoelectronic devices are materials such as low- k (<3) and high- k (>20) and porous dielectrics, copper metallizations, fluoropolymer antireflective coatings (ARCs), special hard masks such as those composed of Ti and TiN, strained wafers of Si/Ge or Ge, and metal capping layers such as those of CoWP and CoWB. These new materials present new and difficult challenges to the device manufacturer.

For example, cleaning of Cu/low- k structures not only requires good cleaning capabilities, but also requires solutions with exceptional substrate compatibilities. Many process technologies that have been developed for the traditional or common semiconductor devices containing Al/SiO₂ or Al (Cu)/SiO₂ structures cannot be applied to Cu/low- k and high- k structures. Vice versa, many Cu/low- k strippers are not suitable for Al metallizations, unless significant adjustments are made.

The manufacturing processes of Cu/low- k and/or high- k structures frequently generate unusually hardened photoresist layers, tough plasma etching and/or ashing residues. Even highly aggressive reagents, such as HF acid, hydroxylamine and strong alkaline solutions, often fail to provide suitable cleaning along with acceptable substrate compatibility.

Aqueous fluorides or HF based solutions have been used extensively as traditional FEOL and BEOL etchants and cleaning agents. Frequently, these types of cleaners are developed as oxide etcher or ash residue removers. For example, diluted HF (dHF) solutions and buffered oxide etch (BOE, consists of HF/NH₄F/H₂O) are effective oxide (silicon oxide) remover and limited residue cleaners, but generally non-effective in stripping photoresist.

A number of organic solvent-based or semi-aqueous solutions containing fluorides or HF have also been used in many BEOL applications. However, most of these products are still weak in multi-purpose applications such as removing plasma hardened photoresist and ARCs. They are also sometimes too aggressive, non-selective enough, or cannot meet new, highly demanding substrate compatibilities and selectivity requirements for advanced FEOL and BEOL applications with new challenging types of materials such as low- κ and high- κ and porous dielectrics, copper metallizations, fluoropolymer antireflective coatings (ARCs), special hard metal gates such as those of Ti and TiN, strained wafers of Si/Ge or Ge, and metal capping layers such as those of CoWP and CoWB. Thus, new and improved stripping or cleaning compositions are needed for multi-purpose applications in connection with these new material being employed on newer microelectronic and nanoelectronic devices.

In order to create ever-smaller microprocessors, memory cells and other semiconductor devices, one of the key strategies is to fabricate Multigate transistors. In addition to the conventional planar, multiple gate transistors, nonplanar double gate (e.g., FinFET), or tri-gate have been developed. Frequently, high- κ materials and metal gates are also used in such advanced technologies (such as 14 nm nodes). The list of materials/substrates is extensive: Al, Cu, W, Ti, TiN, TaN, Nb, RuO₂, Mo, LaO_x, AlO_x, HfSiON, COSi₂, Wsi₂, SiN, SiON, TEOS, ploySi, SiGe, Ge, and their combined alloys and/or adducts. The thickness control of various, frequently ultra-thin Metal Gate (MG), Work Function Metal (WF), and High κ (HK) are critical. There are big challenges involved with introducing cleaning chemistries with enabling (high clean capability for various PR and residues) and wide, very high compatibility for ultra-thin films (e.g., 10 angstrom WF films). For example, etch rates as low as 1 angstrom of TiN can sometimes be too high to be usable. Current or traditional wet clean chemistries can no longer meet these kinds of compatibility demands. There is a need for new enabling clean chemistries with superior substrate compatibilities which can selectively clean photoresist, antireflective coatings (ARC), residual WF metals, and various plasma etch or ash residues.

Fluoride activated (based) cleaning chemistries generally work much more effectively at acidic pH conditions. However, acidic fluoride chemistries, especially HF-containing cleaners, suffer great limitations of metallization and being incompatible with a number of substrates. For example, etch rate of 200:1 DHF at 25°C: Al, >550 /min, TEOS, >30 /min; 200:1 DHF at 35 °C, Al, >2,000 /min, TEOS, >140 /min. Even the highly diluted 600:1 DHF at 35 °C: Al, >750 /min. Other fluoride based cleaners containing fluoride salts are also severely limited with cleaning capabilities or substrate compatibilities: at neutral or basic pH, clean capabilities are generally quite weak and limited to only selected types of residues which can be cleaned; at acidic pH, ammonium fluoride containing cleaners frequently have poor copper compatibilities; alkylammonium fluoride containing cleaners generally have poor aluminum compatibilities. In addition, most fluoride based cleaners show poor compatibilities with a variety of important microelectronic materials, such as TEOS, SiN and low-k.

Anti-reflective coating (ARC) materials have been increasingly used in fabrication of advanced microelectronic devices. One popular ARC is Silicon-containing Bottom Anti-Reflective Coating (SiBARC). However, ARC removers which are based on fluoride activated chemistries frequently suffer serious selectivity issues between providing efficient SiBARC removal and limiting etching damages to important metallizations (e.g. Al, Cu, W, Ti, TiN, TaN) and substrates (e.g. TEOS, SiN, high-k, low-k). Few acidic fluoride clean chemistries have shown improvements by providing better compatibilities. None of them, however, could demonstrate the compatibilities at the levels which meet highly demanding requirements at advanced technology nodes in semiconductor such as 16nm or lower. In special, but critical applications, optimization of Al₂O₃ thickness without damaging Al metallization provides obvious and critical performance. Furthermore, special cleaning needs such as selective removal of “Al oxide like”, “Ti oxide like” residues or etched/ashed antireflective coatings with very stringent compatibilities pose great technology challenges. None of known chemistries has met all of these challenges/needs at the same time.

Diluted hydrofluoric acid (DHF) is a unique and effective cleaner in wide microelectronic applications. However, advanced FEOL and BEOL clean demands much diversified substrate and metallization compatibilities than DHF. In addition, other capabilities such as PR (photoresist) stripping are also highly beneficial. Thus, a new cleaning chemistry is needed.

Although fluoride-based cleaners have been largely utilized in the past for various cleaning needs, the use of new materials, alloys and composites, with different sensitivities, have

precluded their use in many new applications. Fluoride containing formulations, for example, are well known to etch silicon oxide at acidic pH and commonly used as silicon oxide etchant. Well known examples are HF- based silicon oxide etchants, such as Buffered Oxide Etchant (BOE), which comprise aqueous solutions of HF and NH_4F at various ratios. Their selectivity of ARC or SiBARC removal vs. TEOS is generally very poor, however. Many previous disclosures use weakly acidic pH ($\text{pH} > 6$), neutral or preferably alkaline pH conditions to suppress these compatibility problems. However, the ARC/SiBARC removal capability and cleaning capabilities are greatly decreased at these pH conditions. One example is US Patent 7,399,365 B2. It teaches to use preferred pH ranges of 6.5 to 8.

The art includes attempts to remedy this problem, including providing a fluoride source as an activating species without differentiation. U.S. Patent No. 6,777,380, for example includes a cleaner with fluoride sources of hydrofluoric acid, ammonium fluoride, tetramethylammonium fluoride, ammonium bifluoride, and others. These examples however, do not provide the wide compatibilities necessary for current applications, or the selectivity enhancing also necessary.

There is a need, therefore, for acidic ARC removers/cleaners with preferred pH ranges of 5 or less, thus delivering high clean capability of ARC/SiBARC etch. There is a further need for cleaning compositions capable of achieving wide compatibility and high selectivity vs. many important metallization and substrates, including high compatibilities/low etch rates for Al, Cu, W, Ti, TiN, TaN, TEOS.

SUMMARY

Provided therefore herein is a novel acidic fluoride activated cleaning chemistry with highly effective ARC removal, clean capabilities, and superior compatibilities to wide varieties of materials. This invention describes compositions which provide ARC removal, PR stripping, etch/ash residues clean and CMP residue removal in FEOL, BEOL and FPD applications, while providing excellent substrate compatibility, pH stability, bath stability and free from undesirable surface modifications.

Provided herein is a cleaning composition for micro-electronics applications. The cleaning composition includes from about 0.05% to about 5.0 % by weight of a bifluoride compound, from about 0.01% to about 5% by weight of a pH-stabilizing compatibility enhancer, from about 5% to about 90% by weight of an organic solvent, and from about 5% to about 90% water.

In another embodiment, the cleaning composition includes from about 0.05% to about 1.0 % by weight of a bifluoride compound, from about 0.05% to about 3% by weight of a pH-stabilizing compatibility enhancer, from about 10% to about 70% by weight of an organic solvent, and from about 10% to about 50% water.

In another embodiment, the cleaning composition includes from about 0.1% to about 0.5 % by weight of a bifluoride compound, from about 0.1% to about 1.0% by weight of a pH-stabilizing compatibility enhancer, from about 20% to about 60% by weight of an organic solvent, and from about 20% to about 40% water.

In another embodiment, the cleaning composition has a pH of less than or equal to 5.5. In an embodiment, the cleaning composition has a pH of less than or equal to 5.0, and in another embodiment, the composition has a pH of less than or equal to 4.5.

In another embodiment, the cleaning composition further includes a co-solvent selected from alcohols, alcohol-ethers, and ethers. In an embodiment, the bifluoride compound may be selected from the group of ammonium bifluoride, alkylammonium bifluoride, potassium bifluoride, and alkali metal bifluorides. In an embodiment, the bifluoride compound is selected from any number of commercially available bifluoride compounds known in the art.

In an embodiment, the pH-stabilizing compatibility enhancer is a polyprotic acid, or salt thereof. In an embodiment, the pH-stabilizing compatibility enhancer is selected from the group of citric acid, ammonium citrate monobasic, ammonium citrate dibasic, ammonium citrate tribasic, phosphoric acid, ammonium phosphate monobasic, ammonium phosphate dibasic, ammonium phosphate tribasic, ascorbic acid, ammonium ascorbate monobasic, ammonium ascorbate dibasic, and mixtures thereof.

In an embodiment, the organic solvent of the cleaning composition is a sulfide or an amide. In another embodiment, the organic solvent is selected from dimethyl sulfoxide, N-methyl pyrrolidone (NMP), N-ethyl pyrrolidone (NEP), N-(2-hydroxyethyl)-2-pyrrolidone (HEP), dimethyl 2-piperidone (DMPD), dimethyl acetamide, formamide, and mixtures thereof.

In another embodiment, the cleaning composition of the present invention further includes at least another fluoride source. In an embodiment, the at least another fluoride source is a fluoride salt. In yet another embodiment, the cleaning composition further includes a corrosion control agent. In an embodiment, the corrosion control agent is selected from the group of commercially available control agents known in the art. In another embodiment, the

cleaning composition further includes a surfactant. The surfactant may be selected from the group of commercially available surfactants known in the art.

In another embodiment, the present invention includes a method of cleaning a micro-electronic material, the method including contacting the micro-electronic material with a cleaning composition comprising: about 0.05% to about 5.0 % by weight of a bifluoride compound, about 0.01% to about 5% by weight of a pH-stabilizing compatibility enhancer, about 5% to about 90% by weight of an organic solvent, and about 5% to about 90% water.

For a better understanding of the present invention, together with other and further objects and advantages, reference is made to the following detailed description, taken in conjunction with the accompanying examples, and the scope of the invention will be pointed out in the appended claims. The following detailed description is not intended to restrict the scope of the invention by the advantages set forth above.

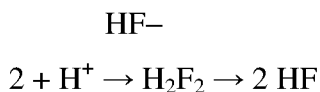
DETAILED DESCRIPTION

This invention solves the difficult challenges of using acidic fluoride based chemistries as anti-reflective coating (ARC) removers, offering broad, superior metallization and substrate compatibilities at the same time. It may also be considered as a Superior diluted hydrofluoric acid (DHF) replacement. It can provide critical cleans for many other advanced front end of the line (FEOL) and back end of line (BEOL) applications. Furthermore, this invention provides enabling wet clean solutions for the highly demanding wide and tight compatibility requirements for High k/Multigate and High k/Metal Gate device fabrications of sub-28nm technologies. Current clean technologies rarely show such tight control or compatibilities (low etch rates) for a wide and long list of metallization and substrate materials. For special applications, the present invention delivers unique one-step optimization of critical aluminum oxide thickness for performance enhancement.

Acidic semi-aqueous compositions comprising at least of (A) bifluoride compounds (HF_2^-) as the primary fluoride-activating agents, (B) "pH-stabilizing, compatibility enhancer" with multiple pKa values, (C) "metal compatibility enhancing" organic solvents, and (D) water. The pH (10% diluted aqueous) should be equal or less than 5.5, more preferably equal or less than 5.0, most preferably equal or less than 4.5. Optional components include other fluoride salts, amines, corrosion control agents and corrosion inhibiting co-solvents. The pH-stabilizing compatibility enhancer can be selected from citric acids, phosphoric acids, citrates and

phosphates. The organic solvents are selected from sulfides, amides, alcohols and ethers. The compositions have the capability to remove hardened silicon containing ARC materials, have wide compatibilities which include Al, Cu, W, TiN, SiN, TaN and others. Preferably, they also show acceptable compatibilities with TEOS, low-k and high-k materials in selected applications.

As used herein, a “bifluoride compound,” or “bifluoride” refers to a compound with two Fluorine atoms. In some embodiments, the bifluoride compound further includes a hydrogen atom, and exists in a salt form. Bifluorides are also known as difluorohydrogenides, and difluorohydrogenates, or hydrogen(difluoride). They may also be represented as an inorganic anion with the chemical formula HF_2^- . In some instances, the fluorohydrogenate group ($-\text{HF}^-$) in anions such as bifluoride can assimilate a proton by recombination:



Because of this capture of a proton (H^+), bifluoride has basic character. Its conjugate acid is the reactive intermediate, μ -fluoro-fluorodihydrogen (H_2F_2), which subsequently dissociates to become hydrogen fluoride. In solution, most bifluoride ions are dissociated.

Because bifluorides may be basic, the compositions of the present invention use pH-compatibility enhancers to try to maintain an acidic nature to the composition. As used herein, the term, “pH-stabilizing compatibility enhancer” refers to any compound which can adjust the pH of the solution to operable levels, most notably to a pH of equal to or less than 5.5.

As used herein, “organic solvent” refers to a substance that is capable of dissolving or dispersing one or more other substances which are non-metallic in nature. Used typically in liquid form, organic solvents are typically hydrocarbons or related substances. Organic solvents usually have a low boiling point and evaporate easily or can be removed by distillation, thereby leaving the dissolved substance behind. Solvents should therefore not react chemically with the dissolved compounds, they should be inert. 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.

These compositions use bifluorides in a preferred format, metallization and dielectrics compatibility enhancing matrices. They deliver unusual ARC removal capability with exceptional selectivity and compatibility. They can also be used for cleaning advanced FEOL and BEOL microelectronic and nanoelectronic structures, including sensitive Al, Cu, high k and low- κ , porous low- κ substrates. They are capable of removing anti-reflective coating (ARC), stripping photoresists and removing etch/ash residues.

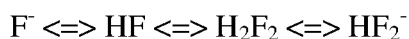
The aforementioned chemical compositions can be formulated as highly non-aqueous to semi-aqueous solutions or slurries. They can be used in removing implanted polymers, stripping ARC and photoresists, cleaning residues from plasma process generated organic, organometallic and inorganic compounds, cleaning residues from planarization process, such as chemical mechanical polishing, and using as additives in planarization slurry/liquids.

Many fluoride based cleaners have been developed and served for various cleaning needs for past and current technologies. However, in new microelectronic applications, frequently old and new materials, alloys and composites, are now used in the same device designs and manufacturing. Thus, the cleaning solutions are required to be highly compatible with many substrates. For example, a cleaner may need to be compatible with Al, Cu, W, TiN, SiN, TaN, and TEOS all at the same time. The allowable loss may be limited to 10 Å or less during the processes. For certain front end of the line (FEOL) applications, some allowable material loss may be 1-2 Å or less. Thus, previously developed chemistries which may have been considered to be “compatible” and acceptable for old technology requirements, are no longer acceptable for future technology requirements. Their uses may lead to serious reliability problems or detrimental performance issues. The invention described herein solves all the aforementioned challenges with novel, innovative designs and chemistries.

As previously stated, fluoride based chemistries at neutral or alkaline pHs are generally weak in clean capabilities. At acidic pH, the present invention provides for the use of bifluorides as the primary fluoride species, which is contrary to the state of the art regarding most fluoride-based cleaners.

By using bifluorides, the present invention provides superiority over all the other fluorides, which are difficult to develop or formulate. The bifluoride compositions of the present invention provide broad compatibility with wide metallization materials and substrates. HF based cleaners are generally not Al compatible. Ammonium fluoride based cleaners have high Cu etch rates. Alkylammonium fluoride based cleaners cause severe Al corrosion issues.

With removing or adding protons, bifluoride based chemistries can be adjusted to give optimum HF concentrations in specially designed solvent matrices through the following proposed equilibrium:



In the present compositions, bifluoride is used as the primary fluoride species. In an embodiment, bifluoride is the only fluoride species in the composition. Many other patents just broadly include and can use any HF or fluoride species as the primary species. This practice frequently results in serious compatibility problems. Thus, these patents do not offer us any valuable teachings. Our invention specify that the pH (10% diluted aqueous) should be equal or less than 5.5, more preferably equal or less than 5.0, most preferably equal or less than 4.5. Our invention may also contain other fluoride species (e.g. fluoride salts or HF), but must be used as one of the minor, co-additives.

Additionally the compositions of the present invention include the use of pH-Stabilizing Compatibility and Selectivity Enhancer with Multiple pKa values. We have found and established surprising effects of selected compounds with multiple pKa values in providing unexpected compatibility enhancements of a number of important substrates, such as SiN, Al. In comparative examples, compositions without these unique enhancers are unable to meet stringent compatibility requirements; hence their uses may lead to serious or detrimental performance issues. The pH stability of many fluoride-based cleaners (e.g. NH₄F- based) known to have poor pH stabilities. The uses of our unique enhancers help to give excellent pH stability and extended bath life.

Buffer capability over wide pH ranges. Our inventions have improved buffering capabilities to minimize the effects of acids or bases which are encountered/added to the cleaners. Our invention describes selections of specific compounds must have multiple pKa values. They include polyprotic acids and their salts, such as citric acid, ammonium citrate monobasic, ammonium citrate dibasic, ammonium citrate tribasic, phosphoric acid, ammonium

phosphate monobasic, ammonium phosphate dibasic, ammonium phosphate tribasic, ascorbic acid, ammonium ascorbate monobasic, ammonium ascorbate dibasic.

An acid dissociation constant, K_a , (also known as acidity constant, or acid-ionization constant) is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for a chemical reaction known as dissociation in the context of acid-base reactions. The larger the K_a value, the more dissociation of the molecules in solution, and thus the stronger the acid. The equilibrium of acid dissociation can be written symbolically as:



where HA is a generic acid that dissociates by splitting into A^- , known as the conjugate base of the acid, and the proton, H^+ , which, in the case of aqueous solutions, exists as the hydronium ion, e.g., a solvated proton.

The dissociation constant is usually written as a quotient of the equilibrium concentrations (in mol/L), denoted by [HA], $[A^-]$ and $[H^+]$:

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

Due to the many orders of magnitude spanned by K_a values, a logarithmic measure of the acid dissociation constant is more commonly used in practice. The logarithmic constant, pK_a , which is equal to $-\log_{10} K_a$, is sometimes also referred to as an acid dissociation constant:

$$pK_a = -\log_{10} K_a$$

The larger the value of pK_a , the smaller the extent of dissociation at any given pH, i.e., the weaker the acid. A weak acid, for example, has a pK_a value in the approximate range -2 to 12 in water. Acids with a pK_a value of less than about -2 are said to be strong acids. A strong acid is almost completely dissociated in aqueous solution, to the extent that the concentration of the undissociated acid becomes undetectable. pK_a values for strong acids can, however, be estimated by theoretical means or by extrapolating from measurements in non-aqueous solvents in which the dissociation constant is smaller, such as acetonitrile and dimethylsulfoxide.

In order to meet the broad and stringent metallization and substrate compatibility requirements, only the selected organic solvent matrices can be used. Surprisingly dramatic solvent effects have been discovered. In a preferred embodiment, the “Metal Compatibility Enhancing” Organic Solvents include sulfides and amides, which are present as the primary

solvents. They also provide higher PR stripping capabilities. Additionally, alcohols, alcohol-ethers and ethers can also be used, which are preferably used as minor co-solvents.

In another embodiment, water is a solvent. The solvent matrices may be semi-aqueous systems. In an embodiment, water content is 5% or more. In yet another embodiment, water content is 20% or more by weight. Comparing to water-free and low water cleaners, the combination of semi-aqueous solvent matrix and fluorides frequently result in serious metal compatibility issues. We have addressed these challenges with the novel use of selected fluoride species, unique compatibility enhancers and compatibility enhancing organic solvents.

The compositions of the present invention also deliver novel selectivity: i) between ARC and substrates, or ii) between ARC and metallizations. The chemistries disclosed herein are capable of delivering selective etch/removal of Silicon-containing Bottom Anti-Reflective Coating (SiBARC), such as DUO 248 material from Honeywell, without significant etch/damages of substrates (e.g. Silicon Oxide, TEOS or silicon nitride) or etch/damages of metallizations (e.g. Al, Cu, W, Ti, TiN, TaN).

It is known that fluorides at acidic pH have higher reactivity and cleaning capabilities. However, it also attacks silicon based materials, such as TEOS. Frequently, it even etches the more durable silicon based materials, such as silicon nitride, at smaller etch rates than TEOS. For advanced applications, even smaller SiN etch rates, such as 5-10 Å/min, are frequently unacceptable. The present invention provides novel etch selectivity among silicon based ARC and other silicon based substrates.

It is also known that acidic fluoride based chemistries, especially HF containing formulations, cannot have broad compatibilities with wide varieties of metallizations at the same time. Our invention delivers unique broad compatibilities with metallizations (e.g. Al, Cu, W, Ti, TiN, TaN) and substrates (e.g. TEOS, SiN, high-k, low-k). Few acidic fluoride clean chemistries have shown improvements by providing better compatibilities. However, none of the prior art could demonstrate the compatibilities at the levels which meet highly demanding requirements at advanced technology nodes in semiconductor such as 16nm or lower.

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. 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 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 alkoxyates, 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, dialkylmorpholinium salts, alkylbenzyltrimethylammonium salts, alkyltrimethylammonium salts, and alkylpyridinium salts. Preferably, the cationic surfactants are halogen-free surfactants. Examples 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 cetoxypopylbetaine (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.

EXAMPLES

The present invention is further exemplified, but not limited, by the following representative examples, which are intended to illustrate the invention and are not to be construed as being limitations thereto.

Ingredients Present by Weight Percentage

Ex. No:	Ammonium bifluoride (ABF)	Ammonium citrate dibasic (ACA)	NH ₄ F (40%)	Ammonium phosphate dibasic (ADP)	Amino trimethylene phosphonic acid	N-(-2 hydroxyethyl) morpholine	Ethylene glycol	Diethylene glycol	Dimethyl siloxane (DMSO)	H ₂ O
1	0.3	0.3					25		59.4	15
2	0.2	0.2					25		59.6	15
3	0.3	0.3					20	5		34.4
4	0.25	0.25		0.2			10		49.3	40
5	0.5	0.5							59	40
6	0.3	0.4	0.6				14	5	49.7	30
7	0.3	0.4	0.6				14	5	49.5	30
8	0.4	0.4					14	5	50	30
9	0.3	0.3				0.3		20	49.2	30
10	0.4	0.4	0.3				14	5	49.9	30
11	0.3	0.4	0.6				14	5	49.5	30
12	0.3	0.4	0.6				10	9	49.5	30
13	0.15	0.3	0.15				14	5	50.4	30
14	0.3	0.4	0.6		0.2		14	5	49.3	30
15	0.3	0.5	0.6		0.2			10	58.4	30
16	0.3	0.4	0.6					10	58.4	30
17	0.3	0.4	0.6		0.1		10		58.6	30
18	0.15	0.3	0.3					15		25
19	0.15	0.3	0.3		0.1			15		25
20	0.3	0.3	0.2				14	5	50.2	30
21	0.15	0.3	0.15		0.1		14	5	50.3	30
22	0.15	0.3	0.15		0.1		10		59.4	30

Additionally, the following examples also include the components listed below:

Example 7 0.2% by weight MTES

Example 11 0.2% by weight polydimethylsiloxane

Example 12 0.5% by weight polydimethylsiloxane

Example 14 0.2% by weight polydimethylsiloxane

Example 16 0.2% by weight 5MBZT

Example 18 59.25% by weight N-(2-hydroxyethyl)-2-pyrrolidone (HEP)

Example 19 59.15% by weight N-(2-hydroxyethyl)-2-pyrrolidone (HEP)

The following tables illustrate the properties of the composition of the present invention, as exemplified through the Examples listed above.

Table I

ARC Removers with Wide Metallization Compatibilities Etch rates are in Angstrom per minute

Ex. No:	Al ER (Å/m)	Cu ER	TEOS ER	SiN ER	TiN ER (CVD)	TaN ER	W ER	Unashed DUO	Ashed DUO	10% pH
11 at 55°C	0.4 (2.1)	2.3	50	3.2	2.2	0.1	1.5	538	333	4.2
11 at 50°C	0.4	0.2	42.5	1.6	1.1	0.3	0	553	217	
6 at 65°C	1.3	1.6	79					>561	335	4.2
100:1 DHF at 25°C (Prior Art)	>1,400							93	415	
200:1 DHF, at 25°C (Prior Art)	590	2.7	31	4.0	0.6	0.4	4.2	62	37	2.5
13 at 45°C	2.7	0.2	0.9	0.3	0		0.2	60	20	
8 at 45°C	2.8	2.6	26	2.5				215	108	4.2
6 at 65°C	1.3	1.6	79					>561	335	4.2
6 at 45°C	0.4	0.8	18					244	41	4.2
7 at 85°C	4.7	7.2	157					>550	335	3.9
7 at 65°C	1.4	3.6	26	5.3				>550	330	3.9

Ex. No:	Al ER (A/m)	Cu ER	TEOS ER	SiN ER	TiN ER (CVD)	TaN ER	W ER	Unashed DUO	Ashed DUO	10% pH
7 at 55°C	1.3	3.1	16	3.4				570	61	
7 at 45°C	1.0	0.7	5.2					144	17	
11 at 45°C	3.1	2.9	34	4.5				559	58	4.1
12 at 55°C	4.0	4.0	51	3.8				546	332	4.1
12 at 45°C	3.4	2.1	35	3.6				212	48	4.1
14 at 45°C	0.6	0.6	38		0.19	1.5		541	203	3.7
14 at 55°C	1.0	1.7	68		0.36	0.7		535	241	
15 at 45°C	0.8	1.5	40		0.14	1.5		549	226	3.8
15 at 55°C	1.7	4.1	79		0.26	1.2		547	204	
16 at 45°C	0.9	1.4	34		0.71	1.2		564	125	3.9
16 at 55°C	1.7	0.8	78		1.60	1.3		480	336	
17 at 45°C	1.3	0.7	32		0.19±0.0 2	1.56± 0.28		152	110	4.1
17 at 55°C	1.0	1.0	67		0.29±0.0 2	0.62± 0.99		>366	343	
19 at 45°C	1.9	1.2	4.0	1.8	0.08±0.0 1		0.3	17	8.5	
19 at 55°C	2.5	2.1	10.9	2.5	0.09±0.0 1		0.4	35	36	
21 at 45°C	3.2	1.2	7	2.1	0.06		0.8	28	18.4	
22 at 45°C	0.8	1.1	7.6	2.5	0.09±0.0 1		1.3	38	22	

Table II

Cleaning Chemistries with Superior Compatibilities
(High Potentials for Critical Cleans for Sub-20nm High k/Multigate/Metal Gate Technologies)

Ex. No.	ER (Å/min)							CD O Low	10% pH
	Al	Cu	TiN (PVD)	TiN (CVD)	W	TEOS	SiN		
13 (35 °C)	2.7	0.2	0.26 ± 0.17	0.16 ± 0.002	0.2		0.9 1.56 ± 0.05	1.4	3.9
21 (35 °C)	1.2	0.8	0 ± 0.09	0.06 ± 0.003	0.7		4.2 2.06 ± 0.07	8.9	3.9
19 (35 °C)	1.3	1.6	0 ± 0.01	0.11± 0.004	0.3	1.6	1.04 ± 0.04	4.3	5.5
13 (45 °C)	5.8	4.8	0.27± 0.21	0.36 ± 0.003	-	4.5	1.82 ± 0.05	2.9	
20 (25°C)	0	0.4	0	0		4.5			3.6
20 (40 °C)	1.0	1.2	9.8	0.8		16.7	2.7 (45C)		3.6
21 (45 °C)	3.2	1.2	0.22± 0.10	0.06 ± 0.002	0.8		7.0 2.08 ± 0.01	15.2	
19 (45 °C)	1.9	1.2	0 ± 0.05	0.08± 0.01	0.3		4.0 1.76 ± 0.04	5.3	
22 (45 °C)	0.8	1.1	0.05± 0.12	0.09± 0.005	1.3	7.6	1.8	16.8	3.9
19 (55 °C)	2.5	2.1	0 ± 0.03	0.09± 0.01	0.4	10.9	2.5	27	

CDO Low k: k value is at the range of 2.4-2.5

Table III
Bath Life Study showing good pH and etch rate stabilities

Ex. No.	Process Time (@45C)	Wt Loss (%)	Al ER (Å /min) o (45 C) @ 600 rpm stirring Rate	Cu ER (Å /min) o (45 C) @ 600 rpm stirring Rate	10% pH
8	0 hr	-	1.9	3.7	3.5
	6 hr	0.8%	1.7	3.5	3.5
	12 hr	1.8%	1.5	3.3	3.5
	24 hr	3.0%	1.4	3.3	3.5
	48 hr	4.7%	1.4	3.4	3.5
	72 hr	6.9%	1.0	3.7	3.5
	96 hr	10.1%	0.6	3.7	3.5

Table IV
Bath Life Study Showing Good pH and Etch Rate Stabilities

Ex. No.	ΔWt.	ΔpH	Al, ΔER (Å /min)	Cu, ΔER (Å /min)	TEOS, ΔER (Å /min)	Clean Capability	Bath Life
8	10%	0	< ± 1	< ± 0.3	< ± 5	Product	> 4 days
10	9%	0	< ± 1	< ± 1	< ± 5	No Change	> 4 days

Table V
Bath Life Study Showing Good pH and Etch Rate Stabilities

Ex. No.	Process Condition	Al ER (Å /min) (ii 40 C @ 600 rpm Stirring Rate)	Cu ER (Å /min) (ii 40 C @ 600 rpm Stirring Rate)	TiN ER (Å /min) (ii 40 C @ 600 rpm Stirring Rate)	TEOS ER (Å /min) (ii 40 C @ 600 rpm Stirring Rate)	10% pH
20	0 hr	1.0	1.2	0.8	16.7	3.6
	After 7 days, RT	1.3	1.4	0.7	16.5	3.7
	After 7 days, 35C	1.2	1.4	0.7	17.4	3.7
	After 7 days, 45C	1.5	1.5	0.9	23.7	3.8

Table VI

Ex. No.	Process Condition	Wt Loss (%)	Water Content	Fluoride Content
20	0 hr, RT	-	31.32%	0.28%
	After 7 days, RT	-0.1%	31.55%	0.27%
	After 7 days, 35C	0.5%	29.54%	0.27%
	After 7 days, 45C	6.7%	24.63%	0.27%

Table VII – Additional Examples
Ingredients Present by Weight Percentage

Ex. No:	Ammonium bifluoride (ABF)	Ammonium citrate dibasic (ACA)	NH ₄ F (40%)	Carbitol® (Diethylene glycol monoethyl ether)	Diethylhydroxyl amine (DEHA)	Ethylene glycol	Diethylene glycol	Dimethyl siloxane (DMSO)	H ₂ O
30	0.35	0.35	0.15	20	0.25		9.9	49.0	20
31	0.35	0.35	0.15	16	0.25		4.9	48.0	30
32	0.35	0.35	0.15	17	0.25		4.9	42.0	35
33	0.3	0.3			0.2		20	49.2	30
34	0.4	0.4	0.3			14	5	49.9	30
35	0.15	0.3	0.15			14	5	50.4	30

In tests, examples 30-35 performed similarly in all categories shown in tables II – VI as the other examples. Thus while there have been described what are presently believed to be preferred embodiments of the invention, those skilled in the art will realize that changes and modifications may be made thereto without departing from the spirit of the invention, and it is intended to claim all such changes and modifications as fall within the true scope of the invention.

Claims

1. A cleaning composition for micro-electronics applications comprising 0.05% to 5.0 % by weight of a bifluoride compound, 0.01% to 5% by weight of a pH-stabilizing compatibility enhancer, 5% to 90% by weight of an organic solvent, and 5% to 90% water, wherein a pH of said cleaning composition is less than or equal to 5.5, wherein said pH-stabilizing compatibility enhancer is a polyprotic acid, or salt thereof.
2. The cleaning composition of claim 1 comprising 0.05% to 1.0 % by weight of a bifluoride compound, 0.05% to 3% by weight of a pH-stabilizing compatibility enhancer, 10% to 70% by weight of an organic solvent, and 10% to 50% water.
3. The cleaning composition of claim 1 comprising 0.1% to 0.5 % by weight of a bifluoride compound, 0.1% to 1.0% by weight of a pH-stabilizing compatibility enhancer, 20% to 60% by weight of an organic solvent, and 20% to 40% water.
4. The cleaning composition of claim 1 wherein a pH of said cleaning composition is less than or equal to 5.0.
5. The cleaning composition of claim 1 wherein a pH of said cleaning compositions is less than or equal to 4.5.
6. The cleaning composition of claim 1 further comprising a co-solvent selected from alcohols, alcohol-ethers, and ethers.
7. The cleaning composition of claim 6 wherein said co-solvent is ethylene glycol, diethylene glycol, or a combination thereof.
8. The cleaning composition of claim 1 wherein said bifluoride compound is selected from the group consisting of ammonium bifluoride, alkylammonium bifluoride, potassium bifluoride, and alkali metal bifluorides.
9. The cleaning composition of claim 8 wherein said bifluoride compound is ammonium bifluoride.
10. The cleaning composition of claim 1 wherein said pH-stabilizing compatibility enhancer is selected from the group of citric acid, ammonium citrate monobasic, ammonium citrate dibasic, ammonium citrate tribasic, phosphoric acid, ammonium phosphate monobasic, ammonium phosphate dibasic, ammonium phosphate tribasic, ascorbic acid, ammonium ascorbate monobasic, ammonium ascorbate dibasic, aminotrymethylenephosphonic acid, and mixtures thereof.

11. The cleaning composition of claim 1 wherein said organic solvent is a sulfide or an amide.
12. The cleaning composition of claim 11 wherein said organic solvent is selected from dimethyl sulfoxide, N-methyl pyrrolidone (NMP), N-ethyl pyrrolidone (NEP), N-(2-hydroxyethyl)-2-pyrrolidone (HEP), N-(2-hydroxyethyl)morpholine, dimethyl 2-piperidone (DMPD), dimethyl acetamide, formamide, and mixtures thereof.
13. The cleaning composition of claim 1 further comprising another fluoride source.
14. The cleaning composition of claim 13 wherein said another fluoride source is a fluoride salt.
15. The cleaning composition of claim 1 further comprising a corrosion control agent.
16. The cleaning composition of claim 1 further comprising a surfactant.
17. A method of cleaning a micro-electronic material comprising contacting said microelectronic material with a cleaning composition comprising: 0.05% to 5.0 % by weight of a bifluoride compound, 0.01% to 5% by weight of a pH-stabilizing compatibility enhancer, 5% to 90% by weight of an organic solvent, and 5% to 90% water, wherein a pH of said cleaning composition is less than or equal to 5.5, wherein said pH-stabilizing compatibility enhancer is a polyprotic acid, or salt thereof.