APPARATUS FOR CONTAMINATION REMOVAL USING MAGNETIC PARTICLES

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ABSTRACT

Methods and apparatus are provided for cleaning a substrate (e.g., wafer) in the fabrication of semiconductor devices utilizing a composition of magnetic particles dispersed within a base fluid to remove contaminants from a surface of the substrate.
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CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a divisional of U.S. patent application Ser. No. 12/483,518, filed Jun. 12, 2009, pending, the disclosure of which is hereby incorporated herein in its entirety by this reference.

TECHNICAL FIELD

[0002] Embodiments of the invention relate to methods and apparatuses for cleaning surfaces of a substrate.

BACKGROUND OF THE INVENTION

[0003] A common occurrence during semiconductor device fabrication is the accumulation of particulate contaminants on semiconductor device surfaces. Various processes and cleaning solutions have been used for the removal of small residual particles and other contaminants from surfaces, such as a wafer surface in the fabrication of semiconductor-based structures and devices. A post-process clean is typically conducted to remove contaminants remaining on a surface after a processing step such as etching, planarization, polishing, sawing, film deposition, etc., prior to performing another device fabrication step such as a metallization, gate or device formation, etc. If residues or contaminants remaining from a process step are not effectively removed, various fabrication problems and defects in the finished integrated circuit device can result. For example, metal contaminants that remain on a surface feature can cause shorts between capacitor electrodes or other electrical failures, and non-conductive contaminants on a feature such as particles (e.g., SiO₂, polysilicon, nitride, polymers, etc.) remaining after a chemical-mechanical planarization or polishing (CMP) or other process can cause the failure in adhesion of subsequent layers, a loss of critical dimension of the formed feature, or pattern deformation in that area leading to yield loss. Current technology nodes (e.g., 65 nm and smaller) require a high level of surface cleaning, including the removal of remnant particles, residues and other contaminants while maintaining other surface materials intact.

[0004] One example of a known cleaning technique used to remove unwanted surface materials is an RCA clean, which conventionally includes first applying an aqueous alkaline cleaning solution known as a Standard Clean 1 (SC1) to remove particle contaminants. SC1 typically consists of a dilution of ammonium hydroxide/hydrogen peroxide (NH₄OH/H₂O₂) followed by a deionized (DI) water rinse. An example of a cleaning technique to remove metal contaminants is an aqueous acidic cleaning solution known as a Standard Clean 2 (SC2) composed of a hydrochloric acid/hydrogen peroxide (HCl/H₂O₂) dilution followed by a second DI water rinse. Other wet cleaning methods used for cleaning residues from structures include, for example, a piranha clean using a sulfuric acid-based mixture (e.g., H₂SO₄/H₂O₂), a buffered oxide etch solution, and fluoride-based aqueous chemistries.

[0005] Small particles or other contaminants resulting from fabrication steps can be held to a surface by electrostatic and/or other forces and can become adhered, typically requiring relatively large forces to remove them. Cleaning solutions are often applied in conjunction with acoustic energy (i.e., ultrasonic or megasonic energy), high pressure spraying techniques, mechanical scrubbing techniques with a pad or brush, etc., to enhance the cleaning action of the solution. However, acoustic cleaning and spraying techniques apply cleaning forces in a manner that is difficult to control, which can cause damage to surface structures or alter critical dimensions without effectively removing all of the particulate contaminants from the substrate. In addition, many cleaning solutions can attack and/or dissolve the structures formed in the fabrication step.

[0006] Other techniques involve forcing solid particles (e.g., salts of fatty acid solids, paraffin, wax, polymers, etc.) dispersed within a continuous phase to a substrate surface to disengage surface contaminants, which can damage to line elements and other surface structures. For example, some techniques apply a chemical or foam that contains salts of fatty acid solids (e.g., crystals of stearic acid salts) by dispensing from a rotary head or proximity cleaning head. However, stearic acid crystal size and its velocity in a dynamic foam are difficult to control, resulting in damage to surface structures (e.g., line elements) by poorly controlled parameters within the foam.

[0007] It would be desirable to provide a process for removing contaminants from a surface without adversely affecting structures and/or surface materials on a substrate that overcomes these problems.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Embodiments of the present disclosure are described below with reference to the following accompanying drawings, which are for illustrative purposes only. Throughout the following figures, reference numerals will be used in the drawings, and the same reference numerals will be used throughout the several figures and in the description to indicate same or like parts.

[0009] FIG. 1 is a diagrammatic elevational cross-sectional view of an apparatus for removing contaminants from a substrate according to an embodiment of the invention.

[0010] FIG. 2 is a cross-sectional view of the apparatus shown in FIG. 1 at a subsequent processing stage showing the application of a magnetic field; FIG. 2A is a top plan view of the apparatus of FIG. 2, taken along line 2A-2A.

[0011] FIG. 3 is a diagrammatic top plan view of an apparatus for removing contaminants from a substrate according to another embodiment of the invention, showing multiple magnetic field generators positioned about a containment vessel.

[0012] FIG. 4 is a diagrammatic elevational cross-sectional view of an apparatus for removing contaminants from a substrate according to another embodiment of the invention, showing magnetic field generators situated at each side, above and/or below a containment vessel.

[0013] FIG. 5 is a cross-sectional view of the apparatus shown in FIG. 2 at a subsequent processing stage.

[0014] FIG. 6 is a cross-section view of the substrate shown in FIG. 5 at a subsequent processing stage.

[0015] FIG. 7 is diagrammatic elevational cross-sectional view of an apparatus for removing contaminants from a substrate according to another embodiment of the invention; FIG. 7A is a top plan view of the apparatus of FIG. 7, taken along line 7A-7A.
DETAILED DESCRIPTION

[0016] The following description, with reference to the drawings, provides illustrative examples of apparatus and methods according to embodiments of the present disclosure. Such description is for illustrative purposes only and not for purposes of limiting the same.

[0017] The terms “wafer” and “substrate” are interchangeable and are to be understood as a semiconductor-based material including silicon, silicon-on-insulator (SOI) or silicon-on-sapphire (SOS) technology, doped and undoped semiconductors, epitaxial layers of silicon supported by a base semiconductor foundation, and other semiconductor structures. Furthermore, when reference is made to a “wafer” and/or “substrate” in the following description, previous process steps may have been utilized to form regions or junctions in or over the base semiconductor structure or foundation. Additionally, when reference is made to a “substrate assembly” in the following description, the substrate assembly may include a wafer with materials including dielectrics and conductors, and features such as transistors, formed thereon, depending on the particular stage of processing. In addition, the semiconductor need not be silicon-based, but may be based on silicon-germanium, silicon-on-insulator, silicon-on-sapphire, germanium, or gallium arsenide, among others.

[0018] Embodiments of the invention, the composition is a fluid suspension composed of magnetic particles dispersed in a carrier or base fluid that is chemically compatible with the materials to be treated. In embodiments, the carrier fluid is a continuous phase selected so as not to damage or adversely affect surface materials and/or structures situated on a substrate, with suitable chemical and thermal stability over the temperature range of the application. The carrier fluid should have a wide temperature range with a low freezing point and a high boiling point (e.g., from about 40°C to about 400°C). The pH of the composition can be from about 1 to about 13, or any value or sub-range therebetween.

[0019] The carrier fluid can be an aqueous solution, for example, water or a buffer such as saline, phosphate, borate, acetate, citrate, carbonate, bicarbonate or other buffer, with a pH of about 3-11, or a value or sub-range therebetween. In other embodiments, the carrier fluid can be water with appropriate surfactants to stabilize the magnetic particles in suspension.

[0020] In other embodiments, the carrier fluid can be a non-aqueous liquid, including, for example, silicone oils such as polyalkyl, polyaryl, polyalkoxy, or polyaryloxy/siloxane oils and silicone oils (e.g., polydimethyl siloxanes, liquid methyl phenyl silicones, tetraethyl silicate, etc.); mineral oils; vegetable oils (e.g., sunflower oil, rapeseed oil, soybean oil, etc.); hydrocarbons including paraffin oils, naphtha lenes, chlorinated paraffins, olefin oligomers and hydrogenated olefin oligomers (e.g., polysiloxylene, ethylene-propylene copolymers, etc.); polyphenylethers; polyesters (e.g., perfluorinated polyesters, etc.); dibasic acid esters; neopen tylpolyl esters; phosphate esters; glycol esters and ethers (e.g., polyalkylene glycol, etc.); aromatic-type oils (e.g., benzoic acid, phthalic acid, etc.); alkyne oxide polymers and inter polymers, and derivatives thereof (e.g., methylpolyisopropylene glycol, etc.); carbon tetrachloride; fluorocarbons; chlorofluorocarbons; ketones; and alcohols, among others.

[0021] The carrier fluid should have a viscosity that permits movement of the magnetic particles within the suspension when applied to a substrate in the presence of a magnetic field. The viscosity of the carrier fluid can be varied according to the type and concentration of the magnetic particles from a relatively low viscosity carrier fluid, such as isopropyl alcohol (IPA), acetone and propanol, to a relatively high viscosity carrier fluid, such as an ethylene glycol/sulfuric acid mixture. The viscosity of the carrier fluid can be determined according to known techniques, for example, using a viscometer.

[0022] The magnetic particles are typically composed of a ferromagnetic, ferrimagnetic, paramagnetic, or superparamagnetic material combined with and/or coated with a material that is functionalized to have surface functional reactive groups to bind with or repel contaminants on the surface of a substrate. The composition of the magnetic particles determines characteristics including hydrophobic/hydrophilicity and charge (positive/negative), which can affect coupling to or repulsion of contaminants.

[0023] Methods for producing magnetic particles are known in the art, as described, for example, in U.S. Pat. No. 5,091,206 to Wang et al. (assigned to Baxter Diagnostics Inc.), U.S. Pat. No. 6,133,047 to Elaisiari et al. (assigned to Bio Merieux), U.S. Pat. No. 6,682,660 to Sucholelki et al. (assigned to MDS Proteomics, Inc.), U.S. Pat. No. 7,186,398 to Andres et al. (assigned to Purdue Research Foundation), and U.S. Pat. No. 7,214,427 to Huang et al. (assigned to Aviva Biosciences Corporation).

[0024] In embodiments of the invention, the magnetic particles can be composed of a magnetic material dispersed in a polymer matrix that includes ligands or reactive functional groups presented on the surface of the magnetic particle such that binding moieties are available for interaction with a target contaminant(s). In other embodiments, the magnetic material can be combined with a polymeric material, ceramic material, semiconductor material, etc., to form a core particle and then surface coated with a polymeric material that provides surface reactive functional groups.

[0025] In another embodiment, a magnetic material (e.g., metal oxide) can be mixed with monomer(s) and coated onto a polymeric core particle (e.g., polystyrene particles), ceramic material core particle, semiconductor material core particle, etc., which can be coated with a layer of functionalized polymer to provide functional groups such as carboxyl, amino or hydroxyl groups for covalent coupling of contaminant materials. Magnetic particles (or core particles) can be overcoated with the same or a different polymer than used for forming a polymer/magnetic material core particle. In yet other embodiments, a magnetic material (e.g., a metal oxide) can be formed as a core particle and coated with a polymeric material that provides surface reactive functional groups.

[0026] Non-limiting examples of magnetic materials that can be utilized include iron, iron oxides, iron nitrides, iron carbides, silanized iron oxides, carbonyl iron, chromium dioxide, low carbon steel, silicon steel, nickel, cobalt, etc., or combinations or alloys of such materials, for example, Fe—Co compounds and alloys (e.g., CoFe), Fe—Ni compounds and alloys (e.g., Ni8Fe), Mn—Zn ferrite, Ni—Zn ferrite, AlNiCo alloys, and ceramic ferrites such as magnetite (Fe3O4), maghemite (Fe2O3) magnesiomerite (MgFe2O4), jacobite (MnFe2O4), trevorite (NiFe2O4), pyrohite (Fe3(Fe2+ + Si)O8(Si = 0 to 0.2)), greigite (Fe[II]Fe[III])3S4, and rare earth magnets such as neodymium magnet (NdFeB magnet or Neo magnet) and samarium cobalt magnet alloys (generally SmCo5), etc., among others.

[0027] The reactive functional groups can be incorporated onto the surface of the magnetic particles, for example, by using a functionalized monomer or a mixture of monomers
and functionalized monomers with a magnetic material during formation of magnetic particles composed of a polymeric and magnetic material. In other embodiments, a magnetic material or a polymer/magnetic material core particle can be coated with a thin layer of functionalized monomer (or monomer/functionalized monomer mixture) to form a polymeric outer layer. Inclusion of an effective amount or percentage of functionalized monomers can eliminate adding materials having functionalized groups after formation of the particles.

[0028] Polymeric materials can be produced using monomers having reactive functional groups including, for example, groups containing C—O bonds, such as carboxyl groups, aldehyde groups, carbonyl (ketone) groups, ether groups, ester groups, peroxy groups, etc.; hydroxyl functional groups; hydrazide functional groups; hydrocarbon functional groups, such as alkyl (methyl) groups, alkyl (alkene) groups, alkynyl (alkyne) groups, vinyl groups, phenyl groups, benzyl groups, etc.; nitrogen-containing functional groups, such as amide groups, amine (amino) groups, imine groups, azo groups, nitrile (cyan) groups, nitro groups, nitroso groups, pyridyl groups, isocyanate groups, isothiocyanate groups, etc.; functional groups containing a carbon-halogen bond, such as halide groups, fluoro groups, chloro groups (e.g., chloromethyl groups), etc.; sulfur-containing functional groups, such as sulfite groups, etc.; and groups containing phosphorus and sulfur, such as phosphodiester groups, sulfoxyl (thiol) groups, phosphorus sulfide groups, etc.; and combinations thereof.

[0029] The polymeric material can be produced by conventional methods including emulsion polymerization, suspension polymerization or other polymerization process, with or without the use of a cross-linking agent (e.g., divinyl benzene, etc.). Monomers that can be utilized to produce the polymeric material include vinyl monomers such as styrene, vinyl toluene, and substituted styrenes (e.g., chloromethyl styrene), acrylates and methacrylates (e.g., methylmethacrylate, 2-hydroxyethyl methacrylate, 2-aminoethyl methacrylate, etc.), among others, including copolymers and multiblock copolymers (e.g., styrene-divinylbenzene copolymer, styrene-butadiene copolymer, styrene/vinyltoluene copolymer, etc.).

[0030] In other embodiments, a ligand having a reactive functional group can be attached to the surface of the magnetic particles, for example, through covalent attachment, non-covalent binding, chemical coupling, or adsorption by hydrophobic (van der Waals) attraction, hydrophilic attraction or ionic interaction, according to conventional methods for surface functionalization. Metal and ceramic material can generally be functionalized through covalent bonds such as a metal-oxygen bond, a metal-sulfur bond, or a metal-carbonyl bond according to conventional methods. Ligands can also be attached to metal surfaces electrostatically. See, e.g., Bunton, Marie-Isabelle (ed.), Synthesis, Functionalization and Surface Treatment of Nanoparticles, American Scientific Publishers, Valencia, Calif., 323 pp. (2003), and Sigma-Aldrich, Inc., Surface Functionalized Nanoparticles at www.sigmaaldrich.com/materials-science/material-science-products.html?tabId=16377718.

[0031] Ligands can be attached to the magnetic particles, for example, using an absorption buffer (e.g., phosphate buffered saline (PBS), bovine buffer, acetate buffer, citrate phosphate buffer, carbonate-bicarbonate buffer, MES buffer, etc.). Optionally, a blocker can be adsorbed onto the magnetic particles to reduce nonspecific binding between the magnetic particle and non-target molecules and self-aggregation of the magnetic or core particles (e.g., BSA, non-ionic surfactants such as TWEEN® 20 and TRITON® X-100, polyethylene glycol, etc.). In some embodiments, a linker molecule (e.g., a cleavable linker) that includes difunctional groups can be used to covalently couple a ligand having a reactive functional group to a magnetic material, and/or to a polymer magnetic material core particle, etc. A linker (e.g., BSA, polylysine, or molecule having an alkane, alkene, ester, ether or other group, etc.) can also function as a spacer to extend a small molecule with a reactive functional group from the magnetic particle and reduce steric hindrance.

[0032] In other embodiments of the invention, the magnetic particles can be formed without ligands or reactive functional groups. An additive material bearing a ligand having a reactive functional group (e.g., a functionalized monomer, monomer/functionalized monomer mixture, etc.) can be added to the carrier fluid with the non-functionalized magnetic particles, wherein the additive material will react, for example, to covalently couple the magnetic particles with the contaminants. For example, the magnetic particles can be composed of a magnetic material with a core of a polymeric material, a ceramic material, a semiconductive material, etc. In other embodiments, the magnetic particles are composed of a magnetic material combined with a polymeric material, a ceramic material, a semiconductive material, etc., to form a composite particle. In other embodiments, the magnetic particles are composed of a core of a magnetic material overcoated with a polymeric material, a ceramic material, a semiconductive material, etc.

[0033] Magnetic particles can be prepared, for example, from an aqueous suspension of a magnetic material and monomer(s), with or without a cross-linking agent such as divinylbenzene (e.g., ferrofluid (magnetite)/styrene/divinylbenzene) that is polymerized to trap the magnetic materials (e.g., magnetite) in a polymer matrix to form a core particle. The core particle can be encapsulated by a polymer material with reactive functional groups, for example, carboxyl (—COOH) or amine groups that are available on the surface of the magnetic particle to react with contaminants on the substrate. Such magnetic particles are commercially available, for example, as COMPET™ superparamagnetic particles, composed of a magnetite/polymer matrix coated with a polymer with carboxyl (—COOH) surface groups (mean diameter of about 3-8 μm; density of about 1.1-1.2 g/cm³) available from Bungs Laboratories, Inc., (Fishers, Ind., USA).

[0034] The size and shape(s) of the magnetic particles can be varied according to the contaminant to be removed and for effective substrate cleaning without damaging the substrate or the structures and materials on the substrate. In embodiments of the invention, the magnetic particles can have an average particle size (particle diameter) of about 1-100 times the size of the contaminant to be removed, for example, about 0.01-100 μm (as measured by transmission electron microscopy (TEM)), or any value or sub-range therebetween, e.g., about 0.1-40 μm, about 1-10 μm, etc. The shape of the magnetic particles can be regular or irregular, spherical or nonspherical, and can be in the form of a powder, fibers, spheres, rods, plates, core-shell structures, and the like, including, nano-sized rods (e.g., 10 nm to 100 nm) and microspheres.

[0035] The volume fraction (concentration) of magnetic particles in the composition should be sufficient to provide the desired effect or performance. The concentration of magnetic particles is such that the particles can be maintained as
a dispersion in the base fluid without settling, and to allow the composition to maintain a relatively low viscosity for application onto the substrate. Generally, the concentration of magnetic particles in the base fluid can be in a range of about 0.1-30% by weight of the total composition, or any value or sub-range therebetween, and in some embodiments at about 20-30% by weight, about 10-30% by weight, about 1-10% by weight, etc. The weight percentage of the magnetic particles can be adjusted according to the density of the fluid phase and/or the amount of contaminants to be removed. In other embodiments, the density of the particles can be matched with a base fluid for dispersion of the magnetic particles within the composition. The magnetic particle loading in the dispersion can be varied according to the desired weight % or according to the dispersion of the magnetic particles in the fluid carrier (loading before flocculation), which is dependent, at least in part, on particle surface chemistry, the fluid carrier or dispersion medium, particle size, and/or additives.

Optionally, the composition can contain typically used additives, generally at about 0.1-10% by weight of the total composition, or about 0.5-6% by weight. Typical additives include, for example, co-solvents, pH modifiers, chelating agents, antioxidants, rheology modifiers (e.g., polymers, particulates, polyglycopolymers, etc.), polar solvents, and surfactants or dispersing agents (dispersants) to enhance the dispersion stability of the suspension against sedimentation and aggregation or agglomeration of the magnetic particles. Examples of surfactants include block copolymers, dedecyl alcohol, fatty acids and amines, glycerol, glycerol esters, glycerol monooleates, hydrocarbon polymers, sodium oleate, and tin oxide, among others. The composition can also include a chemical compound to modify or bind to the available reactive group on the magnetic particle, for example, a cross-linking agent to activate groups having a low reactivity to the contaminant (e.g., carbodiimide for binding to COOH groups) or to join non-reactive groups. The composition should not contain compounds or additives that will interfere with or compete with the binding reaction of the magnetic particles with contaminants.

In some embodiments, an additive material bearing a ligand having a reactive functional group (e.g., a functionalized monomer, monomerfunctionalized monomer mixture, etc.) that is not bound to the magnetic particles may be added to the carrier fluid with magnetic particles that have not been functionalized and/or with functionalized magnetic particles.

An embodiment of a method according to the invention for removing contaminants from a substrate to be processed is described with reference to FIGS. 1-2A.

FIG. 1 depicts an embodiment of an apparatus, designated generally as 10, which can be utilized in methods of the invention. The apparatus 10 generally includes a containment vessel (or container) 12 for receiving and containing a fluid, and a magnetic field generator 14. As shown, a substrate 16 to be treated, which is a wafer in the present example, can be placed onto a substrate support 18 within the containment vessel 12. The containment vessel 12 can be composed of an insulating material such as glass, plastic, polyvinylidene fluoride (PVDF), etc.

The apparatus 10 can be connected to other processing units/systems, for example, by a conveyor mechanism (not shown) for conducting the substrate 16 through a processing system, including a pre-cleaning apparatus and/or a post-cleaning apparatus (not shown). The various processing units can be electrically coupled to a microprocessor, which may be programmed to carry out particular functions as is known in the art. A pre-cleaning apparatus can be designed to physically loosen or etching of the substrate 16, which can be performed, for example, by a Standard Clean (SCI) clean or dilute hydrofluoric acid (DHF) clean, followed by a rinse (e.g., DI rinse). This can serve to reduce the treatment required for removal of contaminants. A post-cleaning can be applied to remove remaining particles.

As depicted in FIG. 1, the substrate 16 to be treated is contacted by a composition 20, according to the invention, composed of magnetic particles 22 in a base fluid 24. The substrate 16 can comprise structures 26 such as conductive or insulative lines, shallow trench isolation (STI) structures, bond pads, contacts and interconnects, among other elements, exposed at a surface 28 of the substrate 16. Contaminants 30 composed of conductive, insulative and/or semiconductive materials such as oxides, nitrides, silicon materials, carbon, polymer resist, metals and metal-containing materials (e.g., W, WSi2, TiN, Ta2O5, etc.), among others, can remain adhered to the structures 26 and/or the surface 28 of the substrate 16 as a result of earlier processing (e.g., an SCI clean, etc.).

The composition 20 can be applied to the substrate 16, for example, from a dispensing device 32. In some embodiments, the dispensing device 32 can be structured to deliver the composition 20 under pressure onto the surface 28 of the substrate 16. In other embodiments, the containment vessel 12 can include an inlet and an outlet for passage of the composition 20 into and out of the vessel 12.

In embodiments of the invention, the magnetic particles 22 are allowed to react with contaminants 30 for a time and at a temperature to permit substantial interaction to form contaminant-conjugated magnetic particles 34. Optionally, the composition 20 can be mixed (continuously or intermittently) during the reaction period. Reaction time can vary, for example, according to the nature and concentration of contaminants 30, the mechanism by which binding occurs, and the affinities of the reactive functional groups 36 that are used.

Reactive functional group(s) 36 on the surface of the magnetic particles 22 can chemically and/or physically interact with one or more contaminants 30, for example, by adsorption, covalent bonding, or a non-covalent interaction (e.g., hydrogen bond, ionic bond, van der Waals forces, etc.) to form contaminant-conjugated magnetic particles 34. In some embodiments, the reactive functional group(s) 36 on surfaces of the magnetic particles can provide a repelling force to cause contaminants 30 to be displaced and/or separated from the surface 28 of the substrate 16 and structures 26. The magnetic particles 22 are structured with reactive functional groups 36 that will provide an interaction with contaminants 30 that is stronger than the reactive force of the surface 28 of the substrate 16 or structures 26 with the target contaminant. The chemical composition of the contaminants 30 and the surface 28 of the substrate 16 and structures 26 will determine, at least in part, the ultimate strength of adhesion of contaminants 30 to the substrate 16 and surface structures. The interaction of magnetic particles 22 with contaminants 30 can be enhanced, for example, by the inclusion of a surfactant or dispersing agent to maintain the magnetic particles as a dispersion in the composition 20, by adjusting the pH, by...
application of the magnetic field, and/or by the inclusion of a chemical agent to enhance reactivity of the surface functional groups.

Referring to FIGS. 2 and 2-A, a magnetic field (arrows \( \rightarrow \)) is applied to attract (or repel) contaminant-conjugated magnetic particles 34 (and non-conjugated, magnetic particles 22) at a low force to draw and disengage the contaminants 30 from the surface 28 of the substrate 16 and structures 26. The interaction of the magnetic particles 22 with the contaminants 30 and movement of magnetic particles 22 in response to the magnetic field(s) provides removal of contaminants 30 without damage to the device structures (e.g., lines, etc.) on the surface 28 of the substrate 16. Devices for magnetic separation of particles in solution are generally described, for example, in U.S. Pat. No. 6,562,239 (Foy et al.), U.S. Pat. No. 6,572,778 (Sterman et al.), U.S. Pat. No. 6,689,615 (Murto et al.), U.S. Pat. No. 7,258,799 (Ras et al.), and Bangs Laboratories, Inc., TechNote 102, Rev. 005, Jan. 6, 2004 (at www.bangslabs.com).

In any of the described embodiments, the magnetic field generator 14 can be a permanent magnet, electromagnet (connected to a power source) or superconducting magnet, and can be composed, for example, of ferromagnetic or rare earth magnets. An insulator (not shown) can be positioned between the magnetic field generator 14 and the containment vessel 12 or the substrate 16 to block or shield the substrate from a magnetic field. In some embodiments, the magnetic field generator can be incorporated into a containment vessel, e.g., embedded in a sidewall of the vessel.

In the embodiment illustrated in FIGS. 1-2A, a magnetic field generator 14 is positioned along one side of the containment vessel 12 such that a magnetic field is applied in a single direction relative to the substrate 16. When the composition 20 is exposed to a sufficiently high magnetic field from the magnetic field generator 14, the magnetic particles (both unbound, non-conjugated magnetic particles 22 and conjugated magnetic particles 34) will move in response to the magnetic field that is generated, i.e., attracted toward the magnetic field (arrows \( \rightarrow \)) as shown in FIG. 2, or repulsed away. The velocity at which the contaminant-conjugated magnetic particles 34 are moved can be varied, for example, by adjusting the strength of the magnetic field and/or the position of the magnetic field generator 14 with respect to the substrate 16.

The magnetic field generator 14 can be positioned relative to the substrate 16 to apply a magnetic field to draw magnetic particles 22 in a lateral direction (arrows \( \rightarrow \)) across the substrate 16. For example, a magnetic field generator can be situated at one location as depicted in FIG. 2A, or one or more magnetic field generators can surround a substrate (partially or completely) as illustrated in FIGS. 3 and 4. In embodiments of the invention, a plurality of magnetic field generators (e.g., 14a\(_1\) to 14a\(_n\) in FIG. 3; 14a\(_{1n}\), 14a\(_{2n}\) in FIG. 4) can be positioned around the substrate at multiple locations to apply a magnetic field in more than one direction relative to the substrate. As further illustrated in FIG. 4, in some embodiments, a magnetic field generator can be situated above (as shown by magnetic field generator 14b\(_{1n}\)) and/or below (as shown by magnetic field generator 14b\(_{2n}\)) the substrate 16 to draw magnetic particles in an upward (\( \uparrow \)) or a downward (\( \downarrow \)) direction relative to the substrate 16.

Multiple magnetic field generators can be independently controlled, for example, using a dedicated power supply in the case of electromagnets, by the positioning of an insulator to shield one or more of the magnetic field generators from the substrate, or by using a field generator control by connecting the magnetic field generator(s) in communication with a controller comprising a computer device configured under control of a program to control the magnetic field, e.g., when the magnets are turned off and on.

In embodiments of the invention, a magnetic field can be applied in a single direction relative to the substrate to draw (or repel) the magnetic particles including the contaminant-conjugated magnetic particles, laterally in a single direction, which can reduce damage to the substrate and/or structures on the substrate.

In other embodiments, a magnetic field can be applied in multiple directions to enhance contact and interaction of magnetic particles with contaminants and the removal of contaminants from the substrate. Two or more magnetic field generators can be activated simultaneously, in succession, in an alternating sequence, in pairs, or in other combinations or sequences. For example, referring to FIG. 3, magnetic field generators 14a\(_{1n}\), 14a\(_{2n}\) and 14a\(_{3n}\), 14a\(_{4n}\) on opposing sides of a substrate 16 can be activated to generate magnetic fields (arrows \( \rightarrow \)) to attract and draw magnetic particles 22 in a lateral direction (arrows \( \rightarrow \)) to opposite sides of the substrate 16 and containment vessel 12.

In some embodiments, a magnetic field can be applied in a first direction and then in a second direction. In yet other embodiments of the invention, the magnetic field can be oscillated, for example, by pulsing the magnetic field (s), by cyclically or repeatedly applying and terminating the magnetic field(s) and/or by increasing and decreasing the strength of the magnetic field(s), which can cause the magnetic particles and contaminant-conjugated magnetic particles to move (e.g., rock or oscillate) with a low force to enhance the interaction of magnetic particles with contaminants.

In yet other embodiments, the magnetic field generator(s) can be movable to vary its position relative to the substrate. For example, a magnetic field generator 14c\(_{1n}\) (FIG. 4) can be first positioned below a containment vessel 12 to draw magnetic particles downward (arrows \( \downarrow \)) relative to a surface 28 of a substrate 16, then moved to above the substrate 16 (e.g., magnetic field generator 14b\(_{1n}\)) to draw magnetic particles upward (arrows \( \uparrow \)) relative to the substrate surface, then moved to one side of the containment vessel 12 (e.g., 14a\(_{2n}\)) to draw magnetic particles in a lateral direction (arrows \( \downarrow \)), and/or to a second position at another side of the containment vessel 12 (e.g., magnetic field generator 14a\(_{2n}\)) to draw magnetic particles in a second lateral direction (arrow \( \rightarrow \), or other combination or sequence.

The magnetic particles will accumulate in response to the magnetic field. For example, in the embodiment depicted in FIGS. 2 and 2A, magnetic particles 22 and contaminant-conjugated magnetic particles 34 will accumulate at the side of the containment vessel 12 in proximity to the magnetic field generator 14. The accumulated magnetic particles 22 and contaminant-conjugated magnetic particles 34 can then be removed, for example, by terminating the magnetic field and discharging the liquid composition 20 from the containment vessel 12, for example, through a discharge outlet 38, as shown in FIG. 2.

In some embodiments, the composition 20 including the magnetic particles 22 and contaminant-conjugated magnetic particles 34 can be passed through the outlet 38 by gravity, optionally by applying force or a pressure differential...
(e.g., vacuum or suction). In other embodiments, as illustrated in FIG. 2, a magnetic field generator 40 can be positioned at the outlet to generate a magnetic field to attract and draw the magnetic particles 22 and contaminant-conjugated magnetic particles 34 toward and into the outlet 38. The apparatus 10 can further include a collection device 42 for receiving and collecting the magnetic particles 22 and contaminant-conjugated magnetic particles 34 of the discharged composition 20. The collection device 42 can be structured, for example, with a filter 43 that can be positioned within or proximal to the outlet 38 to isolate and collect the magnetic particles 22 and contaminant-conjugated magnetic particles 34, for example, a glass fiber filter, porous membrane, paper filter, woven fabric filter, etc. The magnetic particles 22 and contaminant-conjugated magnetic particles 34 can also be recovered from the discharged composition 20 by centrifugation or other known method.

[0056] In embodiments of the invention, a collected material can then be processed to separate and recover the magnetic particles 22 from contaminants 30, particulates and other components. In some embodiments, the magnetic particles 22 can be separated or cleaved off from the contaminants 30 by an optical, chemical or other suitable cleavage method. For example, the magnetic particles 22 can be separated from contaminants 30 by applying an appropriate elution buffer, applying a magnetic field to draw off the magnetic particles 22, and removing the supernatant containing the contaminants 30.

[0057] As illustrated in FIG. 5, a rinse water or other aqueous medium 44 can then be applied (arrows ↓↓↓) to remove the composition 20, including magnetic particles 22 and/or contaminant-conjugated magnetic particles 34, from the substrate 16. The aqueous medium 44 can be applied, for example, from a dispensing device 46 under non-damaging conditions by dispensing, by aerosol spraying, by megasonic rinsing, etc.

[0058] Referring now to FIG. 6, a post-clean procedure (arrows ↓↓↓) can then be conducted to apply a cleaning agent to remove remaining residual material (e.g., remaining composition, magnetic particles, etc.) from the substrate 16 leaving a cleaned surface 28. For example, a post-clean can be conducted through the use of an SC1 clean or DHF clean (e.g., about 500:1 water:HF) in conjunction with a spray or megasonic system, followed by a water rinse. Subsequent processing of the substrate 16 and features 26 can then be conducted as desired.

[0059] In another embodiment of the method of the invention illustrated in FIGS. 7 and 7A, a composition 20" according to the invention containing magnetic particles 22" can be applied to remove contaminants 30" from a substrate 16" having a non-planar topography, for example, one or more structures 26" that project or protrude from the surface 28". In some embodiments, the substrate 16" can comprise a plurality of structures 26" that protrude from the surface 28" and extend over the substrate 16" separated by a channel or recess 48". The structures 26" can be, for example, a gate runner, wordline, bit line, conductive line (e.g., conductive metal trace line, interconnect, etc.), insulative line, spacer line, etc., of a material (e.g., conductive, semiconductor, insulative, etc.), such as oxides, nitrides, silicon materials, carbon, polymer resist, metals and metal-containing materials, carbon materials, resists, metals, metal-containing materials, etc. The substrate 16" can comprise a plurality of elements, for example, contacts, bond pads, ball pads, ball contacts, transistors, isolation structures (e.g., shallow trench isolation (STI) structures), etc., that project from the surface 28" of the substrate 16", and, in some embodiments, can be situated in generally parallel-aligned linear arrays.

[0060] Contaminants 30" composed of conductive, insulative and/or semiconductive materials such as oxides, nitrides, silicon materials, carbon, polymer resist, metals and metal-containing materials, among others, can remain adhered to the structures 26" and/or the surface 28" of the substrate 16" as a result of earlier processing. A composition 20" can be applied to the substrate 16" by delivery from a dispensing device or, as illustrated, by flowing into the containment vessel 12" through an inlet, as shown in FIG. 7.

[0061] In some embodiments, contaminants 30" can be removed from the non-planar surface 28" of the substrate by applying a composition according to the invention and applying one or more magnetic fields to draw and remove the contaminant-conjugated magnetic particles 34" using a low force in a lateral direction across the substrate (and/or in an upward or downward direction), as previously described with respect to FIGS. 1-4.

[0062] In another embodiment of the invention, magnetic field generators 14a", 14b" can be positioned on opposing sides as shown in FIG. 7A, or on one side of the substrate 16", at or about a perpendicular orientation relative to the axis of line element structures 26". Upon the application of a magnetic field (arrows from one or both magnetic field generators 14a", 14b"), the magnetic particles 22" and contaminant-conjugated magnetic particles 34" can be drawn in a lateral direction (arrows ↓↓↓) within and along the channels 48" and relatively parallel to the line element structures 26". This arrangement and application of magnetic field(s) from magnetic field generators 14a", 14b" in a parallel direction relative to the axis of elevated structures 26" (e.g., lines) on the surface 28" of the substrate 16" can reduce contact by the magnetic particles 22" and contaminant-conjugated magnetic particles 34" that can result in damage to the structures 26".

[0063] Although specific embodiments have been illustrated and described herein, it will be appreciated by those of ordinary skill in the art that any arrangement that is calculated to achieve the same purpose may be substituted for the specific embodiments shown. This application is intended to cover any adaptations or variations that operate according to the principles of this disclosure as described herein. It is therefore intended that such changes and modifications be covered by the appended claims and the equivalents thereof. The disclosures of patents, references and publications cited in the application are incorporated by reference herein.

1. An apparatus for cleaning a substrate, the apparatus comprising:
   a containment vessel for receiving and containing a fluid composition therein;
   a substrate support configured to hold a substrate, the substrate comprising a semiconductor device structure;
   a source of the fluid composition, the fluid composition comprising magnetic particles having functional reactive groups formulated to conjugate with contaminants on the substrate; and
   at least one magnetic field generator configured to generate a sufficient magnetic field to draw contaminant-conjugated magnetic particles from the substrate without causing damage to the semiconductor device structure.
2. The apparatus of claim 1, wherein the at least one magnetic field generator comprises a plurality of magnetic field generators.

3. The apparatus of claim 1, wherein the at least one magnetic field generator comprises a plurality of magnetic field generators situated on opposing sides of the containment vessel.

4. The apparatus of claim 2, wherein the plurality of magnetic field generators at least partially surround the containment vessel.

5. The apparatus of claim 2, wherein the plurality of magnetic field generators are situated at a plurality of positions surrounding the containment vessel.

6. The apparatus of claim 1, wherein the at least one magnetic field generator is situated beneath a base of the containment vessel.

7. The apparatus of claim 2, wherein the at least one magnetic field generator is positioned above the containment vessel.

8. The apparatus of claim 2, wherein the at least one magnetic field generator is movable about the containment vessel.

9. The apparatus of claim 1, wherein the containment vessel comprises an outlet for discharging a fluid composition therefrom.

10. The apparatus of claim 9, further comprising a magnetic field generator situated proximal to the outlet of the containment vessel.

11. The apparatus of claim 1, wherein the at least one magnetic field generator is in communication with a controller comprising a computer device configured under control of a program to control the magnetic field.

12. An apparatus for cleaning a substrate, the apparatus comprising:

   a substrate support configured to hold a substrate comprising protruding structures with a recess therebetween;

   a containment vessel for receiving and containing a fluid composition therein;

   a source of the fluid composition, the fluid composition comprising magnetic particles having functional reactive groups formulated to conjugate with contaminants on the substrate; and

   a magnetic field generator configured to laterally move contaminant-conjugated magnetic particles in a single direction across the substrate and substantially parallel to the protruding structures.

13. The apparatus of claim 12, further comprising a dispensing device for applying the fluid composition to the substrate.

14. The apparatus of claim 12, wherein the containment vessel comprises an inlet and an outlet for passage of the fluid composition into and out of the containment vessel.

15. The apparatus of claim 12, further comprising an insulator between the magnetic field generator and the containment vessel or the substrate to shield the substrate from a magnetic field generated by the magnetic field generator.

16. The apparatus of claim 12, wherein the magnetic field generator is incorporated into the containment vessel.

17. An apparatus for cleaning a substrate, the apparatus comprising:

   a substrate support configured to hold a substrate comprising semiconductor structures in linear arrays;

   a containment vessel for receiving and containing a fluid composition therein;

   a source of the fluid composition, the fluid composition comprising magnetic particles having functional reactive groups configured to conjugate with contaminants on the substrate; and

   a magnetic field generator perpendicular to the linear arrays of semiconductor structures, the magnetic field generator configured to move contaminant-conjugated magnetic particles in a lateral direction parallel to the linear arrays of semiconductor structures.

18. The apparatus of claim 17, wherein the magnetic field generator is configured to laterally move contaminant-conjugated magnetic particles without damaging the semiconductor structures.

19. The apparatus of claim 17, further comprising:

   an outlet for discharging the fluid composition; and

   a collection device within or proximal to the outlet to isolate and collect the magnetic particles and the contaminant-conjugated magnetic particles.

20. The apparatus of claim 17, further comprising a device for applying a dilute ammonium hydroxide/hydrogen peroxide (SC1) solution or a dilute hydrofluoride solution to the substrate.