PROCESS AND APPARATUS FOR REMOVING RESIDUES FROM SEMICONDUCTOR SUBSTRATES

(1) Field of the Invention

[0001] The present invention generally relates to a process and apparatus for cleaning substrates. More particularly, the present invention relates to processes for removing residues including etch, metal, and non-metal residues from semiconductor substrates. The instant invention finds application in many processes such as commercial silicon wafer production.

(2) Background

[0002] The semiconductor industry faces challenges to produce devices with increasingly smaller features to increase electrical component density per unit area on a wafer and to enhance operating speed of the semiconductor. Electrical components of semiconductor devices are now approaching sizes and/or dimensions such that surface tension generated by conventional aqueous and semi-aqueous cleaning solutions during manufacturing may damage the extremely delicate electrical components and/or features. Ultimately the surface tension exerted in these liquids on the small wafer surface features and patterns will exceed the critical stress, the point of structural failure, making conventional aqueous and semi-aqueous fluids unsuitable or at worst obsolete for next-generation processing and cleaning of substrates, wafers, and/or semiconductors. New cleaning fluids and approaches or processes that address

the fundamental surface tension limitation that remain reactive toward tenacious surface residues are needed. The term "tenacious residues" describes the typically high molecular weight and heterogenous residues comprising combinations of metallic and/or non-metallic residues introduced to a substrate surface during wafer processing (e.g., plasma etching) and which become partially or fully polymerized or bound to a polymer matrix or are otherwise physically trapped or confined within a bulk residue.

[0003] The substrates in semiconductor or wafer processing are conventionally multilayered composites comprising silicon and other thinly layered and/or deposited materials or films. During wafer processing and production, various and dynamic combinations of etch and/or metal residues are routinely sputtered and deposited onto a surface in, on, or around the macro and micro structures or patterns located thereon. For example, metal residues including copper (Cu), aluminum (Al), and iron (Fe) or other transition metal residues, as well as non-metal residues including carbon (C), nitrogen (N), oxygen (O), phosphorus (P), sulfur (S), or others (F, Cl, I, Si,) may be deposited on a surface on various patterned structures (i.e., vias) in the form of particulates, crumbs, mounds, striations, films, and molecular layers. Presence of such residues following processing may lead to a faulty or failed device. Thus, commercial production requires residues to be removed from the wafer.

[0004] Densified fluids including near-critical and supercritical fluids can address the fundamental surface tension limitation associated with aqueous and semiaqueous fluids without risking structural collapse of features. However, a major drawback of densified fluid systems is that they are non-reactive, having

no ability to directly chemically modify and remove tenacious metal and non-metal residues generated during wafer processing.

[0005] Accordingly, there remains a need to show an effective system for removing tenacious residues from semiconductor substrates and/or surfaces that addresses critical surface tension limitations. We present a "reactive" system wherein 1) removal of tenacious residues is effected; 2) surface tension approaches zero as compared to aqueous and semi-aqueous fluid systems known in the art; 3) risk of damage to, or structural collapse of, intricate substrate features is minimized; 4) polarity in the continuous phase is maintained; and 5) speed of cleaning is enhanced. The present invention thus represents a new advancement relative to wafer and semiconductor surface processing.

SUMMARY OF THE INVENTION

[0006] The present invention relates to a "reactive" system and process for effecting removal of tenacious residues found on substrates and surfaces such as a semiconductor (e.g., silicon) surface. Residues may include, but are not limited to, the group of organic residues, metal residues, etch residues, non-metal residues, polymeric residues, and combinations thereof. The term "reactive" in reference to the systems of the present invention describes chemical processes or reactions wherein combinations of chemically reactive agents or constituents present in the densified fluid and/or reverse micelle core react with and chemically modify residues thereby effecting removal from the substrate or surface. Reactions effecting residue removal may include, but are not limited to, the group of chemical, oxidation, reduction, molecular-weight

reduction, fragment cracking, exchange, association, dissociation, complexation (including polar head group reactions within the inner polar cores of the reactive reverse micelles or aggregates), and combinations thereof.

[0007] The reactive systems of the present invention are distinguished from other densified fluid cleaning systems known in the art in at least the following key areas. First, the present invention embodies reactive approaches for effecting residue removal and/or cleaning that are viable and applicable to commercial wafer and/or semiconductor processing. Test results show, for example, that residue removal is effected to industry accepted contamination standards or better. One such measure for commercial processing is the atomic monolayer standard for residue per unit area. For example, a monolayer of pure silicon on a wafer surface may be calculated to comprise a coverage of approximately 2×10^{15} atoms per square centimeter (e.g., atoms/cm^2). The systems of the present invention have been shown to remove residues to a level of about 4×10^{11} atoms/cm^2 or better, making them ultimately viable for commercial use. Secondly, systems of the present invention offer enhanced speeds and/or efficiencies for effecting removal of residues. For example, residue removal occurs in a maximum period up to 15 minutes. Typical periods for residue removal occur in 5 minutes or less on average. Periods of 15 seconds are presently ideal. Thirdly, and significantly, the systems embodied in the present invention exert low surface tension stresses on small wafer features, thus being ultimately useful for commercial processing applications into the next generation of feature development and beyond.

[0008] The process of the present invention generally comprises 1) providing a densified fluid wherein the fluid is a gas at standard temperature and

pressure wherein the density of the fluid is above the critical density of the fluid; 2) providing a cleaning component; 3) intermixing the densified fluid and the cleaning component whereby a reactive cleaning fluid is formed comprising reactive reverse-micelles or reactive aggregates; and 4) contacting a residue on a substrate with the reactive cleaning fluid for a time t_r whereby the residue is chemically modified and removed from the substrate. The cleaning component comprises at least one reverse micelle-forming surfactant and/or co-surfactant and/or at least one reactive chemical agent, and combinations thereof. The reactive chemical agent may be added independently of the surfactant/co-surfactant or may be integral to the surfactant itself.

[0009] Reaction between the residues of interest and the components in the system (reverse micelles, reactive chemical agents, etc.) chemically modify the residues thereby removing them from the substrate surface. An additional, but optional, step includes rinsing the cleaned surface with a rinsing fluid to aide in the recovery or removal of spent cleaning fluid containing the chemically modified residues.

[0010] The term "densified" as used herein refers to fluid forming materials or compounds that exist as gases under standard temperature and pressure (STP) conditions and which (as fluids) are maintained at a density (ρ) above the critical density (e.g., $\rho > \rho_c$) for the specified fluid material. STP is universally defined as a temperature of 0 °C and a pressure of 1 atm [~1.01 bar]. Densified fluids comprise the group of liquefied gases and/or supercritical fluids. Appropriate temperature and pressure regimes above the critical density may be selected from a plot of reduced pressure (P_r) as a function of reduced density (ρ_r) whereby the corresponding reduced temperature (T_r) isotherms are specified.

The reduced temperature, reduced pressure, and reduced density are further defined by the respective ratios $T_r=T/T_c$, $P_r= P/P_c$, and $\rho_r=\rho/\rho_c$ where T_c, P_c, and ρ_c define the critical temperature, critical pressure, and critical density, respectively. The process of the present invention preferably applies fluids having reduced densities in the range from about 1 to 3. More preferably, fluids are employed having reduced densities in the range from about 1 to 2.

[0011] The densified fluid of the present invention preferably comprises CO_2 given the low surface tension (1.2 dynes/cm at 20 °C, "Encyclopedie Des Gaz", Elsevier Scientific Publishing, 1976, pg. 361) and ultimately useful critical conditions (where T_c= 31 °C, P_c = 72.9 atm (or 1,071 psi), CRC Handbook, 71st ed., 1990, pg. 6-49). For CO_2, the critical density (ρ_c) is approximately 0.47 g/cc ("Properties of Gases and Liquids", 3ed., McGraw-Hill, pg. 633) where ρ_c is defined by the term ($1/V_c$ x Mol. Wt.) where V_c is the critical volume. Other gases that may find potential use as densified fluids include, but are not limited to, ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), butane (C_4H_{10}), sulfurhexafluoride (SF_6), and ammonia (NH_3), including substituted derivatives thereof (e.g., chlorotrifluoroethane) and equivalents, although flammability and toxicity issues present safety concerns to be addressed. The flammability limit for butane, for example, is 1.86% by volume in air (CRC Handbook, 71st ed., 1990, pg. 16-16); NH_3 is poisonous.

[0012] As noted hereinabove, fluid surface tension also remains a significant concern. As the size of features on semiconductor and wafer surfaces continues to decrease and feature density per unit area continues to increase, surface tension in aqueous and semiaqueous fluids will eventually exceed the feature critical stress σ_{crit}, the point of structure failure, collapsing

and/or damaging the features during the drying phase of production to remove water. Surface tension of water at 20 °C is about 73 dynes/cm (CRC Handbook, 71st ed., 1990, pg. 6-8). Dimethyl acetamide, a commercial semiaqueous cleaning fluid, exhibits a surface tension at 30 °C of about 32 dynes/cm (Table of Physical Properties, High Purity Solvent Guide, 2ed., Burdick and Jackson Laboratories, Inc., 1984, pg. 138). In contrast, the surface tension of densified CO_2 at 20 °C is 1.2 dynes/cm ("Encyclopedie Des Gaz", Elsevier Scientific Publishing, 1976, pg. 338), a factor of from 25 to 60 below the surface tension for a comparable semi-aqueous or aqueous fluid, respectively. And, while surface tension for water is negligible in the supercritical phase, dissolution of the wafer substrate becomes significant at the elevated critical temperature for water (T_c = 371.4 °C, CRC Handbook 71st ed., 1990, pg. 6-49). Thus, semi-aqueous and aqueous fluids continue to be problematic cleaning fluids at best. Densified fluids, including densified and liquefied CO_2 gas and supercritical CO_2 fluid can thus be used to address the fundamental surface tension concern associated with aqueous and semi-aqueous cleaning solutions given that surface tension becomes negligible as the fluid approaches the critical point.

[0013] The person of ordinary skill in the art will recognize the wide selection of temperature and pressure profiles usable in conjunction with the systems of the present invention. For example, pressures up to 10,000 psi and temperatures fully encompassing the range of densified and super critical fluids may be envisioned. Thus, no limitation is intended by the disclosure of conditions herein ideally suited substrate processing operations.

[0014] The temperature of densified CO_2 gas (e.g., liquefied CO_2) is preferably in the range from about -80 °C to 150 °C with a pressure up to about

3000 psi inclusive. More preferably, a temperature may be selected of up to and including 60 °C with a pressure in the range from 850 psi up to 3000 psi inclusive. Most preferably, conditions are selected whereby temperature is at or near room temperature (approximately 20-25 °C), pressure is approximately 850 psi, and density in the densified liquid exceeds the critical density of pure CO_2 (e.g., $\rho_c > 0.47$ g/cc).

[0015] Density increases may also be exploited in a densified fluid by effecting changes to pressure and/or temperature in the system. For example, density in a pure liquefied CO_2 fluid at 20 °C and approximately 870 psi (60 bar) is 0.78 g/cc ["Encyclopedie Des Gaz", Elsevier Scientific Publishing, 1976, pg. 338]. At 2900 psi (200 bar), density increases in the fluid to approximately 0.94 g/cc, a 20% increase. Similar or greater effects can be attained in supercritical (SC) fluids whereby higher densities can be exploited as a function of pressure and/or temperature. For example, in a pure supercritical CO_2 fluid at 40 °C and 1300 psi, density is approximately 0.48 g/cc. At 2900 psi, density in the SC fluid increases to 0.84 g/cc, a 75% increase. In general, for a CO_2 fluid system under supercritical fluid (SCF) conditions, the system need only exceed the critical parameters where T_c= 31 °C; P_c = 1,071 psi; and ρ_c. = 0.47 g/cc. Thus, above a temperature of about 32 °C, a pressure for an SCF system need only be selected whereby the density exceeds the critical density of CO_2. Temperatures for SCF systems up to 150 °C are conceptually practicable if the density of the solution mixture is maintained above the critical density. Because the polarity of a densified or supercritical fluid is too low to effect removal of tenacious residues of interest from a substrate surface, additional modifications to the fluid must be made, as described hereinafter.

[0016] Surfactants of the present invention are preferably selected from the group of reverse-micelle forming surfactants and co-surfactants including, but not limited to, CO_2-philic, anionic, cationic, non-ionic, zwitterionic, and combinations thereof. Presently, surfactants preferably comprise a perfluoro-poly-ether (PFPE) backbone or equivalent fluorocarbon-containing tail so as to be soluble in the densified fluid medium. Anionic reverse micelle forming surfactants include, but are not limited to, various classes of fluorinated hydrocarbons, and fluorinated and non-fluorinated surfactants, including PFPE surfactants, PFPE carboxylates (including PFPE ammonium carboxylates), PFPE phosphate acids, PFPE phosphates, fluorocarbon carboxylates, PFPE fluorocarbon carboxylates, PFPE sulfonates (including PFPE ammonium sulfonates), fluorocarbon sulfonates, fluorocarbon phosphates, alkyl sulfonates, sodium bis-(2-ethyl-hexyl) sulfosuccinates, ammonium bis-(2-ethyl-hexyl) sulfosuccinates, and combinations thereof. Cationic reverse micelle forming surfactants include but are not limited to the tetra-octyl-ammonium fluoride class of compounds. Non-ionic reverse micelle forming surfactants include, but are not limited to, the poly-ethylene-oxide-dodecyl-ether class of compounds, their substituted derivatives, and functional equivalents thereof. Zwitterionic reverse micelle forming surfactants include, but are not limited to, the alpha-phosphatidyl-choline class of compounds, their substituted derivatives, and functional equivalents thereof. Co-surfactants include, but are not limited to, the group of alkyl acid phosphates, alkyl acid sulfonates, alcohols of general formula ROH where R is any alkyl or substituted alkyl group (e.g., alkyl alcohols, perfluoroalkyl alcohols), dialkyl sulfosuccinate surfactants, derivatives, salts, and functional equivalents thereof. Co-surfactants are preferably selected from the

group consisting of sodium bis-(2-ethyl-hexyl) sulfosuccinates (e.g., sodium AOT), ammonium bis-(2-ethyl-hexyl) sulfosuccinates (e.g., ammonium AOT), and their functional equivalents or the like. Surfactants and/or co-surfactants not miscible in the bulk densified fluid or solvent (e.g., non-CO_2-philic) may also be rendered soluble and/or capable of forming reverse micelles and thus be suitable for use in the densified fluid provided at least one miscible (e.g., CO_2-philic) reverse-micelle-forming surfactant or co-surfactant is used in the surfactant combination. As such, the person of ordinary skill in the art will recognize that the useful scope of surfactant and co-surfactant classes is wide whereby many effective embodiments of reverse micelle forming surfactants and co-surfactants can be used in conjunction with the present invention. Thus, no limitation in scope is intended by the disclosure of the preferred embodiments.

[0017] Reactive chemical agents of the present invention comprise the group of reagents or modifiers that when added to the densified fluid provide chemical reactivity to the reactive cleaning fluid. The term "reactive" as used herein describes and defines or otherwise refers to the ability of modifiers or chemical agents in the bulk densified fluid and/or reverse micelle(s)/aggregates to chemically modify or react with tenacious residues such that residues are removed from the substrate surface. Agents providing reactivity may be the surfactant/co-surfactant itself and/or components thereof, and/or may be separate chemical modifiers added to the bulk fluid and/or the reverse micelle(s)/aggregate(s). Reactive chemical agents or modifiers are preferably selected from the group of mineral acids, fluoride-containing compounds and acids, organic acids, amines, alkanolamines, hydroxylamine, peroxides and other oxygen-containing compounds, chelates, ammonia, and combinations

thereof. Mineral acids are preferably selected from the group of hydrochloric (HCl), sulfuric (H_2SO_4), phosphoric (H_3PO_4), and nitric (HNO_3), their respective acid dissociation products (e.g., H^+, HSO_4^{-1}, $H_2PO_4^{-1}$, HPO_4^{-2}, etc.) and salts, and combinations thereof. Preferred fluoride-containing compounds and acids include, but are not limited to, F_2, hydrofluoric acid (HF), various dilution acids thereof up to and including ultra-dilute hydrofluoric acid (UdHF: 1:1000 dilution of 49 vol% HF in water). Organic acids include the sulfonic acids (R-SO_3H) and corresponding salts, phosphate acids (R-O-PO_3H_2) and corresponding salts, and phosphate esters and salts, substituted derivatives, and functional equivalents thereof. Preferred alkanolamines and other amines include, but are not limited to, ethanolamine ($HOCH_2CH_2NH_2$) and hydroxylamine (HO-NH_2), derivatives, and functional equivalents thereof. Peroxides include, but are not limited to, organic peroxides (R-O-O-R′), alkyl peroxides (R-C-O-O-R′), t-butyl peroxide [$(H_3C)_3C$-O-O-R′), hydrogen peroxide (H_2O_2), substituted derivatives, and combinations thereof. Oxygen containing compounds include, but are not limited to, oxygen (O_2) and ozone (O_3), and functional or reactive equivalents. Chelates include, but are not limited to, pentandiones; 1,1,1,5,5,5-hexa-fluoro-2,4-pentandione (also known as hexa-fluoro-acetyl-acetonate or 2,4 pentanedione), phenanthrolines; 1,10-phenanthroline ($C_{12}H_8N_2$), oxalic acid [$(COOH)_2$], and aminopolycarboxylic acids including ethylene-di-amine-tetra-acetic-acid (EDTA), derivatives, and salts (e.g., sodium EDTA, etc.) thereof.

[0018] Corrosion inhibitors may be added as constituents or modifiers to the reactive cleaning fluids and systems of the present invention to passivate and inhibit loss of base metal layers comprising copper or other metals. Inhibitors include, but are not limited to, benzotriazoles including 1,2,3-

Benzotriazole, and catechols including catechol, 1,2-Di-hydroxy-benzene (pyrocatechol) and 2-(3,4-Di-hydroxy-phenyl)-3,4-di-hydro-2H-1-benzopyran-3,5,7-triol (catechin), substituted derivatives, and equivalents thereof.

[0019] Intermixing of the densified fluid, the at least one reverse micelle-forming surfactant and/or co-surfactant, and/or the reactive chemical agent generates the reactive cleaning fluid. In one of many possible fluid configurations, intermixing of the components in the fluid forms "reactive" reverse micelle(s) or "reactive" aggregates wherein reactive chemical constituents reside within the polar micellar cores. Alternatively, reactive chemical modifiers may reside in the bulk densified fluid or be distributed both in the bulk fluid and the micellar core. Size of the reverse micelles is defined by the molar water-to-surfactant ratio, e.g., $[H_2O]/[Surfactant]$. The functional "reactive" reverse micelles or aggregates have diameters (tail to tail) preferably in the range from about 50 Å to 5000 Å inclusive. The person of ordinary skill in the art will recognize that sizing and/or dimensions of the reactive reverse micelle(s) can vary depending on molecular weight or size of the surfactants employed, as well as other chemical constituents or modifiers employed in the system. Thus, no limitation in scope is hereby intended by disclosure of the preferred system embodiments.

[0020] The multi-component fluid mixture is subsequently raised to selected temperatures and pressures whereby the density (ρ) in the fluid exceeds the critical density (ρ_c) of the bulk fluid thereby effecting formation of a densified reactive cleaning fluid. The effectiveness of the fluid system toward residues is determined by the reaction between, and reactivity of, the reactive reverse micelle(s) and/or reactive aggregates and the targeted substrate

residues of interest. Optimum removal of residues is achieved by effecting a direct chemical reaction between the residues of interest and the reactive reverse micelle(s) or reactive aggregate(s) in the densified fluid.

[0021] Rinsing fluids may be employed optionally to assist in the recovery or removal of the spent reactive cleaning fluid containing chemically modified residues. Rinsing fluids preferably comprise the pure densified fluid (e.g., CO_2 in a densified liquid or supercritical state) or, alternatively, a fluid containing other CO_2-miscible organic solvents, polar fluids, and/or co-solvents having concentrations up to about 30% by volume in the bulk densified fluid including, but not limited to, alcohols of general formula ROH where R is any alkyl or substituted alkyl group having a carbon number in the range from 1 to 12, iso-propyl-alcohol [iPrOH], methanol [MeOH], and ethanol [EtOH] being representative but not exclusive compounds; carboxylic acids of general formula R-COOH where R is any alkyl or substituted alkyl group having a carbon number in the range from 1 to 11 (e.g., formic acid [HCOOH], etc.); tetrahydrofurans (THF), chlorinated and/or fluorinated hydrocarbons including, but not limited, to chloroform, and methylene chloride; and other polar liquids including, but not limited to, water. Examples include a rinsing fluid comprising 5% iPrOH in the bulk densified CO_2 fluid or alternatively, a densified CO_2 fluid saturated with H_2O. Other soluble and/or miscible polar compounds in liquefied CO_2 as reported by Francis in (J. Phys. Chem., 58, 1099-1114, 1954) are hereby incorporated.

[0022] Effectiveness of a reactive cleaning system for wafer or semiconductor processing is also a function of 1) maintaining a sufficiently low surface tension to minimize damage to the critical or intricate surface structures; 2) retaining dimensional and/or site attributes of the patterned features or

structures of a substrate or wafer surface during processing; 3) retaining a sufficient polarity in the cleaning fluid for solubility among and between the various chemical moieties, modifiers, and constituents; and 4) maintaining reactivity between and among the chemically reactive modifiers and/or constituents in the densified fluid medium so as to effect residue removal.

[0023] Residue analysis results using Scanning Electron Microscopy (SEM) examination and X-Ray Photoelectron Spectroscopy (XPS) show systems of the present invention are distinguished at a minimum from other densified fluid systems known in the art in both in their reactivity and ability to effect removal of tenacious residues that continue to prove problematic to the semiconductor industry, including transition metal residues (e.g., Cu and Fe), other metal residues (e.g., Al), as well as non-metal and/or etch residues (e.g., containing C, N, F, Si, P, etc.). Further, results show a contact time t_r with or in the reactive fluids on the order of 5 minutes or less can effect removal of residues, a significant advancement in the art. In sum, the systems of the instant invention present a new capability for attacking and removing unwanted and tenacious residues from a semiconductor or wafer substrate surface.

[0024] It is an object of the present invention to show a reactive reverse-micelle cleaning system that 1) optimizes wafer cleaning performance by removing etch residues and other metal and non-metal residues; 2) comprises low quantities of chemical modifiers; and 3) exhibits low overall toxicity. The term "modifiers" defines any additive (chemical or otherwise) introduced to the fluids of the present systems to enhance reactivity, cleaning performance, speed, and/or efficiency for removing tenacious residues. Preference is given to modifiers, additives, solvents, and fluids that in the various application aspects

are easily recovered and that lower commercial processing costs. Optimization benchmarks include achieving 1) essentially complete removal of residues; 2) greater efficiency and/or speed of residue cleaning than is currently known in the art; 3) cleaning levels for residues that remain efficacious for commercial wafer and/or semiconductor processing; and 4) a reduction in the number of critical dimension (CD) changes to substrate features and patterns (e.g., vias) or other important substrate structures. The term "critical dimension" changes refers to alterations in the size or dimensions (e.g., pitch) of patterns or structural features such as vias on the wafer substrate or surface. Preference is given to systems that minimize changes to functional components of the wafer surface or substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] A more complete appreciation of the invention will be readily obtained by reference to the following description of the accompanying drawings in which like numerals in different figures represent the same structures or elements. The invention may be embodied in many forms and should not be construed as being limited to the embodiments set forth herein.

[0026] **FIG. 1** illustrates a generalized reaction scheme for a reactive reverse micelle residue cleaning system according to the present invention.

[0027] **FIG. 2** illustrates four representative reactions involving reactive constituents and residues in the cleaning system according to the process of the present invention.

[0028] **FIG. 2A** illustrates a first representative reaction between reactive constituents and residues in the cleaning system to remove chemically modified residues.

[0029] **FIG. 2B** illustrates a second representative reaction between reactive constituents and residues in the cleaning system to remove chemically modified residues.

[0030] **FIG. 2C** illustrates a third representative reaction between reactive constituents and residues in the cleaning system to remove chemically modified residues.

[0031] **FIG. 2D** illustrates a fourth representative reaction between reactive constituents and residues in the cleaning system to remove chemically modified residues.

[0032] **FIG. 3** shows an SEM micrograph of an as-received OSG no barrier open (NBO) wafer substrate containing over-etch processing residues including crumbs, striations, and mounds.

[0033] **FIG. 4** shows exploded cross-sectional views of a mixing chamber and a cleaning vessel according to the present invention.

[0034] **FIG. 5** illustrates a complete wafer cleaning system design showing the combination of mixing vessel, wafer cleaning vessel, syringe pump, valves, and associated transfer lines.

[0035] **FIG. 6** illustrates a reactive reverse micelle system for removing semiconductor residues according to a first embodiment of the present invention comprising PFPE phosphate, alkyl sulfonate (e.g., AOT), and water.

[0036] **FIG. 7** presents an SEM micrograph of a cleaned OSG no barrier open (NBO) test wafer showing effective removal of surface residues using a

reactive reverse micelle system according to a first embodiment of the present invention.

[0037] **FIG. 8** illustrates a reactive reverse micelle system comprising PFPE ammonium carboxylate and hydroxylamine for removing semiconductor residues according to a second embodiment of the present invention.

[0038] **FIG. 9** shows an SEM micrograph of a cleaned OSG no barrier open (NBO) test wafer showing the effective removal of surface residues using a reactive reverse micelle system according to a second embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0039] While the present invention is described herein with reference to the preferred embodiments thereof, it should be understood that the invention is not limited thereto, and various alternatives in form and detail may be made therein without departing from the spirit and scope of the invention. In particular, those of ordinary skill in the art will appreciate that combining and intermixing the various fluids and reactive components as currently practiced and described herein may be effected in numerous and effectively equivalent ways. For example, application of the method steps on a commercial scale may comprise use of high-pressure pumps and pumping systems, and/or transfer systems for moving, transporting, transferring, combining, intermixing, as well as delivering and applying the various cleaning fluids. Associated application and/or processing techniques for utilizing the reactive cleaning fluids of the present

invention for ultimately cleaning substrate surfaces, or for post-processing collection of waste solutions and chemical constituents are also envisioned and encompassed hereby, as would be performed by those of ordinary skill in the art.

[0040] **FIG. 1** shows a generalized reaction and process scheme for a reactive reverse micelle fluid system according to the process of the present invention. CO_2-philic surfactants **106** comprising a polar head group **102** and a CO_2-philic tail **104** combine to form aggregates **120** or reverse micelles **120** in the densified fluid **130**. The polar heads **102** align in close proximity in the aggregate **120** or reactive reverse micelles **120**, forming a polar inner core **112**. Reactive chemical agents **125** in the polar core **112** and/or the bulk densified fluid **130** provide reactivity toward residues **150** in combination with the reactive reverse micelles **120** thus constituting a "reactive" reverse micelle fluid system. More specifically, residues **150** on the surface of the wafer **100** react with the reactive constituents **125** in the fluid system thereby becoming chemically modified residues **155** that are removed or separated from the surface of the substrate **100** and which then subsequently reside within the polar core **112** or the densified fluid **130**. Reactions by which residues **150** become chemically modified residues **155** which can be removed from the surface of the substrate **100** include, but are not limited to, chemical reactions, oxidation, reduction, exchange, molecular-weight reduction, fragment cracking, dissociation, complexation, head-group or inner micelle core binding, and combinations thereof.

[0041] Referring now generally to **FIG. 2**, four representative reaction types involving reactive constituents **225**, reverse micelles **220**, and residues **250** in the densified fluid **230** are illustrated whereby the chemically modified residues

255 are removed from a substrate **200** surface. The person of ordinary skill in the art will recognize the illustrated reactions to be representative of the general types of reactions that may be involved. Thus, no limitation is intended by the disclosure thereof.

[0042] **FIG. 2A** illustrates a first reaction type in which a chemical agent **225** present in the polar micelle core **212** of the reverse micelle **220** reacts with a residue **250** on the surface of a substrate **200** yielding a chemically modified residue **255** that is removed from the substrate **200** and which resides within the polar micelle core **212**, e.g., a reaction whereby a polar and/or water-soluble residue is formed.

[0043] **FIG. 2B** illustrates a second reaction type in which a reactive chemical agent **225** present in the densified fluid **230** reacts with a residue **250** on the surface of a substrate **200** yielding a chemically modified residue **255** that is removed from the surface of a substrate **200** and which resides within the polar micellar core **212**. For example, a reaction between a residue and a chemical agent **225** in the densified fluid **230** whereby a polar and/or water-soluble chemically modified residue **255** is formed.

[0044] **FIG. 2C** illustrates a third reaction type in which a reactive chemical agent **225** in the polar core **212** of the reactive reverse micelle **220** reacts with a residue **250** on the surface of a substrate **200** whereby the resultant chemically modified residue **255** is removed from a surface and resides in the bulk densified fluid **230** separate from the substrate **200** surface. For example, a reaction between an acid (e.g., HF) **225** present in the micellar core **212** with a residue **250** whereby a non-polar and/or neutral moiety (e.g., SiF_4) **255** miscible in the densified fluid **230** is generated. Alternatively, a reaction between a metal

residue **250** (e.g., Cu) on the substrate **200** surface, a chemical agent [i.e., peroxide (H_2O_2)] **225** in the micellar core **212**, and a chemical agent **225** [i.e., 2,4-pentandione, a complexing agent] in the densified fluid **230** yielding a chemically modified residue **255** as a CO_2-philic moiety, i.e., copper-hexa-fluoro-acetyl-acetonate.

[0045] **FIG. 2D** illustrates a fourth reaction type in which a chemical agent **225** present as a constituent or component of the reverse micelle **220** (e.g., a head group) reacts with a residue **250** on the surface of a substrate **200** yielding chemically modified residues **255** ultimately retained in the micellar core **212**. For example, a metal-surfactant complex **255** formed between a chemically modified metal residue (e.g., Cu^{+}) **255** and the anion (e.g., PO_4^{2-}) of a phosphate surfactant head group (e.g., PFPE-PO_4^{2-}) **225** retained in the reverse micelle core **212**. Alternatively, a reaction with a quaternary ammonium fluoride surfactant, i.e., tetra-octyl-ammonium-fluoride.

[0046] The person of ordinary skill in the art will recognize that many reactants, potential reactive mechanisms, and reaction products are possible depending on the types of residues **250** on the surface of a substrate **200**, chemical reagents **225**, composition of the reactive reverse micelles **220** or aggregates **220** utilized, and the chemically modified residues **255** generated. In general, numerous and varied reactive outcomes that result in removal of residues **250** from a surface may be effected by the combined action of the reactive reverse micelles **220** or aggregates **220**, the reactive chemical agents **225** present in the cleaning system and the reactivity and selectivity toward substrate residues **250**. As shown hereinabove, chemically modified residues **255** may become miscible in the bulk densified fluid **230** or within the polar core

212 of the reactive micellar aggregates **220** either as freely mobile and soluble species or alternatively as bound or complexed species with the components or constituents comprising the aggregate **220** whereby the chemically modified residues **255** are ultimately removed from the substrate **200** surface. Other reactive combinations as would be envisioned by the person of ordinary skill in the art are hereby incorporated.

[0047] It should be emphasized that the presence of an inner polar core **212** in a micellar system is, by itself, insufficient to chemically modify or remove high molecular weight residues **250** from the surface of a substrate **200** or the resultant modified residues **255**, as evidenced by the number of simple densified systems known in the art that remain presently ineffective at removing tenacious residues because they constitute non-reactive systems. It has been shown, for example, that the reactive components **225** in the bulk fluid **230** or reverse micelle core **212** must be brought into direct and reactive contact with the substrate residue **250** for a sufficient contact time t_r for the necessary chemical reactions to occur. Reactive agents **225** in the polar core **212** of a reactive reverse micelle **220** or reactive aggregates **220** must interact reactively and directly with surface residues **250** for chemical modification to occur. Only then can the modified residues **255** be removed from the substrate surface as miscible moieties in the densified fluid **230** or as chemically modified species **255** within the polar core **212** of the reactive reverse micelles **220** pending recovery of the components in the densified fluid **230**.

[0048] **FIG. 3** shows an over-etched wafer coupon **300** comprising a base layer **305** of a representative metal, e.g., a transition metal such as copper (Cu) or another metal such as aluminum (Al). In the instant case, the base layer **305**

comprising copper was overlaid with an etch stop (e.g., barrier) layer **310** comprising silicon carbide (SiC) followed by a dielectric material layer **315** comprising organo-silane glass (OSG), a standard interlayer low-K dielectric material known in the art, or another porous low-K dielectric material (LKD), and a coating or insulating overlayer **320** comprising silicon dioxide (SiO_2) or other thin film. In each test wafer **300**, small pattern wells **325** called "vias" **325** were introduced into the OSG **315** (or LKD) layer through the SiO_2 coating layer **320**. The as-received test coupons **300** were generally of a "no barrier open" (NBO) or "barrier open" (BO) configuration purposely "over-etched" to enhance the quantity of surface residues for testing. NBO substrates are representative of wafers encountering a first etching (plasma or chemical) step in a commercial process whereby pattern vias **325** and/or other micro and macro structures are etched into the dielectric material layer **315** (e.g., LKD or OSG) but do not breach the etch stop (barrier) layer **310**. In **FIG. 3**, the over-etched wafer **300** surface is shown comprising residues from plasma etch processing in the form of crumb **330** deposits, mounds **335**, and striations **340** deposited on the walls or in the (1 μm) pattern vias **325**. Further processing that breaches the stop layer (e.g., SiC) constitutes a "barrier open" substrate. The wafer coupons **300** were sized as necessary for testing by scoring and breaking the wafers along the crystal planes.

[0049] **FIG. 4** illustrates simplified wafer cleaning equipment of a benchtop scale design for practicing the process of the present invention. The person or ordinary skill in the art will recognize that equipment is application driven and can therefore be scaled and/or configured as necessary to meet the specific application and/or industrial requirements without deviating from the

spirit and scope of the invention, e.g., scaled to accommodate a 300 mm diameter wafer, etc. Thus, no limitation is hereby intended by the disclosure of the instant equipment design applicable to a small test wafer coupon.

[0050] **FIG. 4** shows both a mixing vessel **420** and a wafer cleaning vessel **440** in cross section. The mixing vessel **420** is comprised of a top vessel section **402** and a bottom vessel section **404** machined preferably of titanium (Ti) metal. The vessel **420** may be lined with any of a number of high strength polymer liner(s) **406** to minimize potential of contaminating metals (including but not limited to Cu, Fe, and Ti) and particulates being introduced into the mixing vessel **420**. The liner **406** is preferably made of poly-ether-ether-ketone, also known as PEEK™, available commercially (Victrex USA, Inc., Greenville SC 29615) or an alternative such as poly-tetra-fluoro-ethylene (PTFE), also known as Teflon™, available commercially (Dupont, Wilmington, DE 19898). When assembled, the top vessel section **402** and bottom vessel section **404** define a mixing chamber **408** with an internal diameter of 1.14 inches and a length of 1.75 inches, and an internal volume of approximately 30 mL. Contents of the vessel **420** are stirred with a magnetically coupled Teflon™ stir bar via a standard temperature controlled heating plate. A sapphire observation window **410** available commercially (Crystal Systems, Inc., Salem, MA 01970) is inserted into the top vessel section **402** for observing fluids introduced into the vessel **420** and for inspecting the phase behavior in the mixing solutions. The window **410** has dimensions of about 1-inch in diameter and 0.5 inches in thickness. The vessel sections **402** and **404** and window **410** are assembled and secured in place with a clamp **412** that slidably mounts to close over securing rim edge portions **414** and **416** machined into each of the top **402** and bottom **404** vessel sections,

respectively, thereby effecting a pressure seal within the mixing vessel **420**. The clamp **412** is secured in place via a locking ring **413** positioned and aligned about the perimeter of the clamp **412**.

[0051] The mixing vessel **420** is further configured with a port **418** to the mixing chamber **408** used as an inlet port **418** and a port **419** from the mixing chamber **408** used as an exit port **419**. Fluid flow into the mixing chamber **408** is reversible as ports **418** and **419** may be used interchangeably as exit or inlet ports depending on desired flow direction. Both ports **418** and **419** have dimensions preferably in the range from 0.020 inches I.D. to 0.030 inches I.D.

[0052] The wafer cleaning vessel **440** is comprised of a top vessel section **442** and a bottom vessel section **444** machined preferably of titanium (Ti) metal and lined with a high strength polymer liner **406** to minimize potential of contaminating metals being introduced into the cleaning vessel **440**. When assembled, the top **442** and bottom **444** sections define a wafer cleaning chamber **446**. Sections **442** and **444** are assembled and secured in place with a clamp **412** that slidably mounts to close over securing rim portions **448** and **450** machined into each of the top **442** and bottom **444** vessel sections, respectively, thereby effecting a pressure seal within the cleaning vessel **440**. The clamp **412** is secured in place via a locking ring **413** positioned and aligned about the perimeter of the clamp **412**.

[0053] The cleaning vessel **440** is further configured with an inlet port **452** into the cleaning chamber **446** and an outlet port **454** from the cleaning chamber **440**, each port having dimensions preferably in the range from 0.020 inches I.D. to 0.030 inches I.D. The wafer vessel **440** has an internal diameter of 2.5 inches and a height of 0.050 inches defining a total internal volume of approximately

500 µL. Cleaning fluids are introduced via transfer line **451** from the mixing vessel **420** to the cleaning vessel **440** and into the cleaning chamber **446** through a small inlet hole **456** introduced in the top vessel section **442** through the PEEK™ liner **406**. The top vessel section **442** includes a 0.020 inch vertical channel head space **458** above the wafer surface **400** whereby fluids introduced into the chamber **446** producing a radial flow field that spreads tangentially outward across the wafer **400** surface.

[0054] **FIG. 5** illustrates a complete cleaning system **500** of a benchtop scale design according to the apparatus of the present invention. The mixing vessel **420** is shown in fluid connection with the cleaning vessel **440** via a series of high-pressure liquid chromatography (HPLC) transfer lines **451**. Transfer lines **451** are preferably 0.020 inch I.D. by 1/16-inch O.D. HPLC lines made of PEEK™ available commercially (Upchurch Scientific, Inc., Whidbey Island, WA). Pressure is maintained in the system using a feed pump **505** (for example, a 500 mL model #500-D microprocessor-controlled syringe pump **505** available commercially [ISCO, Inc., Lincoln, NB]) in fluid connection with a tank **507** of ultra-high-purity CO_2.

[0055] A valve **510** (for example, a model 15-15AF1 three-way/two-system combination valve **510** available commercially [High Pressure Equipment Co., Erie, PA 16505]) is inserted in the transfer line **451** leading from the pump **505** forming two independent fluid flow paths **515** and **520**. The first flow path **515** defines a cleaning loop **515** extending from the valve **510** to the inlet port **418** and into the mixing vessel **420**. The second flow path **520** defines a rinsing loop **520** extending from the valve **510** to the inlet port **452** and into the wafer cleaning vessel **440**. A T-fitting **525** (for example, a model P-727 PEEK™ Tee [Upchurch

Scientific, Inc., Whidbey Island, WA]) is inserted in the transfer line **451** of the cleaning loop **515** between the exit port **419** of the mixing vessel **420** and inlet port **452** of the cleaning vessel **440**. The fitting **525** further connects with the transfer line **451** of the rinsing loop **520** bringing the cleaning loop **515** and the rinsing loop **520** into fluid connection whereby cleaning fluid from the mixing vessel **420** or rinsing fluid from the syringe pump **505** may be introduced to the wafer cleaning vessel **440**.

[0056] Further incorporated into the transfer line **451** of the cleaning loop **515** between the exit port **419** and the fitting **525** are two inline filters, a 2 μm pre-filter **530** (for example, a model A-410 HPLC Filter Assembly [Upchurch Scientific, Inc., Whidbey Island, WA]) and a 0.5 μm post filter **535** (for example, a model A-431 HPLC Filter Assembly [Upchurch Scientific, Inc., Whidbey Island, WA]) that prevent potential contaminant metals and/or particulates present in the cleaning fluids from being introduced into the wafer cleaning vessel **440**.

[0057] A straight valve **540** (for example, a model 15-11AF1 two-way straight valve [High Pressure Equipment Co., Erie, PA 16505]) connects via standard 0.020-0.030 inch I.D. PEEK™ transfer line **451** to a second T-fitting **525** and to a waste collection vessel **545** via a "restrictor" segment **555** of PEEK™ transfer line **451** having internal dimensions of approximately 0.005 inch I.D. and a length of from 8 to 12 inches. The T-fitting **525** is further connected via transfer line **451** to the exit port **454** of the cleaning chamber **440** and to a pressure transducer **560** in electrical connection with a pressure readout or display device **570** (for example, a model C451-10,000 combination pressure transducer and pressure display [Precise Sensors, Inc., Monrovia, CA 91016-3315]) for monitoring and reading pressure in the system **500**, and to a rupture disc **565**

(for example, a model 15-61AF1 safety head [High Pressure Equipment Co., Erie, PA 16505]) used as a pressure safety vent.

[0058] As shown in **FIG. 5**, the mixing chamber **420** is further illuminated with an optional light source **575** (for example, a model 190 fiber optic illuminator **570** [Dolan-Jenner, St. Lawrence, MA 01843-1060]). The light source **570** preferably comprises a one foot long positional gooseneck fiber optic and a focusing lens equipped with a 30-watt bulb for focusing and directing light through the observation window **410** into the mixing chamber **408**. An optional high performance camera **580** (for example, a Toshiba model IK-M41F2/M41R2 CCD camera available commercially [Imaging Products Group, Florence, SC 29501]) is also preferably coupled to or used in conjunction with the illuminator **575** and a standard video display **585** to image the mixing chamber **408** and contents.

[0059] Intermixing of the components and/or constituents to form the reactive cleaning fluid is done for about 5 to 10 minutes in the mixing vessel **420** by charging the vessel **420** with pure densified fluid **130** prior to transfer to the cleaning vessel **440**. Pressure is programmed into and maintained by the microprocessor-controlled syringe pump **505**. Metering of fluids from the mixing vessel **420** into the cleaning vessel **440** is initiated by opening the straight valve **540** thereby initiating flow through the restrictor segment **555**. Fluids are discharged at a rate of about 30 mL/min. Each transfer of fluid from the mixing vessel **420** involves about 7 mL of pre-mixed cleaning fluid. Closing of the valve **540** traps cleaning fluid in the cleaning vessel **440** whereby a residence or contact time t_r with the wafer effects cleaning. Rinsing fluids comprising the pure densified solvent for rinsing of the wafer are preferably introduced to the cleaning

vessel **440** via the rinsing loop **520**. Rinsing fluids requiring intermixing with other fluids or solvents may be introduced through the mixing vessel **420** to the cleaning vessel **440** via the cleaning loop **515**. Post-processing examination of the test surfaces was conducted using conventional SEM and/or XPS analysis.

[0060] The following examples are intended to promote a further understanding of the reactive systems of the present invention. Examples 1-4 present four different embodiments of a reactive reverse micelle cleaning system according to the process of the present invention.

EXAMPLE 1

REVERSE MICELLE SYSTEM COMPRISING PERFLUOROPOLYETHER PHOSPHATE SURFACTANT/ALKYL SULFONATE CO-SURFACTANT /WATER.

(Residue Cleaning System)

[0061] **FIG. 6** illustrates a reactive reverse micelle(s) system according to a first embodiment of the present invention. Illustrated is a perfluoro-poly-ether (PFPE) phosphate surfactant/alkyl-sulfonate (AOT) co-surfactant/water system for removing etch residues **650** and non-metal residues **650** found to be tenacious and problematic residues for semiconductor and/or wafer substrate surface processing. This system has very attractive attributes for commercial processing including very low quantities of modifiers, very low volatility, ease of fluid recovery, low toxicity, minimal CD changes, and high speed cleaning. Cleaning occurs preferably in a time below about 15 minutes per wafer on average, and more preferably in less than about 5 minutes.

[0062] The system of the present embodiment comprises reactive reverse micelles **620** or reactive aggregates **620** comprising a PFPE phosphate surfactant **606** and a dialkyl sulfosuccinate (AOT) co-surfactant **612** (e.g., sodium-[bis (2-ethyl-hexyl) sulfosuccinate] or a functional equivalent) in a densified CO_2 continuous phase **630**. The PFPE phosphate surfactant is composed of a phosphate headgroup **602** and a PFPE tail **604**. The AOT co-surfactant **612** is composed of a sulfonic acid or sulfonate head group **608** and a di-alkyl tail **610**. The PFPE phosphate head groups **602** and AOT head groups **608** align in a reactive reverse micelle **620** or reactive aggregate **620** thereby forming the reactive core **614** of the reverse micelle **620**. The PFPE tail **604** and AOT tail **610** of the respective surfactant **606** and co-surfactant **612** provide for the solubility in the densified fluid phase **630**. The reactive reverse micelles **620** or reactive aggregates **620** react with residues **650** on a substrate **600** surface yielding chemically modified residues **655** that are removed or separated from the substrate **600** surface. Depending on resulting state (e.g., polarity, charge, oxidation state, etc.), the modified residues **655** may remain in the densified fluid phase **630** or may reside within the inner polar core **614** of the reactive reverse micelles **620**. The reactive cleaning fluid is maintained at a temperature that ensures a density (ρ) in the fluid medium above the critical density (ρ_c) for pure CO_2.

[0063] **Experimental**. A 30 mL mixing vessel **420** was charged with 0.4 mL (1.3%) perfluoro-poly-ether (PFPE) phosphate acid surfactant **606** (Solvay Solexis, Inc., Thorofare, NJ 08086), 0.15g (0.5%) of sodium AOT sulfonate co-surfactant **612** (Aldrich Chemical Company, Milwaukee, WI 53201), and 25 µL de-ionized, distilled H_2O (0.1%) **614**. As an alternative, ammonium AOT

sulfonate co-surfactant may be substituted for sodium AOT **606**. Solid constituent materials (e.g, surfactants) were added to the bottom vessel section **404** of the mixing vessel **420**; liquid constituents (e.g., H_2O) were subsequently added. The bottom vessel section **404** was subsequently capped with the top vessel section **402** forming the mixing chamber **408**. The sapphire window **410** was inserted into the upper vessel **402** and the vessel clamp **412** and clamping ring **413** were secured in place thereby effecting a pressure seal in the mixing vessel **420**. The mixing vessel **420** was then charged with densified CO_2 **630** via the inlet port **416** and the multi-component fluid was allowed to intermix for about 5 to 10 minutes. The cleaning vessel **440** was also pre-loaded with a commercially processed OSG "no barrier open" (NBO) test wafer coupon **700** (**FIG. 7**) having dimensions in the range from 1 to 1.75 inches on a side and comprising a series of 1 μm pattern vias **725**. Thickness of the wafer **700** was about 725 μm, an industry standard. The cleaning vessel **440** was charged with pure densified CO_2 **630** via the inlet port **452**. Transfer of the reactive cleaning fluid into the mixing vessel **420** was effected via opening of a two-way straight valve **540** in pressure connection with the cleaning vessel **440** thereby initiating flow through the restrictor **555**. Cleaning occurs preferably in a time below about 15 minutes per wafer on average, and more preferably in about 5 minutes or less. In the instant case, the wafer coupon **700** had a contact time t_r in the densified reactive cleaning fluid of about 5 minutes.

[0064] Temperature in the cleaning vessel **440** was maintained at about 20 °C to 25 °C with a pressure of 2900 psi thereby maintaining a density of the fluid mixture above the critical density for the bulk continuous CO_2 fluid (about 0.47 g/cc) **630**. A rinsing fluid comprising pure densified CO_2 fluid was

subsequently introduced to the cleaning vessel **440** through the rinsing loop **520** to aide the removal and recovery of spent reactive cleaning fluid containing the chemically modified substrate residues **655**.

[0065] **Results**. **FIG. 7** shows an SEM micrograph of the surface of an over-etched OSG NBO test wafer substrate **700** cleaned using the reactive reverse micelle cleaning fluid comprising PFPE phosphate **606**/AOT **612**/water **614**. As shown in **FIG. 7**, complete removal of crumbs **330**, mounds **335**, and striations **340** was observed in the post cleaned sample **700** from both the rims and walls of the pattern vias **725**.

EXAMPLE 2

REVERSE MICELLE SYSTEM COMPRISING PERFLUOROPOLYETHER AMMONIUM CARBOXYLATE SURFACTANT/ HYDROXYLAMINE/WATER

(Residue Cleaning System)

[0066] **FIG. 8** illustrates a reactive micelle system according to a second embodiment of the present invention. Illustrated is a PFPE-ammonium carboxylate/hydroxylamine system for removing etch and non-metal residues **850** found to be tenacious and problematic residues for semiconductor substrate and wafer surface processing.

[0067] The system of the instant embodiment comprises reactive reverse micelles **820** or reactive macro-molecular aggregates **820** comprising a fluorinated reverse micelle-forming surfactant, perfluoro-poly-ether (PFPE) ammonium carboxylate **806**, in a densified CO_2 phase **830**. The surfactant **806** comprises a carboxylate headgroup **802** and a perfluoro-poly-ether (PFPE) tail **804**. The carboxylate headgroups **802** align in close proximity to surround and

form the inner polar core **814** of the aggregate **820**. The PFPE tail **804** provides solubility in the densified liquid phase **830**.

[0068] Reactive agents **825** of the instant embodiment are preferably selected from the hydroxylamine class of compounds, hydroxylamine being representative, but not exclusive. Alternatives are preferably selected from the alkanolamine class of compounds, ethanolamine being representative, but not exclusive. The reactive agents **825** in the polar core **814** of the reactive aggregrates **820** react with the residues **850** on a substrate **800** surface chemically modifying them and removing them. Depending on state, the modified residues **855** may reside within the inner polar core **814** of the reactive reverse micelles **620** or alternatively in the densified fluid **830**.

[0069] The instant system has the added benefit of not generating troublesome particulate residues. The ammonium (NH_4^+) counterion as a constituent of the PFPE carboxylate **806** is more easily rinsed from a wafer surface **800** than is sodium ion (Na^+) associated with the surfactant described in Example 1. Concentration of added modifiers (surfactants, co-surfactants, chemical agents, etc.) is preferably below about 30% by volume in the reactive cleaning fluid and more preferably below 2 to 5% by volume for waste minimization, recovery, and/or handling purposes.

[0070] **Experimental**. The PFPE ammonium carboxylate surfactant **806** was prepared for use by chemically derivatizing a pre-surfactant PFPE carboxylic acid surfactant also known as Fluorolink 7004 ™ available commercially (Solvay Solexis, Inc., Thorofare, NJ 08086) using ammonium hydroxide available commercially (Aldrich Chemical Company, Milwaukee, WI 53201) and a molar excess of fluoro-di-chloro-ethane also known as Freon-

113™ available commercially (Alpha-Aesar, Ward Hill, MA 01835). Approximately 30 mL of the Fluorolink 7004 ™ pre-surfactant was mixed in a large beaker under nitrogen gas cover with 20 mL of 25% (by volume in water) ammonium hydroxide, immediately generating a solid paste. The paste was dissolved by addition of about 120 mL of Freon-113™ to the beaker and mixing to a clear solution. The liquid was dried under a nitrogen (N_2) gas purge and cover for approximately one week thereby generating the final PFPE ammonium carboxylate surfactant **806** solid.

[0071] The 30 mL mixing vessel **420** was charged with 1g (3.3%) PFPE ammonium carboxylate **806**, 32 uL of a 50% hydroxylamine solution (Aldrich Chemical Co., Milwaukee, WI 53201) **825** or alternatively 38 µL of a 99% ethanolamine solution **806**. The vessel **420** was charged with pure densified CO_2 **830** at a temperature of about 20 °C to 25 °C and a pressure of 2900 psi and contents were intermixed for a period of from about 5 to 10 minutes thereby forming the reactive cleaning fluid. The 500 µL cleaning vessel **440** was also pre-loaded with a commercially processed OSG NBO test wafer **900** (**FIG. 9**) having dimensions in the range from 1.0 inches to 1.75 inches on a side and further comprising a series of 1 µm pattern vias **925**, a base layer **905** of Cu, and a stop layer **910** of SiC. Thickness of the wafer coupon **900** was an industry standard, about 725 um. The substrate **900** surface was contaminated with quantities of etch and non-metal residues **816**. The cleaning vessel **440** was charged with pure densified CO_2 **830** at a temperature of about 20 °C to 25 °C and pressure of about 2900 psi via the inlet port **452** to maintain density in the fluid **830** above the critical density of pure CO_2 (0.47 g/cc). Transfer of the reactive cleaning fluid into the mixing vessel **420** was effected via opening of a

two-way straight valve **540** in pressure connection with the cleaning vessel **440** thereby initiating flow through the restrictor **555**. Cleaning occurs preferably in a time below about 15 minutes per wafer on average, and more preferably in about 5 minutes or less. In the instant case, the wafer coupon **900** had a contact time t_r in the densified reactive cleaning fluid of about 5 minutes. Temperature in the cleaning vessel **440** was maintained at about 20 °C to 25 °C with a pressure of 2900 psi to maintain a density in the fluid mixture above the critical density for the bulk continuous CO_2 fluid (about 0.47 g/cc) **830**. A rinsing fluid preferably containing pure densified CO_2 fluid **830** was subsequently introduced to the cleaning vessel **440** through the rinsing loop **520** to remove the spent reactive cleaning fluid containing the chemically modified substrate residues **855**.

[0072] **Results**. **FIG. 9** shows an SEM micrograph for the cleaned surface of the over-etched OSG "no barrier open" (NBO) test coupon **900**. As shown in **FIG. 9**, no etch residues (e.g., crumbs or striations) were observed on the rims and/or walls of the pattern via **925** following cleaning, showing the successful removal of residues from the wafer **900** surface. Maximum removal of residues was accomplished in this system in about 5 minutes or less on average.

[0073] The instant embodiment has been shown to be a reactive system given that chemical agent(s) in the densified medium react and chemically modify residues **816** removing them from the surface. Hydroxylamine **825**, for example, is corrosive with many plastics, organic acids, and esters and serves to hydrolyze Si-X bonds from the surface substrates. Hydroxylamine **825** may also produce hydroxide that chemically aides in the cleaning process. Results show the reactive agents **825** of the instant system in combination effectively remove

surface etch residues **855** to a commercial level of clean satisfactory for semiconductor processing. Overall, the system exhibits attractive commercial processing attributes, including low quantities of modifiers (less than about 3 to 5% by volume total), relatively low volatility lending to ease of recovery of system constituents, low toxicity, minimal CD change, and high speed cleaning (less than about 5 minutes on average).

[0074] It should be noted that the presence of a reverse micelle forming surfactant **806** is not sufficient or effective alone in removing residues **850**. Further, hydroxylamine is not soluble in the neat densified CO_2. It is the combination of constituents in the system that effects removal of residues **850**. Direct contact with, and reaction between, the reactive reverse micelles **820**, the reactive chemical agent(s) **825** and residues **855** of interest is critical.

EXAMPLE 3

REVERSE MICELLE SYSTEM COMPRISING FLUOROCARBON PHOSPHATE ACID SURFACTANT/ALKYL SULFONATE CO-SURFACTANT/ BENZOTRIAZOLE (BTA)/ WATER.

(Metal Residue Cleaning System)

[0075] In a third embodiment of the present invention, a surfactant/co-surfactant/corrosion inhibitor/water system has been shown to be effective for removing metal residues (e.g., Cu, Fe, Al, etc.) found to be tenacious and problematic residues for semiconductor (e.g., silicon) substrate and wafer surface processing. The instant system has very attractive attributes for commercial processing including very low quantities of modifiers, very low

volatility, ease of fluid recovery, low toxicity, minimal CD changes, and high speed cleaning (less than about 5 minutes per wafer on average).

[0076] Testing was conducted on a porous low-K dielectric (LKD) "barrier-open" (BO) wafer coupon **600** (e.g., LKD BO) having significant levels of copper residue **650**. The system of the present embodiment is composed of reactive reverse micelle(s) **620** or reactive aggregates **620** comprising a perfluoro-poly-ether (PFPE) phosphate surfactant **606** having a phosphate headgroup **602** and a PFPE tail **604** and a [bis (2-ethyl-hexyl) sulfosuccinate] (e.g., sodium AOT acid sulfonate) co-surfactant **612** having a sulfonic acid or sulfonate headgroup **608** and a dialkyl (e.g., 2-ethyl-hexyl) tail **610**, all present in a densified CO_2 continuous phase **630**. In the present embodiment, a corrosion inhibitor was also added to the fluid system to passivate the base metal layer (e.g., Cu) of the BO substrate **600**. The phosphate head groups **602** and/or sulfonic head groups **608** react with metal residues **650** to yield chemically modified surface residues **655** that are removed from the substrate **600** and may reside in the reverse-micelle core **614** and/or in the densified fluid **630**. For example, chemical oxidation of metal residues **650** such as Cu(0) and/or Cu(I) that yield chemically modified residues **655** such as Cu(I) and/or Cu(II), when removed from the surface of the substrate **600** may migrate to the inner micellar core **614** where head groups **602** and **608** in the reactive aggregate **620** can bind or complex with the modified residues **655**.

[0077] **Experimental**. A 30 mL mixing vessel **420** was charged with 0.4 mL (1.3%) perfluoro-poly-ether (PFPE) phosphate acid surfactant **606** (Solvay Solexis, Inc., Thorofare, NJ 08086), 0.15g (0.5%) of sodium AOT sulfonate co-surfactant **612** (Aldrich Chemical Company, Milwaukee, WI 53201), 25 µL de-

ionized, distilled H_2O (0.1%), and 5 mg 99% BTA (Aldrich Chemical Co., Milwaukee, WI 53201), or alternatively 0.023g (0.1%) 95% catechol (Aldrich Chemical Co., Milwaukee, WI 53201). As an alternative, ammonium AOT sulfonate co-surfactant may be substituted for the sodium AOT **606**. Solid constituent materials (e.g, surfactant) were added to the bottom vessel section **404**; liquid constituents (e.g., H_2O) were subsequently added. The bottom vessel section **404** was subsequently capped with the top vessel section **402** forming the mixing chamber **408**. The sapphire window **410** was inserted into the upper vessel portion **402** and the vessel clamp **412** and clamping ring **413** were secured in place on the mixing vessel **420** thereby effecting a pressure seal in the vessel **420**. The vessel **420** was then charged with densified CO_2 **630** via the inlet port **416** and the multi-component fluid was allowed to intermix for about 5 to 10 minutes. The cleaning vessel **440** was also pre-loaded with a commercially processed test wafer **100** of a barrier-open (BO) type having dimensions in the range from 1 to 1.75 inches on a side. Thickness was an industry standard of about 725 μm. The cleaning vessel **440** was charged with pure densified CO_2 **630** via the inlet port **452**. Transfer of the reactive cleaning fluid into the mixing vessel **420** was effected by opening a two-way straight valve **530** in pressure connection with the cleaning vessel **440** thereby initiating flow through the restrictor **555**. Cleaning occurs preferably in a time below about 15 minutes per wafer on average, and more preferably in about 5 minutes or less. In the instant case, the wafer coupon **600** had a contact time t_r in the densified reactive cleaning fluid of about 5 minutes. Temperature in the cleaning vessel **440** was maintained at about 20 °C to 25 °C with a pressure of 2900 psi to

ensure a density in the reactive cleaning mixture or fluid above the critical density for CO_2 of about 0.47 g/cc.

[0078] A rinsing fluid comprising about 5% iPrOH by volume in the densified CO_2 fluid was preferably introduced to the cleaning vessel following residue removal to aide the recovery of the spent cleaning fluid containing modified residues **655** from the wafer surface **600**.

[0079] **Results**. Table 1 presents XPS analysis results for residual copper for an OSG BO test wafer coupon **600** following cleaning using the PFPE phosphate/alkyl sulfonate/BTA/water system including rinsing with a rinsing fluid comprising 5% iPrOH in densified CO_2.

TABLE 1. XPS surface analysis results for residual copper for a OSG BO wafer coupon following cleaning with a reactive reverse-micelle system comprising PFPE phosphate/AOT/BTA/water including a rinse with 5% iPrOH in densified CO_2, according to a third embodiment of the present invention.

Clean Type	Wafer Type	XPS Surface, Cu (atoms/cm^2)
Untreated	OSG BO	1.0 E+13
Reactive Reverse Micelle-Treated	OSG BO	4.0 E+11

[0080] A residue concentration below about 2 X 10^{12} atoms/cm^2 is considered viable for commercial wafer processing by current semiconductor industry standards. As shown in Table 1, copper residues on the test substrate **600** were reduced to about 4 X 10^{11} atoms/cm^2, substantially below the industry standard for metal residue cleaning showing the present system to be efficacious at removing metal residues **650**. Maximum removal of metal residues **650** was accomplished in this system in about 5 minutes or less on average. In addition, results showed the base metal layer (e.g., Cu) of the BO substrate **600** was

preserved by addition of the corrosion inhibitor as a modifier in the instant system.

[0081] The instant system has been shown to be a reactive system given that chemical agent(s) in the densified medium react with substrate residues chemically modifying and removing them from the surface. Results further show the reactive constituents of the instant system in combination effectively remove surface residues to a commercial level of clean, including preservation of the substrate layers, satisfactory for semiconductor processing. Concentration of added modifiers including surfactants, water, hydroxylamine, etc. is preferably below about 30% by volume in the reactive cleaning fluid and more preferably below about 2 to 5% by volume for waste minimization and/or handling purposes.

[0082] Again, it should be noted that the presence of a reverse micelle forming surfactant is not sufficient or effective in removing residues alone. It is the combination of constituents in the system that effects removal of residues. Direct contact with, and reaction between, the reactive reverse micelles, the reactive chemical agent(s) and the residues of interest is critical.

EXAMPLE 4

REVERSE MICELLE SYSTEM COMPRISING PERFLUOROPOLYETHER CARBOXYLATE SURFACTANT/HYDROXYLAMINE/WATER

(Metal Residue Cleaning System)

[0083] In a fourth embodiment of the present invention, cleaning and removal of tenacious metal residues (e.g., Cu, Al, Fe, etc.) has been

demonstrated using a perfluoro-poly-ether (PFPE) ammonium carboxylate surfactant/hydroxylamine/water system, as detailed herein below.

[0084] The system of the instant embodiment comprises a fluorinated hydrocarbon surfactant **806** of PFPE-ammonium carboxylate **806** having a carboxylate headgroup **802** and a PFPE tail **804** in a densified CO_2 phase **830**. Again, the NH_4^+ counterion for the salt is preferred as it is more easily rinsed from the wafer surface than is Na^+ ion. The fluorinated hydrocarbon surfactant **806** forms macro-molecular reactive aggregates **820** or reactive reverse micelles **820** in the densified CO_2 medium **830** wherein the carboxylate headgroups **802** align in close proximity to surround and form the inner polar core **814** of the reactive aggregates **820**. The PFPE tail **804** provides solubility in the densifed fluid **830**. Dimensions of the inner core **814** and reactive aggregates **820** are defined primarily by the presence of the trace quantities of reactive constituents or agents **825** residing within the polar core **814**. Depending on state, reactive agents **825** may also reside within the bulk densified fluid **830**.

[0085] In the instant example, reactive agents **825** present in the polar core **814** of the reactive aggregrates **820** react with metal residues **850** of interest yielding chemically modified residues **855** which are removed from the substrate surface **800**. Depending on the resulting state, modified residues **855** may reside in the polar reverse-micelle core **814** or alternatively in the densified fluid **830**. Reactive agents **825** of the instant embodiment are preferably selected from the amine class of compounds, hydroxylamine being representative, but not exclusive. Alternatives are preferably selected from the alkanolamine class of compounds, ethanolamine being representative, but not exclusive. Concentration of added modifiers (surfactants, co-surfactants,

chemical agents, etc.) is preferably below about 30% by volume in the reactive cleaning fluid and more preferably below 2 to 5% by volume for waste minimization, recovery, and/or handling purposes.

[0086] **Experimental**. The PFPE ammonium carboxylate surfactant **806** was prepared for use as in Example 2 above. The 30 mL mixing vessel **420** was charged with 1g (3.3%) PFPE ammonium carboxylate surfactant **806**, 32 uL of a 50% hydroxylamine solution (Aldrich Chemical Co., Milwaukee, WI 53201) **825** or alternatively 38 µL of a 99% ethanolamine solution. No corrosion inhibitor was added in the current system. Contents of the vessel **420** were intermixed for a period of from 5-10 minutes by charging with pure densified CO_2 **830** at a temperature of about 20 °C to 25 °C and pressure of 2900 psi thereby forming the reactive cleaning fluid. The 500 µL cleaning vessel **440** was also pre-loaded with an over-etched commercially processed LKD "barrier open" (BO) test wafer **100** (e.g., LKD BO) having dimensions in the range from 1.0 inches to 1.75 inches on a side. The surface was contaminated with quantities of metal residues **850** (e.g., Cu). Thickness of the wafer coupon **800** was an industry standard of about 725 µm. The cleaning vessel **440** was charged with pure densified CO_2 **830** at a temperature of about 20 °C to 25 °C and pressure of 2900 psi via the inlet port **452** to maintain density in the fluid above the critical density of pure CO_2 (0.47 g/cc). Transfer of the reactive cleaning fluid into the mixing vessel **420** was effected via opening of a two-way straight valve **530** in pressure connection with the cleaning vessel **440** thereby initiating flow through the restrictor **555**. The wafer coupon **800** had a contact time t_r in the densified reactive cleaning fluid of about 5 minutes or less. Temperature in the cleaning vessel **440** was maintained at about 20 °C to 25 °C with a pressure of 2900 psi to

ensure a density in the fluid mixture above the critical density for CO_2 of about 0.47 g/cc. The wafer substrate **800** was rinsed from 2 to 5 times with a rinsing fluid comprising the densified CO_2 fluid to ensure complete removal of the reactive cleaning fluid containing the modified residues **855** cleaned from the wafer surface **800**.

[0087] **Results**. Table 2 presents XPS analysis results for residual copper for a LKD BO ("barrier open") test coupon **800** cleaned using the PFPE ammonium carboxylate/hydroxylamine system.

TABLE 2. XPS surface analysis for residual copper of a LKD BO wafer coupon following cleaning with a reactive reverse-micelle system comprising PFPE-ammonium carboxylate/hydroxylamine according to a fourth embodiment of the present invention.

Clean Type	Wafer Type	XPS Surface, Cu (atoms/cm^2)
Untreated	LKD BO	6.4 E+12
Reactive Reverse Micelle-Treated	LKD BO	1.0 E+12

[0088] A residue concentration below about 2 X 10^{12} atoms/cm^2 is considered viable for commercial wafer processing by current semiconductor industry standards. As shown in Table 2, copper residues in the test substrate were reduced to about 1 X 10^{12} atoms/cm^2, evidence of the viability of the instant embodiment for commercial wafer processing. As in Example 3, results further showed the base metal layer (e.g., Cu) of the BO substrate **800** was preserved by addition of the corrosion inhibitor as a modifier in the instant system. Maximum removal of metal residues was accomplished in about 5 minutes or less on average.

[0089] The instant system has been shown to be a reactive system given that chemical agent(s) in the densified medium react with substrate residues chemically modifying and removing them from the surface. Results further show the reactive constituents of the instant system in combination effectively remove surface residues to a commercial level of clean, including preservation of the substrate layers, satisfactory for semiconductor processing. Results further show a corrosion inhibitor is not required to achieve an effective level of cleaning. Overall, results show this system exhibits attractive commercial processing attributes, including low quantities of modifiers, relatively low volatility of constituents lending to ease of recovery from the bulk fluid, low toxicity, minimal CD change, and high speed cleaning (about 5 minutes on average or less).

[0090] As with the other system embodiments presented herein, the presence of a reverse micelle forming surfactant is not sufficient or effective in removing residues alone. It is the combination of constituents in the system that effects removal of residues. Direct contact with, and reaction between, the residues of interest, the reactive reverse micelles, and the reactive chemical agent(s) is critical.

[0091] While the preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the spirit and scope of the invention.

CLAIMS

WE CLAIM:

1. A process for removing residues from a semiconductor substrate, comprising the steps:

providing a densified fluid wherein said fluid is a gas at standard temperature and pressure and wherein the density of the fluid is above the critical density;

providing a cleaning component;

intermixing said densified fluid and said cleaning component whereby a reactive cleaning fluid is formed comprising reactive reverse-micelle(s) or reactive aggregates; and contacting a residue on a substrate with said reactive cleaning fluid for a contact time t_r whereby said residue is chemically modified and removed from said substrate.

2. The process according to claim 1, wherein said cleaning component is selected from the group consisting of at least one reverse micelle-forming surfactant, at least one reverse micelle-forming co-surfactant, at least one reactive reverse micelle-forming surfactant or reactive reverse micelle-forming co-surfactant, at least one reactive chemical agent, and combinations thereof.

3. The process according to Claim 2, wherein said co-surfactant is an alkyl acid phosphate, alkyl acid sulfonate, alkyl alcohol, substituted alkyl alcohol, perfluoroalkyl alcohol, dialkyl sulfosuccinate, bis-(2-ethyl-hexyl) sulfosuccinate,

AOT, sodium AOT, ammonium AOT, derivatives, salts, and functional equivalents thereof.

4. The process according to Claim 2, wherein said co-surfactant is a non-CO_2-philic surfactant used in conjunction with a CO_2-philic surfactant.

5. The process according to Claim 1, further comprising the step of rinsing said substrate with a densified rinsing fluid comprising up to about 30% modifiers by volume.

6. The process according to Claim 5, wherein said rinsing fluid is the pure densified fluid.

7. The process according to Claim 5, wherein said rinsing fluid is a mixture of densified CO_2 and a modifier selected from the group consisting of iPrOH, H_2O, MeOH, EtOH, or combinations thereof.

8. The process according to Claim 7, wherein said rinsing fluid comprises up to about 15% by volume iPrOH.

9. The process of Claim 1, wherein said densified fluid is a liquid with a temperature from about 20 °C to 25 °C inclusive, a pressure from about 850 psi to 3000 psi inclusive, and a density above a critical density for the densified fluid.

10. The process according to Claim 1, wherein said chemical modification of said residue comprises at least one reaction selected from the group consisting of chemical, oxidation, reduction, molecular weight reduction, fragment cracking, exchange, association, dissociation, or combinations thereof whereby dissolution, solubilization, complexation, or binding of residues occurs whereby said residues are removed from said substrate.

11. The process according to Claim 1, wherein said reactive cleaning fluid has a reduced density in the range from about 1 to 3 inclusive.

12. The process according to Claim 1, wherein said reactive cleaning fluid has a temperature and pressure above the critical temperature and critical pressure of said densified fluid.

13. The process according to Claim 1, wherein said densified fluid is a member selected from the group consisting of carbon dioxide, chlorodifluoromethane, ethane, ethylene, propane, butane, sulfur hexafluoride, ammonia, and combinations thereof.

14. The process according to Claim 1, wherein said reverse micelle forming surfactant is a member selected from CO_2-philic, anionic, cationic, non-ionic, zwitterionic, and combinations thereof.

15. The process according to Claim 14, wherein said anionic reverse-micelle forming surfactant is selected from the group consisting of PFPE surfactants,

PFPE carboxylates, PFPE sulfonates, PFPE phosphates, alkyl sulfonates, bis-(2-ethyl-hexyl) sulfosuccinates, sodium bis-(2-ethyl-hexyl) sulfosuccinate, ammonium bis-(2-ethyl-hexyl) sulfosuccinate, fluorocarbon carboxylates, fluorocarbon phosphates, fluorocarbon sulfonates, and combinations thereof.

16. The process according to Claim 14, wherein said cationic reverse-micelle forming surfactant is selected from the tetraoctylammonium fluoride class of compounds.

17. The process according to Claim 14, wherein said non-ionic reverse-micelle forming surfactant is selected from the poly-ethyleneoxide-dodecyl-ether class of compounds.

18. The process according to Claim 14, wherein said zwitterionic reverse-micelle forming surfactant is selected from the alpha-phosphatidyl-choline class of compounds.

19. The process of Claim 1, wherein said reactive chemical agent is selected from the group consisting of mineral acids, fluoride-containing compounds and acids, organic acids, oxygen-containing compounds, amines, alkanolamines, peroxides, chelates, ammonia, and combinations thereof.

20. The process according to Claim 19, wherein said mineral acids are selected from the group consisting of HCl, H_2SO_4, H_3PO_4, HNO_3, HSO_4^-, H_2PO_4, HPO_4^{2-},

phosphate acids, acid sulfonates, their dissolution products, their salts, and combinations thereof.

21. The process according to Claim 19, wherein said fluoride-containing compounds and acids are selected from the group consisting of F_2, HF, dilute HF, UdHF, and combinations thereof.

22. The process according to Claim 19, wherein said organic acids are selected from the group consisting of sulfonic acids, phosphate acids, phosphate esters or their salts, their substituted derivatives, and combinations thereof.

23. The process according to Claim 19, wherein said oxygen-containing compounds are selected from the group consisting of O_2, ozone, functional or reactive equivalents, and combinations thereof.

24. The process according to Claim 19, wherein said alkanolamine is an ethanolamine.

25. The process according to Claim 19, wherein said amine is hydroxylamine.

26. The process according to Claim 19, wherein said chelate is a member of the group consisting of pentanediones; 2,4 pentanediones; phenanthrolines; 1,10 phenanthroline; EDTA, sodium EDTA, oxalic acid, or combinations thereof.

27. The process according to Claim 19, wherein said peroxides are selected from the group consisting of organic peroxides, alkyl peroxides, t-butyl peroxides, hydrogen peroxide, substituted derivatives, and combinations thereof.

28. The process in accordance with Claim 1, wherein said reactive cleaning fluid comprises up to about 30% by volume of reactive reagents and/or modifiers.

29. The process in accordance with Claim 28, wherein said reactive cleaning fluid comprises about 2 to 5% modifiers by volume including PFPE acid phosphate, AOT, H_2O, or combinations thereof.

30. The process in accordance with Claim 28, wherein said reactive cleaning fluid comprises about 3 to 5% modifiers by volume including PFPE carboxylate, alkanolamines, hydroxylamine, H_2O, or combinations thereof.

31. The process in accordance with Claim 28, wherein said reactive cleaning fluid further comprises a corrosion inhibitor having a concentration in the range from about 0.1% to 1% inclusive by volume.

32. The process in accordance with Claim 31, wherein said corrosion inhibitor is selected from the group of benzotriazoles; 1,2,3-benzotriazole; catechols; catechol; 1,2-di-hydroxy-benzene; 2-(3,4-di-hydroxy-phenyl)-3,4-di-hydro-2H-1-benzopyran-3,5,7-triol, substituted derivatives, and combinations thereof.

33. The process according to Claim 28, wherein said reactive cleaning fluid further comprises about 5% modifiers by volume including PFPE carboxylates, amines, alkylamines, hydroxylamine, benzotriazoles, catechols, and combinations thereof.

34. The process of Claim 1, wherein time t_r is about 15 minutes inclusive.

35. The process of Claim 1, wherein time t_r is less than about 5 minutes.

36. The process of Claim 1, wherein said residue is selected from the group consisting of organic residues, metal residues, etch residues, non-metal residues, polymeric residues, and combinations thereof.

37. The process of Claim 1, wherein said residue is a transition metal.

38. The process of Claim 1, wherein said residue is selected from the group consisting of Cu, Al, Fe, Ta, and combinations thereof.

39. The process of Claim 1, wherein said reactive cleaning fluid has a temperature of about 20 °C to 25 °C, a pressure of about 850 to 3000 psi, and a fluid density above the critical density of the densified fluid.