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(71) Applicant: **APPLIED MATERIALS, INC.** [US/US]; P.O. Box 450A, Santa Clara, CA 95052 (US).

(72) Inventors: **CHEN, Haojiang**; 10582 White Fir Court, Cupertino, CA 95014 (US). **PAPANU, James, S.**; 351 Holly Drive, San Rafael, CA 94903 (US). **KAWAGUCHI, Mark**; Apt. #16, 911 S. Winchester Boulevard, San Jose, CA 95128 (US). **HERCHEN, Harald**; 3094 Mattique Drive, San Jose, CA 95135 (US). **HWANG, Jeng, H.**; 20835 Scofield Drive, Cupertino, CA 95014 (US). **JIN, Guangxiang**; 1738 Fumia Drive, San Jose, CA 95131 (US). **PALAGASHVILI, David**; 49 Showers Drive, K431, Mountain View, CA 94040 (US).

(74) Agents: **BERNADICOU, Michael, A.** et al.; Blakely, Sokoloff, Taylor & Zafman LLP, 7th floor, 12400 Wilshire Boulevard, Los Angeles, CA 90025 (US).

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(54) Title: SUBSTRATE CLEANING APPARATUS AND METHOD

(57) Abstract: A method of processing a substrate (30) comprises exposing the substrate (30) to an energized process gas to etch features (67) on the substrate (30) and exposing the substrate (30) to an energized cleaning gas to remove etchant residue (70) and/or remnant resist (60) from the substrate (30). To enhance the cleaning process, the substrate (30) may be treated before, during or after the cleaning process by exposing the substrate (30) to an energized treating gas comprising a halogen species.

SUBSTRATE CLEANING APPARATUS AND METHOD

BACKGROUND

The present invention relates to cleaning a substrate.

In the manufacture of integrated circuits, active and passive devices are formed on a substrate, such as a semiconductor wafer, by alternately depositing and etching layers of dielectric, semiconducting, and conducting materials, such as silicon dioxide, polysilicon, and metal compounds and alloys. These layers may be etched to form a pattern of etched features by providing a resist layer of photoresist and/or oxide hard mask on the substrate, and using lithography or energized gas to expose and pattern the resist layer. The portions of the layers adjacent to the patterned resist features are etched to form a predefined pattern of gates, vias, contact holes, trenches, and/or metal interconnect lines. Etching is typically performed using a capacitively or inductively coupled plasma of halogen-containing gases, as for example described in Silicon Processing for the VLSI Era, Vol. 1, Chapter 16, by Wolf and Tauber, Lattice Press, 1986, which is incorporated herein by reference.

The etching process may leave remnant resist and etchant residue on the substrate. Remnant resist are those residual resist portions that are not etched by the etchant gases, and which remain on the substrate after the etching process. The etchant residue may comprise residual species and/or sidewall deposits on the sidewalls of the etched features. The residual species may result from adsorption of halogen-containing etchants on the etched features which may lead to corrosion of the metal-containing features. The sidewall deposits may be formed during the etching process by reaction of the etchant gases, the metal-containing layers, and the resist, and by condensation of the reaction residue on the sidewalls of the features. One method of cleaning an etched substrate is a dry cleaning method in which a plasma of a gas is used to remove remnant resist remaining on the substrate in a stripping (or ashing) process and to remove or inactivate residual halogen-containing species in a passivating process. The sidewall deposits on the substrate are typically removed by wet chemical etching methods or they can be at least partially removed in a dry cleaning process.

Conventional stripping methods which use a plasma of oxygen, nitrogen or water vapor, can be used to strip remnant resist from the substrate. These conventional stripping techniques are sometimes ineffective at stripping all the resist from the substrate, particularly when the polymeric resist is hardened by exposure to a plasma. For oxide hard mask resists, the oxide layer can be stripped or can be left on the substrate. Typically, remnant oxide hard mask is left on the substrate and a dielectric layer is deposited on the remnant oxide in a subsequent process step. In addition, adequate stripping processes generally compromise process throughput. The stripping process may also harden sidewall deposits making the deposits difficult to remove.

In passivating techniques, the etchant residue on the substrate is removed or inactivated to, for example, reduce post-etch corrosion problems by using a passivating gas, such as ammonia and/or water vapor. One limitation of conventional passivating techniques is that they often only prevent post-etch corrosion of the substrate for short periods, typically ranging from about 1 to 5 hours after exposure of the substrate to ambient moisture. The short corrosion resistant period is undesirable because post-etch processing steps may need to be performed within 1 to 2 hours after the substrate is first exposed to the atmosphere, resulting in a tight or inflexible production schedule. Often, the substrate cannot be etched, or if already etched, cannot be removed from the chamber in order to avoid corrosion.

Due to the shortcomings of the conventional dry cleaning processes, remnant resist and/or etchant residues are often removed in a wet-cleaning process in which the substrate is exposed to wet solvents . However, the wet-cleaning process also suffers from several disadvantages. For example, residue removal is often not complete, resulting in inconsistently processed substrates. In addition, the solvents may attack the metal-containing features on the substrate, particularly when very small features are etched on the substrate. The solvents used may also be costly and may generate hazardous chemical waste that is difficult to dispose of.

Thus, there is a need for a process and apparatus for cleaning a substrate to, for example, remove remnant resist and etchant residue on the substrate. It is further desirable to reduce post-etch corrosion. It is still further

desirable to be able to clean a substrate while reducing the need to expose the substrate to a wet solvent.

SUMMARY

The present invention satisfies these needs. In one aspect of the present invention, a substrate processing method comprises exposing a substrate to an energized process gas to etch the substrate, exposing the substrate to an energized cleaning gas, and before, during, or after exposing the substrate to an energized cleaning gas, exposing the substrate to an energized treating gas comprising a halogen species and a hydrogen species.

In another aspect of the invention, a substrate processing method comprises exposing a substrate to an energized process gas to etch the substrate and exposing the substrate to an energized treating gas comprising a chlorine species.

In another aspect of the invention, a substrate processing method comprises exposing a substrate to an energized process gas to etch the substrate and exposing the substrate to an energized treating gas comprising a fluorine species and a hydrogen species.

In another aspect of the invention, a method of treating an etched substrate comprises exposing the etched substrate to an energized process gas comprising a first halogen species and exposing the etched substrate to an energized process gas comprising a second halogen species.

In another aspect of the invention, a method of cleaning an etched substrate comprises exposing a substrate to a cleaning gas; and after this, exposing the substrate to an energized treating gas comprising one or more of NH_3 and H_2.

In another aspect of the invention, a substrate processing method comprises exposing a substrate to an energized process gas to etch the substrate in a process zone and exposing the substrate to an energized treating in the process zone.

In another aspect of the invention, a method of treating an etched substrate comprises exposing the etched substrate to an energized process gas comprising oxygen species while maintaining the substrate at a temperature of at least about 200°C, treating the substrate with a treating gas and rinsing the substrate with de-ionized water to remove etchant residue on the substrate.

DRAWINGS

These features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings which illustrate examples of the invention. However, it should be understood that each of the features can be used in the invention in general, not merely in the context of the particular drawings, and the invention includes any combination of these features, where:

Figure 1a is a schematic sectional side view of a substrate with metal-containing layers thereon;

Figure 1b is a schematic sectional view of the substrate of Figure 1a following etching;

Figure 2 is a schematic view of a multi-chamber apparatus having an etching chamber and a cleaning chamber;

Figure 3 is a schematic sectional side view of an etching chamber;

Figure 4 is a schematic sectional side view of a cleaning chamber;

Figures 5a and 5b are flow charts illustrating substrate cleaning processes;

Figures 6a and 6b are flow charts illustrating other versions of substrate cleaning processes; and

Figures 7a-7c are flow charts illustrating other versions of substrate cleaning processes.

DESCRIPTION

The process and apparatus of the present invention are useful for processing substrates, such as semiconductor wafers, but may also be used for other processes or for processing other substrates, such as printed circuit boards, flat panel displays, and liquid crystal displays. Thus, the description represents illustrative embodiments of the invention and is not intended to limit the invention.

In one version of the present invention, a substrate **30**, such as a substratum **35** having one or more materials, such as layers **40, 45, 50**, thereon as shown in Figure 1a, may be processed. These layers are often superimposed on one another and may comprise dielectric layers comprising, for example, silicon dioxide, undoped silicate glass, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), Si_3N_4, or TEOS deposited glass; semiconducting layers comprising, for example, silicon-containing layers such as polysilicon or a silicon compound; and electrically conducting layers such as metal-containing layers comprising, for example, aluminum, copper, titanium, titanium nitride, or metal silicide such as tungsten silicide and cobalt silicide. Suitable etchant gases for etching layers on the substrate **30**, include for example, HCl, BCl_3, HBr, Br_2, Cl_2, CCl_4, $SiCl_4$, SF_6, F_2, NF_3, HF, CF_3, CF_4, CH_3F, CHF_3, $C_2H_2F_2$, $C_2H_2F_4$, $C_2H_4F_2$, C_2F_6, C_3F_8, C_4F_8, C_2HF_5, C_4F_{10}, CF_2Cl_2, $CFCl_3$, O_2, N_2, He, and mixtures thereof. The etchant gas is selected to provide high etch rates, and highly selective etching of the particular layers or materials that are being etched. When multiple layers are sequentially etched, multiple etchant gas compositions having first, second, third, etc. compositions may be sequentially introduced into the chamber to etch each particular layer.

Figure 1a shows a version of a substrate **30** having material formed on a substratum **35**. The substratum **35** may comprise semiconducting material, such as silicon, gallium arsenide, and the like. The material on the substratum **35** may comprise (i) a diffusion barrier material **40** comprising, for example, silicon oxynitride, organic anti-reflective layer (ARC), titanium, tungsten, titanium-tungsten, or titanium

nitride, (ii) an electrically conductive material **45** comprising, for example, titanium, tungsten, aluminum, copper or similar metal or alloys thereof, and optionally silicon, and (iii) an anti-reflective material **50** comprising, for example, silicon, titanium nitride, or titanium tungsten. An oxide layer (not shown), such as SiO_2, may also be provided below the diffusion barrier layer **40**. A patterned etch-resistant material **60** of, for example, photoresist, such as polymeric photoresist, or electron-beam resist overlies the layers. Etchant gas may be provided to etch the exposed portions of the layers to form apertures **65**, such as lines, trenches, holes or vias, that extend through one or more of the layers and which form features **67** on the substrate **30**, as schematically illustrated in Figure 1b.

After the etching process, remnant resist **60** and etchant residue **70** remaining on the substrate **30** may be removed in one or more cleaning processes to provide a clean substrate surface for subsequent processing that is substantially resistant to corrosion. The remnant resist **60** is the portion of the resist material that remains on the substrate **30** after the etching process and may comprise any material that is relatively resistant to etchant gas used to etch one or more underlying materials on the substrate **30**. In one version, the remnant resist **60** comprises residual polymeric photoresist or oxide hard mask. Suitable polymeric photoresist materials are commercially available from Shipley Co., Marlboro, Massachusetts, or Tokyo Ohka Kogyo (TOK) Co., Ltd., Kawasaki, Japan. The etchant residue **70** on the features may comprise (i) residual species **75**, for example residual halogen radicals, such as chlorine or fluorine, metal containing species, such as one or more metal oxides, or byproduct compounds
that are formed when residual halogen radicals react with the metal in the etched layers that remain on the substrate **30** after etching, and/or (ii) sidewall deposits **80** which are formed on the sidewalls of the etched features **67** during etching. The sidewall deposits may comprise (i) organic compounds containing carbon and hydrogen, (ii) metal from the metal-containing layers, such as aluminum or titanium, and (iii) etchant gas species such as chlorine, boron and/or nitrogen. The composition and stoichiometry of the sidewall deposits **80** depend upon the chemical composition of the material being etched, the resist material **60**, and the etchant gases used to etch the features **67**. In one version, the etchant residue **70** comprises both residual species **75** and sidewall deposits **80**. The residual species may comprise one or more

of Al_2O_3, TiO_2, CuO, and SiO_2. The sidewall deposits may comprise one or more of carbon, hydrogen, nitrogen, one or more halogens, oxygen, silicon, and metals. By "cleaning" it is meant that one or more of the remnant resist, residual species, and sidewall deposits is at least partially removed from a substrate **30** or inactivated.

Referring to Figure 2, the substrate **30** may be etched and cleaned in a multi-chamber apparatus **100** comprising one or more etching chambers **110** for etching the substrate **30**, and one or more cleaning chambers **120** for removing remnant resist **60** and/or removing or inactivating etchant residue **70** that remain on the substrate **30** after the etching process. The etching chamber **110**, cleaning chamber **120**, a transfer chamber **125**, and a load lock chamber **130** may be interconnected in a vacuum sealed environment that may be maintained at a low pressure to reduce contamination of the substrate **30**. During processing, a robotic arm **135** transfers a substrate **30** from the load lock chamber **130** to the transfer chamber **125** and then to one of the processing chambers.

The substrate **30** may be etched in a process chamber **110**, such as for example, a DPS type Metal Etch Centura chamber, schematically illustrated in Figure 3, and from Applied Materials, Inc. in Santa Clara, California. The particular embodiment of the process chamber **110** shown herein is provided only to illustrate the invention, and should not be used to limit the scope of the invention. The chamber **110** comprises a support **140** within a process zone **145** in the chamber **110**. A substrate **30** may be positioned on the support **140** by the robotic arm **135**. The substrate **30** may be held in place during the etching process using a mechanical or electrostatic chuck **150** with grooves **155** in which a coolant gas, such as helium, is held to control the temperature of the substrate **30**.

During processing of the substrate, the chamber **110** may be maintained at a low pressure and process gas may be introduced into the chamber **110** through a gas supply **160** having a gas source **162** and gas inlets **164** peripherally disposed about the substrate **30**. Alternatively, a showerhead gas distributer (not shown) may be positioned above the substrate **30**. The process gas may be energized by a gas energizer that couples an energetic electromagnetic field into the process zone **145**, such as an inductive, capacitive, or microwave field. In the version shown in Figure

3, an inductor coil **165** adjacent to the process chamber **110** forms an inductive electric field in the chamber **110** when powered by a coil power supply **170** operated using, for example, an RF voltage at a source power level that may be from about 200 Watts to about 2000 Watts. Alternatively or additionally, a capacitive electric field may be formed in the chamber **110**. At least a portion of the support **140** may be electrically conductive to serve as a cathode electrode **175**. The cathode electrode **175**, in conjunction with sidewalls of the chamber **110** which may be electrically grounded to serve as an anode electrode **180**, form process electrodes in the process zone **145** that may capacitively couple to energize the process gas. The cathode **175** may be powered by an electrode power supply **185** operated using, for example, an RF voltage at a power level of from about 10 Watts to about 1000 Watts. The capacitive electric field is substantially perpendicular to the plane of the substrate **30**, and may accelerate the plasma species toward the substrate **30** to provide more vertically oriented anisotropic etching of the substrate. The frequency of the RF voltage applied to the process electrodes **175,180**, and/or the inductor coil **165** is typically from about 50 KHz to about 60 MHz, and more typically about 13.56 MHz. In one version, the cathode **175** is also an electrode in a dielectric in the electrostatic chuck **150**.

The ceiling **190** of the process chamber **110** can be flat or rectangular shaped, arcuate, conical, dome-shaped, or multi-radius dome-shaped. In one version, the inductor coil **165** covers at least a portion of the ceiling **190** of the process chamber **110** in the form of a multi-radius dome-shaped inductor coil having a "flattened" dome shape that provides more efficient use of plasma source power and increased plasma ion flux uniformity directly over the substrate **30** center.

When capacitively generated, the plasma formed in the process zone **145** may also be enhanced using magnetically enhanced reactors (not shown), in which a magnetic field generator, such as a permanent magnet or electromagnetic coils, are used to apply a magnetic field in the process zone **145** to increase the density and uniformity of the plasma. The magnetic field may comprise a rotating magnetic field with the axis of the field rotating parallel to the plane of the substrate **30**, as described in U.S. Patent No. 4,842,683, which is incorporated herein by reference in its entirety.

Spent process gas and etchant residue are exhausted from the process chamber **110** through an exhaust system **195** capable of achieving a low pressure in the process chamber **110**. A throttle valve **200** is provided in the exhaust for controlling the pressure in the chamber **110**. Also, an optical endpoint measurement system (not shown) may be used to determine completion of the etching process for a specific layer by measuring, for example, the change in light emission of a particular wavelength corresponding to a detectable gaseous species or by other interferometric techniques.

To perform an etching process in the process chamber **110**, an energized process gas comprising etchant gas may be provided in the process zone **145**. By "energized process gas" it is meant that the process gas is activated or energized to form one or more dissociated species, non-dissociated species, ionic species, and neutral species. The etchant gas composition may be selected to provide high etch rates, and highly selective etching of a particular layer or layers that are being etched. When etching a metal-containing material, such as conductive material **45**, the etchant gases may comprise one or more of halogen-containing gases, such as one or more of Cl_2, BCl_3, CCl_4, $SiCl_4$, CF_4, NF_3, SF_6, Br_2, HBr, BBr_3, CHF_3, C2F2, and the like, and optionally, one or more additive gases, such as inert or non-reactive gases, such as H_2, N_2, O_2, He-O_2, and the like. In an exemplary process, the anti-reflective material **50** is etched by exposing the substrate **30** to an energized process gas comprising etchant gas comprising, for example, about 90 sccm Cl_2 and about 30 sccm BCl_3 at a pressure of about 8 mTorr, a source power level of about 1600 Watts, a bias power level of about 145 Watts, a backside helium pressure of about 4 Torr and a cathode temperature of about 50°C. The electrically conductive material **45** may then be etched by an energized process gas comprising etchant gas comprising, for example, about 80 sccm Cl_2, about 5 sccm BCl_3, and about 10 sccm CHF_3 at a pressure of about 14 mTorr, a source power level of about 1600 Watts, a bias power level of about 150 Watts, a backside helium pressure of about 8 Torr and a cathode temperature of about 50°C. Thereafter, the diffusion barrier layer **40**, and optionally a portion of the oxide layer, may be etched by introducing an energized process gas comprising etchant gas comprising, for example, about 30 sccm Cl_2, about 5 sccm BCl_2, and about 30 sccm N_2 or Ar at a pressure of about 10 mTorr, a source power

level of about 1600 Watts, a bias power level of about 125 Watts, a backside helium pressure of about 8 Torr and a cathode temperature of about 50°C.

After completion of the etching process, the substrate **30** may be dechucked and lifted from the support **140** by, for example, a pneumatic lifting apparatus which raises lift pins (not shown) in the support **140** to raise the substrate **30** from the surface of the support **140**. The robotic transport arm **135** may be inserted between the substrate **30** and the support **140** to lift the substrate **30** off the lift pins. Thereafter, the lift pins are retracted into the support **140**, and the robotic arm **135** transports the substrate **30** out of the etching chamber **110** and into the transfer chamber **125**.

To remove the etchant residue **70** and remnant resist **60**, the substrate **30** may be transferred from the transfer chamber **125** to a cleaning chamber **120**, such as for example, an Advanced Strip and Passivation, (ASP) chamber, schematically illustrated in Figure 4, and commercially available from Applied Materials Inc. in Santa Clara, California. The cleaning chamber **120** shown herein is provided only to illustrate the process of the present invention, and should not be used to limit the scope of the invention, because other cleaning chambers can also be used to clean the substrate **30**, including the process chamber **110** shown in Figure 3. The substrate **30** is placed on a support **210** by the robotic arm **135**, and optionally held in place during processing by a mechanical or electrostatic chuck **212**.

In the cleaning chamber **120** of the type illustrated in Figure 4, an energized process gas comprising cleaning gas is provided to clean the substrate **30** held on the support **210** in a process zone **215**. The support **210** supports the substrate **30** in the process zone **215** and may optionally comprise an electrostatic chuck **212**. Within or below the support **210**, a heat source, such as infrared lamps **220**, can be used to heat the substrate **30**. The process gas comprising cleaning gas may be introduced through a gas distributor **222** into a remote plasma generation zone **225** in a remote chamber **230**. By "remote" it is meant that the center of the remote chamber **230** is at a fixed upstream distance from the center of a process zone **215** in the cleaning chamber **120**. In the remote chamber **230**, the cleaning gas is activated by coupling microwave or RF energy into the remote chamber **230**, to

energize the cleaning gas and cause ionization or dissociation of the cleaning gas components, prior to its introduction through a diffuser **235**, such as a showerhead diffuser, into the process zone **215**. Alternatively, the process gas may be energized in the process zone **215**. Spent cleaning gas and residue may be exhausted from the cleaning chamber **120** through an exhaust system **240** capable of achieving a low pressure in the cleaning chamber. A throttle valve **245** in the exhaust **240** is used for maintaining a chamber pressure from about 150 mTorr to about 3000 mTorr.

In the version illustrated in Figure 4, the remote chamber **230** comprises a tube shaped cavity containing at least a portion of the remote plasma zone **225**. Flow of cleaning gas into the remote chamber **230** is adjusted by a mass flow controller or gas valve **250**. The remote chamber **230** may comprise walls made of a dielectric material such as quartz, aluminum oxide, or monocrystalline sapphire that is substantially transparent to microwaves and is non-reactive to the cleaning gas. A microwave generator **255** is used to couple microwave radiation to the remote plasma zone **225** of the remote chamber **230**. A suitable microwave generator **255** is an "ASTEX" Microwave Plasma Generator commercially available from the Applied Science & Technology, Inc., Woburn, Massachusetts. The microwave generator assembly **255** may comprise a microwave applicator **260**, a microwave tuning assembly **265**, and a magnetron microwave generator **270**. The microwave generator may be operated at a power level of about 200 to about 3000 Watts, and at a frequency of about 800 MHz to about 3000 MHz. In one version, the remote plasma zone **225** is sufficiently distant from the process zone **215** to allow recombination of some of the dissociated or ionized gaseous chemical species. The resultant reduced concentration of free electrons and charged species in the activated cleaning gas minimizes charge-up damage to the active devices on the substrate **30**, and provides better control of the chemical reactivity of the activated gas formed in the remote plasma zone **225**. In one version, the center of the remote plasma zone **225** is maintained at a distance of at least about 50 cm from the center of the process zone **215**.

A cleaning process may be performed in the cleaning chamber **120** by exposing the substrate **30** to energized process gas comprising cleaning gas to, for example, remove remnant resist **60** and/or to remove or inactivate etchant residue **70**

remaining on the substrate after the substrate is etched. Remnant resist **60** may be removed from the substrate **30** in a stripping (or ashing) process by exposing the substrate **30** to energized process gas comprising stripping gas. Stripping gas may comprise, for example, one or more of O_2, N_2, H_2, H_2O, NH_3, CF_4, C_2F_6, CHF_3, $C_3H_2F_6$, $C_2H_4F_2$, or CH_3F. In one version, a suitable stripping gas for stripping polymeric resist material comprises (i) oxygen, and optionally (ii) an oxygen activating gas or vapor, such as water vapor, nitrogen gas, or fluorocarbon gas, the fluorocarbon gases including any of those listed above. The oxygen activating gas increases the concentration of oxygen radicals in the stripping gas. The stripping gas composition may comprise oxygen and nitrogen in a volumetric flow ratio of about 6:1 to about 200:1, and more preferably from about 10:1 to about 12:1. For a 5-liter process chamber **120**, a suitable gas flow rate comprises 3000 to 3500 sccm of O_2 and 300 sccm of N_2. In one version, a stripping gas comprises about 3500 sccm O_2, about 200 sccm N_2 and optionally about 300 sccm H_2O, that is energized at a power level of about 1400 Watts and introduced into the cleaning chamber **120** at a pressure of about 2 Torr for about 15 seconds. In one version, the water vapor content in the stripping gas should be less than about 20% by volume of the combined oxygen and nitrogen gas content to provide adequate stripping rates. A suitable ratio of the volumetric water vapor flow V_{H2O} to the combined volumetric flow of oxygen and nitrogen (V_{O2} + V_{N2}) is from about 1:4 to about 1:40, and more preferably about 1:10. When the remnant resist comprises oxide hard mask, suitable stripping gases are gases capable of stripping oxide, such as halogen containing gases, including CF_4, C_2F_6, CHF_3, $C_3H_2F_6$, $C_2H_4F_2$ and HF. The substrate may be exposed to the stripping gas for a period of time of from about 10 seconds to about 1000 seconds, and more preferably for about 45 seconds. A single stripping step may be performed or multiple stripping steps may be performed, as discussed in U.S. Patent No. 5,545,289, which is incorporated herein by reference in its entirety.

The cleaning process may also comprise post-etch passivation of the substrate **30**, particularly when conductive material **45** has been etched in the etching process, to remove or inactivate corrosive residue species **75** on the substrate **30**. To passivate the substrate **30**, energized process gas comprising passivating gas may be provided in the process zone **215**. The passivating gas composition is selected to remove or inactivate corrosive etchant residue, such as residual species **75** or to

prevent the formation of corrosive or contaminant materials on the etched substrate **30**. Passivating gas may comprise one or more of H_2O, NH_3, H_2O_2, O_2, N_2, CF_4, C_2F_6, CHF_3, H_2, $C_3H_2F_6$, $C_2H_4F_2$, or CH_3F. In one version, any gas or vapor containing hydrogen can serve as the passivating gas, including hydrogen, water vapor, ammonia, methanol, hydrogen sulfide, and mixtures thereof. In another version, the passivating gases include (i) ammonia and oxygen, or (ii) water vapor, with optional oxygen and nitrogen. When the passivating gas comprises ammonia and oxygen, the volumetric flow ratio of ammonia to oxygen is preferably from about 1:1 to about 1:50, more preferably from about 1:5 to about 1:20, and most preferably about 1:10. For a 5-liter capacity chamber **120**, a preferred gas flow comprises 300 sccm NH_3 and 3000 sccm O_2. Alternatively, a passivating gas comprising at least about 80 volume % H_2O, and preferably about 100 volume % H_2O, can be used to passivate the etchant residue **75**. In one version, a passivating gas comprises about 500 sccm H_2O energized at a power level of about 1400 Watts and introduced into the cleaning chamber **120** at a pressure of about 2 Torr for about 15 seconds. When a bubbler is used, an inert carrier gas such as argon or helium can be passed through the bubbler to transport water vapor to the vacuum chamber. Optionally, oxygen, nitrogen or other additive can be added to the passivating gas to enhance passivating. In this version, the passivating gas comprises at least about 20 volume % H_2O. The effect of the oxygen and nitrogen addition depends on the ratio of the volumetric flow rate of water vapor (V_{H2O}) to the combined volumetric flow rates of oxygen and nitrogen ($V_{O2} + V_{N2}$). A suitable volumetric ratio of water vapor flow rate V_{H2O} to combined volumetric flow rates of oxygen and nitrogen ($V_{O2} + V_{N2}$) for use as a passivating gas is at least about 1:2, more preferably from about 1:2 to about 2:1, and most preferably about 1:1. As with the stripping process and as discussed in U.S. Patent No. 5,545,289, the passivation may be either a single step or multiple steps. In one version, the substrate is exposed to the passivating gas for a period of time of from about 10 seconds to about 100 seconds, and more preferably for about 45 seconds. In one version, a multi-cycle passivation process, for example a three cycle process, has been discovered to be particularly effective in preventing corrosion.

In one version, the substrate may be heated during the stripping and/or the passivation processes. For example, when cleaning the substrate **30** in a cleaning chamber **120**, such as the cleaning chamber of Figure 4, the lamps **220** may be used

to heat the substrate to a temperature of at least about 150 °C, and preferably to a temperature of at least about 250°C. Heating the substrate **30** improves the remnant resist removal rate and may also improve the removal rate of some etchant residue, such as Cl in the sidewall deposits **80**, because the Cl can more readily diffuse out of the sidewall deposits. The elevated temperatures also enhance the surface oxidation,when O_2-containing strip density is used, of the etched metal, making them less susceptible to corrosion.

After the substrate **30** is stripped and passivated, the substrate **30** may be transferred to a wet-cleaning chamber (not shown) where the substrate **30** may be exposed for a short period to a solvent to complete the removal of remnant resist **60** and etchant residue **70**. By first cleaning the substrate **30** in the cleaning chamber, the solvent exposure time and/or the solvent strength may be minimized thereby reducing the deleterious effects of the solvent, such as attack of the etched features **67** which may result in sidewall etching and/or critical dimension loss. In some substrate processes, such as those using a thin resist material **60** or those using lightly polymerizing etchant chemistries, the need for exposing the substrate **30** to a wet solvent, such as for example EKC Z65 or similar solvents from EKC Technology, Inc. in Hayward, California, to complete the removal of remnant resist **60** or polymeric sidewall deposits **80**, may be eliminated or replaced by a de-ionized water rinse, significantly improving the substrate fabrication process by substantially preventing damage to the etched features **67** that may otherwise occur in the presence of the wet solvent and by reducing the costs and environmental impact of the process.

It has been discovered that the removal of remnant resist **60** or etchant residue **70** can be improved by exposing the substrate to a process gas comprising a treating gas before, during, or after the cleaning process. The treating gas may be selected to enhance or improve the cleaning of the substrate thereby further reducing the need to expose the substrate **30** to a wet solvent after a cleaning process. The treating process may be performed in the etching chamber **110**, in the cleaning chamber **120**, or in a separate chamber. In one version the treating gas comprises a halogen. In one particular version, the treating gas comprises a hydrogen species and a halogen species. For example, the treating gas may comprise one or more of HCl,

HBr, and HF. Alternatively, the treating gas may comprise H_2 and one or more of Cl_2, Br_2, and F_2, or any composition that provides a hydrogen species, such as one or more of NH_3, CHF_3, CH_2F_2, CH_3F or H_2, H_2O and equivalents, and a halogen species, such as one or more of HCl, HBr, HF, Cl_2, Br_2, F_2, CF_4, NF_3, SF_6, CHF_3, C_2F_6, CH_2F_3, CH_3F and, and equivalents.

In one version, as illustrated in Figures 5a and 5b, the substrate **30** may be pre-treated prior to cleaning by exposing the etched substrate **30** to an energized process gas comprising treating gas. As shown in Figure 5a, the treating gas may be provided in the etching chamber **110** before the substrate **30** is transferred to the cleaning chamber **120**. Alternatively, as shown in Figure 5b, the substrate **30** may be treated in the cleaning chamber **120**. In another version, the etching, treating, and cleaning processes are all performed in the same chamber. In the Figure 5a version, after or just before an etching process has been completed on the substrate **30** or on a layer on the substrate **30**, an energized process gas comprising treating gas is provided in the process zone **145** of the etching chamber **110**. In the Figure 5b version, an energized process gas comprising treating gas is provided in the process zone **215** of the cleaning chamber **120**. After completion of the treating process or during the treating process, cleaning gas is provided in the process zone **215** to remove the remnant resist **60** and/or to remove the etchant residue **70** from the substrate **30**.

It has been discovered that an effective treating gas, particularly when treating the substrate **30** as shown in Figure 5a, comprises chlorine species, and in one version comprises a hydrogen species and a chlorine species. Accordingly, in one version of the invention, the substrate **30** may be exposed to an energized process gas comprising one or more of (i) HCl, (ii) H_2 and Cl_2, and (iii) a hydrogen species containing gas and a chlorine species containing gas. Treating gas comprising a hydrogen species and a chlorine species is effective in at least partially removing sidewall deposits **80**, such as polymeric sidewall deposits, on the substrate **30**. By treating the substrate **30** with the treating gas and by cleaning the substrate **30** with the cleaning gas, it has been shown that sufficient etchant residue **70** is removed to significantly reduce or eliminate the need to expose the substrate to a wet solvent or to a wet solvent other than H_2O. The hydrogen species and chlorine species

containing treating gas is also particularly effective in removing or in aiding in the removal of sidewall deposits **80** on etched features **67** having tapered profiles. It is believed that treating gas comprising HCl or H_2/Cl_2 reacts with sidewall deposits **80** to remove them from the etched features **67**. For example, the chlorine species may react with metal species, such as aluminum, and hydrogen species may react with organic components, such as carbon. In one version, it has been shown to be advantageous to combine a pretreatment process and a passivation process in order to significantly improve corrosion prevention.

Another version of the invention is shown in Figures 6a and 6b. In this version, the substrate **30** is exposed to an energized process gas comprising treating gas after a cleaning process. In the version of Figure 6a, the treating process may be performed in the cleaning chamber **120** after the cleaning process. The treating gas may be provided in the process zone **215** of the cleaning chamber **120** before or after completion of the cleaning process. Alternatively, as shown in Figure 6b, the substrate **30** may be transferred to a treating chamber, such as a second cleaning chamber **120**, where it can be treated. In the versions of Figures 6a and 6b, the treating gas may be selected to remove remnant resist **60** or etchant residue **70** that remains on the substrate **30** after the cleaning process or may soften and/or loosen the remaining resist **60** or etchant residue **70** so that it may be removed in a de-ionized water bath or with a shortened exposure to a wet solvent.

It has been discovered that a treating gas comprising fluorine is effective in treating the substrate **30** by, for example, softening or loosening remaining etchant residue **70** on the substrate **30** after a cleaning process. For example, a treating gas comprising a hydrogen species, such as one or more of NH_3, H_2O, H_2, and a fluorine species, such as NF_3, CF_4, F_2, SF_6, C_2F_6, and CHF_3,has been shown to effectively remove and/or soften polymeric resist and residue on the substrate **30**. In one version, a treating gas comprising NH_3 and a fluorine-containing gas, such as one or more of NF_3, CF_4, has been shown to allow for effective etchant residue **70** removal without the need for exposing the substrate **30** to a wet solvent. It is believed that by energizing the NH_3 and the fluorine-containing gas, hydrogen and fluorine species are generated that react with and solubilize the sidewall deposits **80**, to render the deposits removable by a de-ionized water rinse, for example. In addition, it is believed

that a particular mixture of NH_3 and NF_3, such as for example 3:1 NH_3 to NF_3, can produce a film on the substrate **30** that may release HF when exposed to an aqueous solution or other polar solvent. Accordingly, HF can be liberated and residue removed simultaneously during the wet process steps (e.g. DI rinse).

An advantage of the version of Figure 6a is that the treating gas may also be introduced under process conditions selected to remove process residue from the chamber surfaces, such as surfaces of walls or components in the chamber **120**. For example, residue may be generated during the cleaning process, and the residue may get deposited on the surfaces. By simultaneously treating the substrate **30** and removing the residue from the surfaces in the chamber **120**, the need for a separate chamber cleaning step may be reduced, and throughput and substrate fabrication consistency may be improved. Thus, in one version, a halogen-containing treating gas is introduced in the process zone **215** of the cleaning chamber **120** after or during a cleaning process to simultaneously treat the substrate **30** and to remove residue from the chamber surfaces. The treating gas may be introduced in a volumetric flow rate of about 80 sccm to about 1000 sccm, more preferably about 300 sccm to about 500sccm, and most preferably about 320 sccm, under the following process conditions: 80 sccm NF_3, 240 sccm NH_2, 2 torr, 1.4 kw for 200 mm substrate processing chamber. In one particular version, the treating gas may comprise one or more of H_2, F_2, NH_3, NF_3, CF_4, CH_4, CH_3F, and CHF_3. The treating gas may also be used to clean residue from the chamber surfaces in a version of the invention where the substrate **30** is etched, cleaned, and treated in the same chamber, thereby removing etchant residue and/or cleaning residue from the chamber surfaces. For example, treatment in the etch chamber using HCl or H_2/Cl_2 can remove etchant residues from the wafer and etch by-product deposition from chamber surfaces.

The effectiveness of the treating gas in the processes of Figures 5a and 5b or Figures 6a or 6b may be increased by selecting process conditions that maximally treat the substrate **30** without damaging the etched features **67** thereon. For example, in the version of Figures 5a and 5b, the treating gas may comprise HCl in a volumetric flow rate of from about 80 sccm to about 250 sccm, more preferably from about 100 sccm to about 200 sccm, and most preferably about 150 sccm in the etching chamber **110** or in equivalent volumetric flow rates in the cleaning chamber

120, for 200 mm substrate processing chamber. The substrate **30** may be exposed to the treating gas for a period of at least about 30 seconds, more preferably at least about 120 seconds, and most preferably about 240 seconds with the chamber **110** maintained at a pressure of about 25 mTorr, a source power of about 500 watts, and a temperature of about 150°C. In the version of Figures 6a and 6b, the treating gas may comprise NH_3 in a volumetric flow rate of from about 80 sccm to about 1000 sccm, more preferably from about 100 sccm to about 400 sccm, and most preferably about 240 sccm and NF_3 in a volumetric flow rate of from about 5 sccm to about 200 sccm, more preferably from about 20 sccm to about 120 sccm, and most preferably about 80 sccm in the cleaning chamber **120**. The volumetric flow ratio of NH_3 to NF_3 may be from about 1:1 to about 10:1, more preferably from about 2:1 to about 4:1, most preferably 3:1.

The effectiveness of the treating gas may also be increased by applying a bias to the substrate **30**. For example, in the version of Figures 5a and 5b, a bias power of from about 0 watts to about 150 watts, more preferably from about 20 watts to about 100 watts, and most preferably about 50 watts may be applied to the process electrode **175** in the etching chamber **110**. The application of bias power has been shown by scanning electron microscope (SEM) data to significantly improve the resist material **60** and the etchant residue **70** removal during the treating process, leaving less resist **60** and residue **70** to be removed during the cleaning process. It is believed that the ion flux resulting from the applied bias power together with the reaction of the treating gas with sidewall deposits **80** helps to remove the sidewall deposits **80** from the etched features **67**. Bias power may also increase the effectiveness of the treating process of Figures 6a and 6b and may be, for example, from about 0 to 600 watts, more preferably from about 50 watts to about 300 watts, and most preferably about 150 watts.

The temperature of the substrate **30** may also be selected to increase the effectiveness of the cleaning and the treating processes. For example, in the treating process of Figures 6a and 6b, it has been determined that a substrate temperature of from about 20°C to about 100°C is effective in treating the substrate **30**, for example by solubilizing the sidewall deposits **80**. This is believed to be due to enhancing adsorption of the reactive species onto the substrate and minimizing

chemical attack of the substrate. Accordingly, in one version of the invention, the substrate **30** is maintained at a temperature of from about 20°C to about 100°C. In one particular version, the substrate is cleaned in a stripping and passivating process at a temperature of about 250°C and then cooled to a temperature of about 50°C to about 100°C to treat the substrate. When the substrate **30** is cleaned and treated in the same chamber, for example as shown in Figure 6a, the substrate may be rapidly cooled, such as by circulating a heat transfer fluid through the support **210** in the chamber. Alternatively, when different chambers are used, for example as shown in Figure 6b, one chamber may be maintained at a first temperature, such as about 250°C, and the second chamber may be maintained at a second temperature, such as from about 30°C to about 100°C. By providing two chambers at different temperatures or by rapidly cooling the substrate **30**, process throughput may be increased, as discussed in commonly owned U.S. Patent Application Serial No. 09/595,336, filed on June 14, 2000, entitled "Substrate Cleaning Apparatus and Method" by Yun et al, attorney docket number 3148/USA/EMET, which is incorporated herein by reference in its entirety.

The integrated process sequence of the versions described above provides effective and improved remnant resist **60** and etchant residue **70** removal. The cleaned substrate often does not require wet solvent exposure. The versions of Figures 5a, 5b, 6a, and 6b provide a large process window for etch processes by providing improved strip/residue removal. The invention allows for the removal of resist **60** and residue **70** at relatively low temperatures with a de-ionized water rinse following exposure of the substrate **30** to to relatively high temperature oxygen-containing and/or water vapor containing gases. This is advantageous because the high temperature provides high strip rates and improved corrosion control. In addition, the invention provides the ability to incorporate additional processes, such as high temperature nitrogen exposure, which can improve corrosion resistance, but which necessitates wet solvent exposure of the substrate **30** in conventional processes.

In another version, as shown in Figures 7a, 7b, and 7c, the substrate **30** may be exposed to an energized process gas comprising a first treating gas before a cleaning process and exposed to an energized process gas comprising a second

treating gas after the cleaning process. This version provides increased removal of resist **60** and etchant residue **70** and even further reduces the need to expose the substrate **60** to a wet solvent. The first and second treating gases may be the same gas or different gas. In one version, one of the treating gases may comprise chlorine. In another version, one of the treating gases may comprise fluorine. In one particular version, the first treating gas comprises a hydrogen species and a chlorine species, such as HCl, and the second treating gas comprises a hydrogen species and a fluorine species, such as one or more of NH_3 and H_2 and one or more of NF_3, CF_4, and SF_6. As shown in Figure 7a, the first treating gas may be introduced in the etching chamber **110** after or during an etching process, and the second treating gas may be introduced in the cleaning chamber after or during a cleaning process. In Figure 7b, the cleaning process and the second treating process are performed in separate chambers. In the version of Figure 7c, the first and second treating gases are provided in the cleaning chamber. Alternatively, the etching, cleaning and first and second treating processes may be performed in the same chamber.

Although the present invention has been described in considerable detail with regard to the preferred embodiments thereof, other embodiments are possible. For example, the order of stripping and passivating and treating may be changed. Additionally, a treating gas comprising fluorine may be introduced before the cleaning process. Other similar modifications can be made without departing from the scope of the invention. Therefore, the appended claims should not be limited to the descriptions of the preferred embodiments contained herein.

What is claimed is:

1. A substrate processing method comprising:

(a) exposing a substrate to an energized process gas to etch the substrate;

(b) exposing the substrate to an energized cleaning gas; and

(c) before, during, or after (b), exposing the substrate to an energized treating gas comprising a halogen species and a hydrogen species.

2. A method according to claim 1 wherein the cleaning gas comprises a stripping gas comprising one or more of O_2, N_2, H_2O, NH_3, CF_4, C_2F_6, CHF_3, $C_3H_2F_6$, $C_2H_4F_2$, and CH_3F provided under process conditions selected to at least partially remove remnant resist material on the substrate.

3. A method according to claim 1 wherein the cleaning gas comprises a passivating gas comprising one or more of H_2O, NH_3, H_2O_2, O_2, N_2, CF_4, C_2F_6, CHF_3, $C_3H_2F_6$, $C_2H_4F_2$, or CH_3F provided under process conditions selected to passivate the substrate.

4. A method according to claim 1 wherein the treating gas comprises a chlorine species.

5. A method according to claim 1 wherein the treating gas comprises a fluorine species.

6. A method according to claim 1 wherein the treating gas comprises one or more of NH_3 and H_2.

7. A method according to claim 6 wherein the treating gas comprises one or more of NF_3, CF_4, C_2F_6 and SF_6.

8. A method according to claim 1 wherein the treating gas comprises one or more of HCl, HBr and HF.

9. A method according to claim 1 wherein the treating gas comprises

H_2 and one or more of Cl_2, Br_2 and F_2.

10. A method according to claim 1 wherein the treating gas comprises one or more of (i) H_2O, (ii) H_2O_2, and (iii) H_2 and O_2 and (iv) H_2 and H_2O.

11. A method according to claim 1 wherein the substrate is exposed to the etching gas in a first process zone and wherein the substrate is exposed to the cleaning gas in a second process zone.

12. A method according to claim 11 wherein the substrate is exposed to the treating gas in the first process zone.

13. A method according to claim 11 wherein the substrate is exposed to the treating gas in the second process zone.

14. A substrate processing method comprising:

(a) exposing a substrate to an energized process gas to etch the substrate; and

(b) exposing the substrate to an energized treating gas comprising a chlorine species.

15. A method according to claim 14 wherein the treating gas is provided under process conditions selected to enhance removal of etchant residue or remnant resist on the substrate.

16. A method according to claim 14 further comprising:

(c) exposing the substrate to an energized cleaning gas.

17. A method according to claim 16 wherein (c) occurs after (b).

18. A method according to claim 16 wherein (b) and (c) are in different process zones.

19. A method according to claim 14 wherein the treating gas comprises a hydrogen species.

20. A method according to claim 19 wherein the treating gas comprises HCl.

21. A method according to claim 19 wherein the treating gas comprises H_2 and Cl_2.

22. A substrate processing method comprising:

(a) exposing a substrate to an energized process gas to etch the substrate; and

(b) exposing the substrate to an energized treating gas comprising a fluorine species and a hydrogen species.

23. A method according to claim 22 wherein the treating gas is provided under process conditions selected to enhance removal of etchant residue or remnant resist on the substrate.

24. A method according to claim 22 further comprising:

(c) exposing the substrate to an energized cleaning gas.

25. A method according to claim 24 wherein (b) occurs after (c).

26. A method according to claim 24 wherein (b) and (c) are in the same process zone.

27. A method according to claim 22 wherein the treating gas comprises a compound comprising a fluorine species and a hydrogen species a compound comprising a fluorine species and a hydrogen species.

28. A method according to claim 22 wherein the treating gas comprises H_2 and F_2.

29. A method according to claim 22 wherein the treating gas comprises one or more of NH_3 and H_2 and one or more of NF_3, CF_4, C_2F_6, and SF_6.

30. A method of treating an etched substrate, the method comprising:

exposing the etched substrate to an energized process gas comprising a first halogen species and

exposing the etched substrate to an energized process gas comprising a second halogen species.

31. A method according to claim 30 wherein the first halogen species comprises chlorine species.

32. A method according to claim 30 wherein the second halogen species comprises fluorine species.

33. A method of cleaning an etched substrate, the method comprising:

(a) exposing a substrate to a cleaning gas; and

(b) after (a), exposing the substrate to an energized treating gas comprising one or more of NH_3 and H_2.

34. A method according to claim 33 wherein the treating gas further comprises one or more of NF_3, CF_4, C_2F_6, and SF_6.

35. A method according to claim 33 wherein the cleaning gas comprises a stripping gas comprising one or more of O_2, N_2, H_2O, NH_3, CF_4, C_2F_6, CHF_3, $C_3H_2F_6$, $C_2H_4F_2$, and CH_3F provided under process conditions selected to at least partially remove remnant resist material on the substrate.

36. A method according to claim 33 wherein the cleaning gas comprises a passivating gas comprising one or more of H_2O, NH_3, H_2, H_2O_2, O_2, N_2, CF_4, C_2F_6, CHF_3, $C_3H_2F_6$, $C_2H_4F_2$, or CH_3F provided under process conditions selected to passivate the substrate.

37. A substrate processing method comprising:

exposing a substrate to an energized process gas to etch the substrate in a process zone and

exposing the substrate to an energized treating in the process zone.

38. A method according to claim 37 wherein the treating gas comprises a halogen species.

39. A method according to claim 37 wherein the treating gas comprises a haolgen species and a hydrogen species.

40. A method according to claim 39 wherein the treating gas comprises HCl.

41. A method according to claim 39 wherein the treating gas comprises H_2 and Cl_2.

42. A method according to claim 37 further comprising exposing the substrate to an energized cleaning gas.

43. A method according to claim 37 further comprising exposing the substrate to an energized cleaning gas in a second process zone.

44. A method of treating an etched substrate, the method comprising:

(a) exposing the etched substrate to an energized process gas comprising oxygen species while maintaining the substrate at a temperature of at least about 200°C;

(b) treating the substrate with a treating gas; and

(c) rinsing the substrate with de-ionized water to remove etchant residue on the substrate.

45. A method according to claim 44 wherein (b) comprises exposing the substrate to an energized treating gas.

46. A method according to claim 44 wherein the treating gas comprises a halogen species.

47. A method according to claim 44 wherein the treating gas comprises a halogen species and a hydrogen species.

48. A method according to claim 44 wherein the treating gas comprises NH_3 and one or more of NF_3, CF_4, C_2F_6, and SF_6.

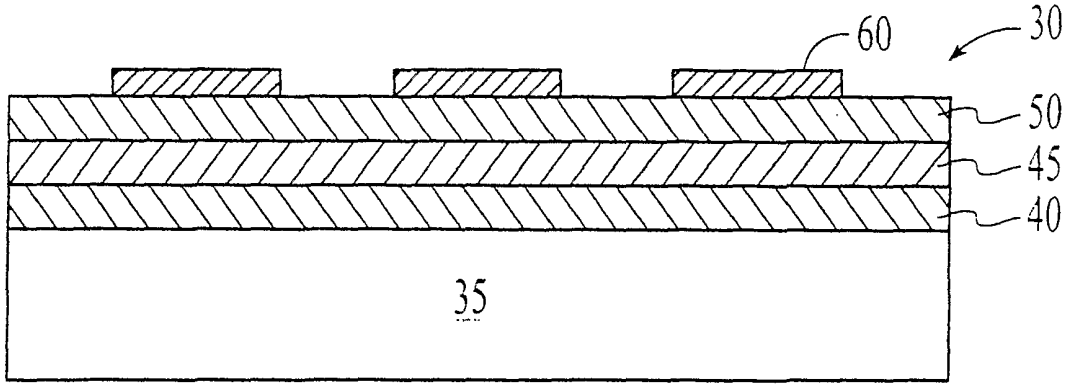


FIG. 1A

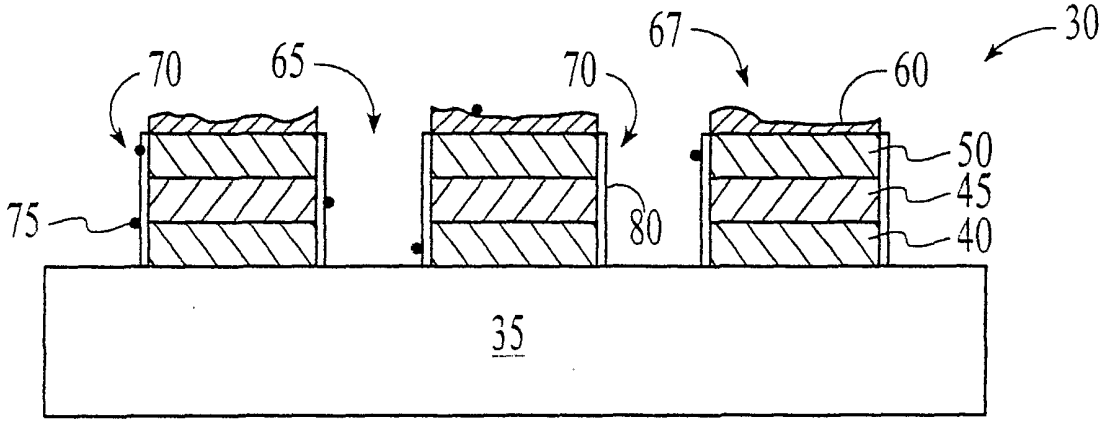


FIG. 1B

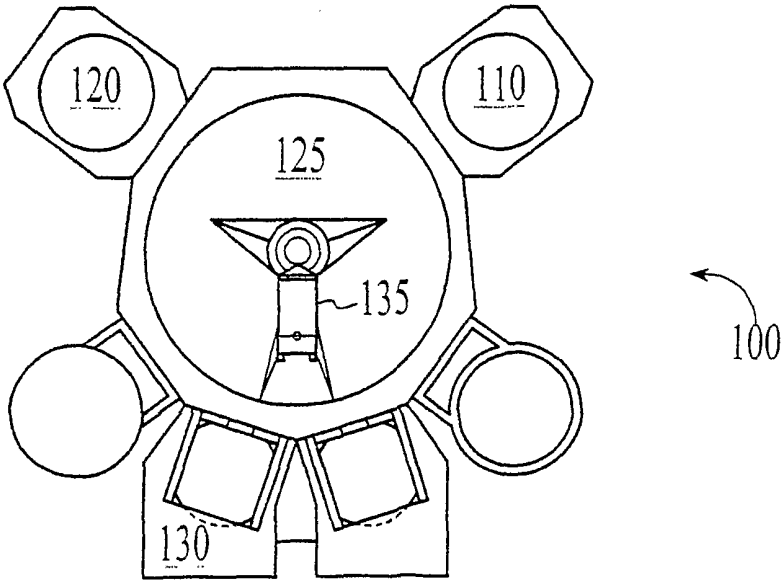


FIG. 2

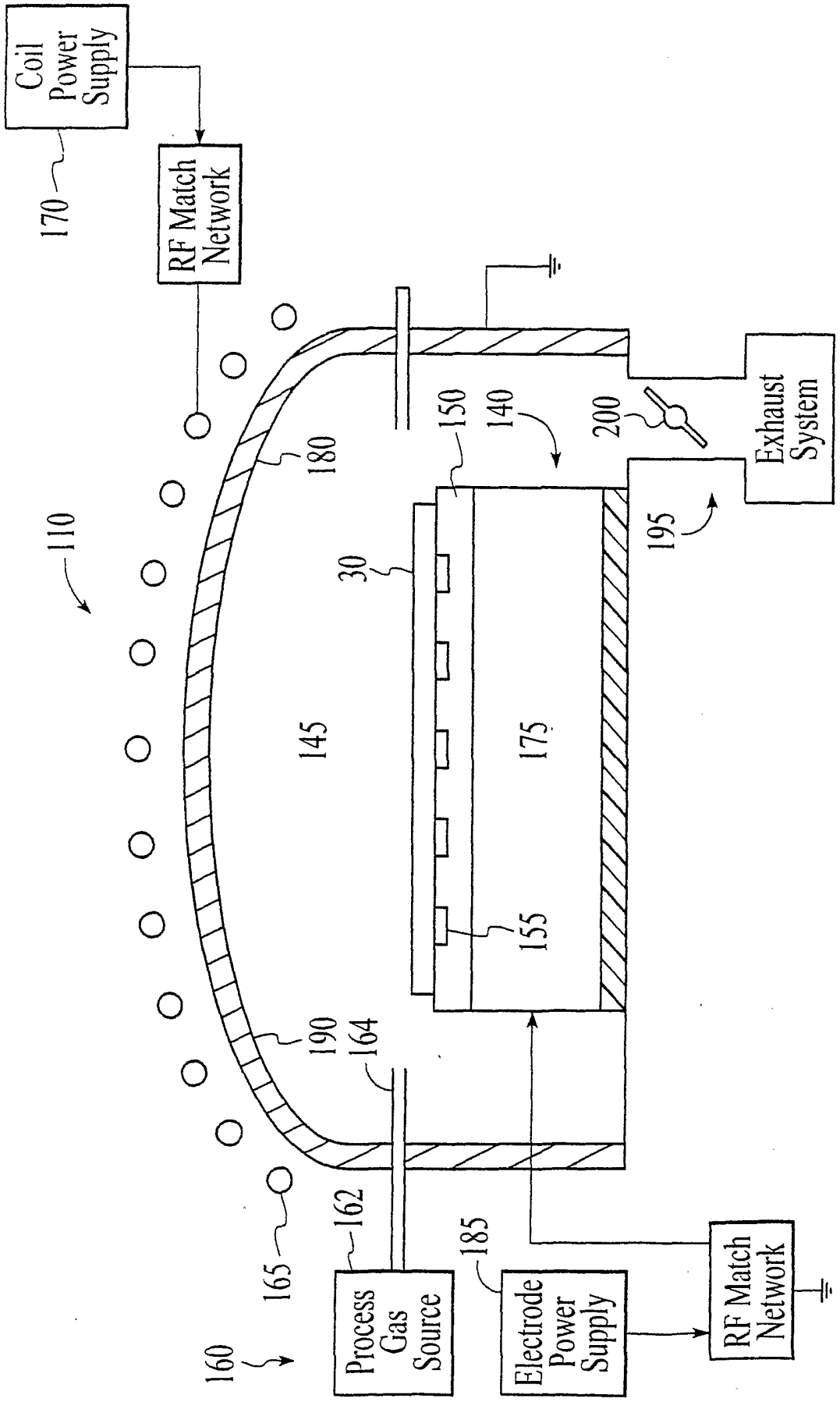

Coil Power Supply
170
RF Match Network
110
180
150
140
200
Exhaust System
195
30
145
175
155
190
164
162
165
160
Process Gas Source
185
Electrode Power Supply
RF Match Network

FIG. 3

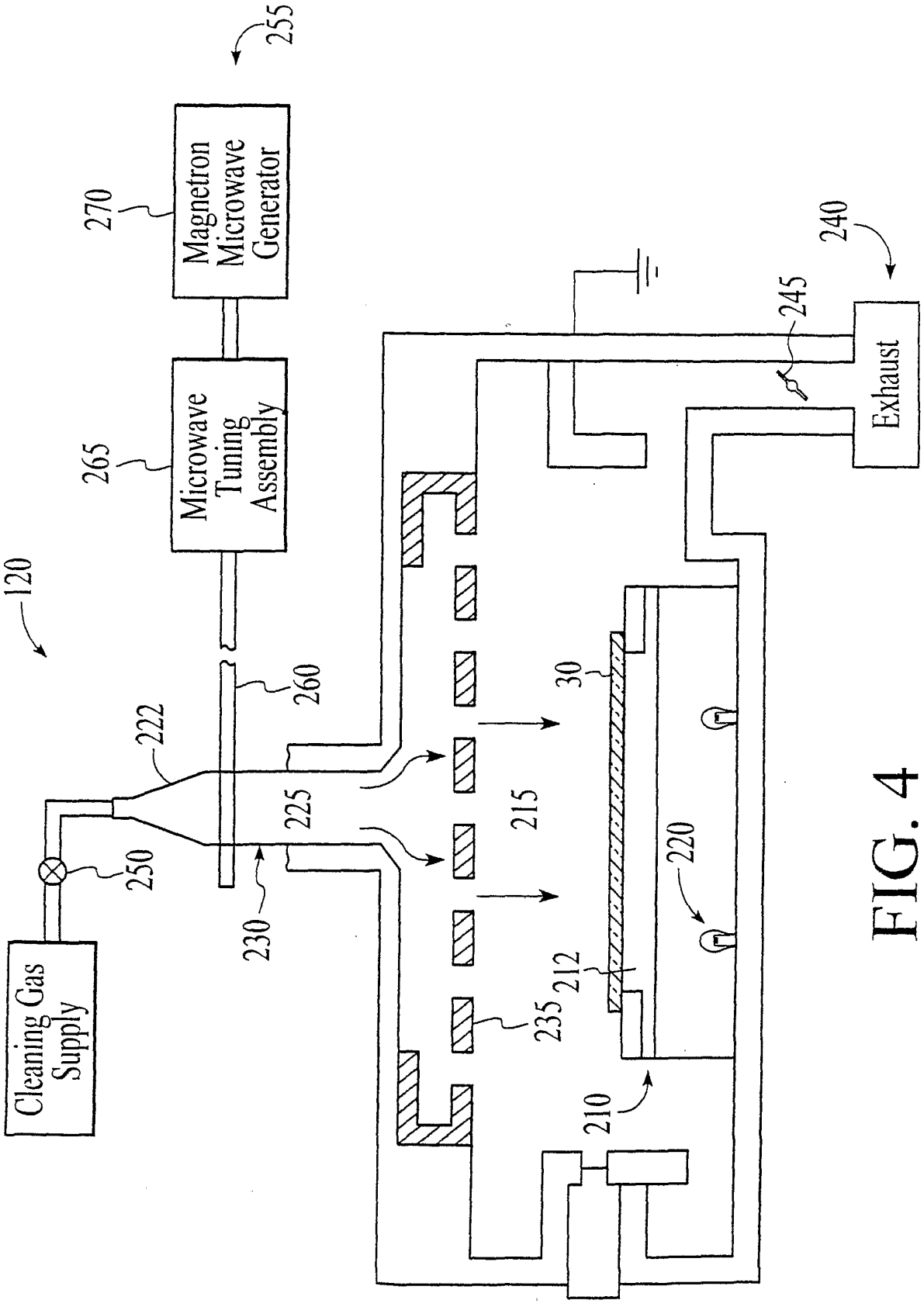

255
270
Magnetron Microwave Generator
265
Microwave Tuning Assembly
120
260
222
225
250
230
Cleaning Gas Supply
30
215
220
212
235
210
240
245
Exhaust

FIG. 4

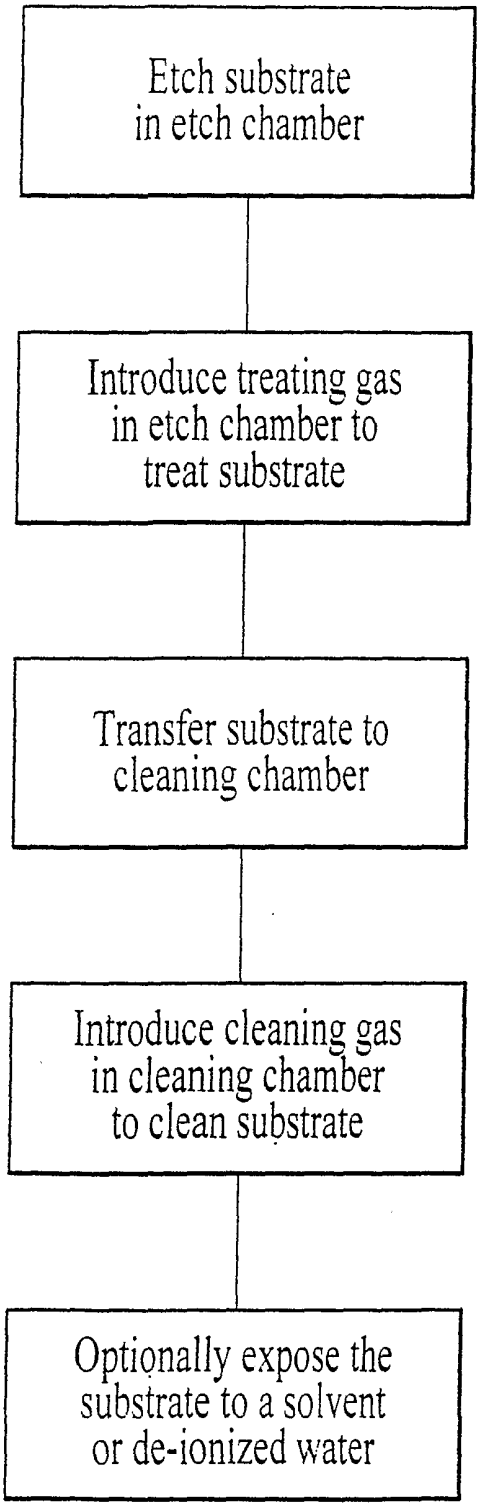

Etch substrate in etch chamber
Introduce treating gas in etch chamber to treat substrate
Transfer substrate to cleaning chamber
Introduce cleaning gas in cleaning chamber to clean substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 5A

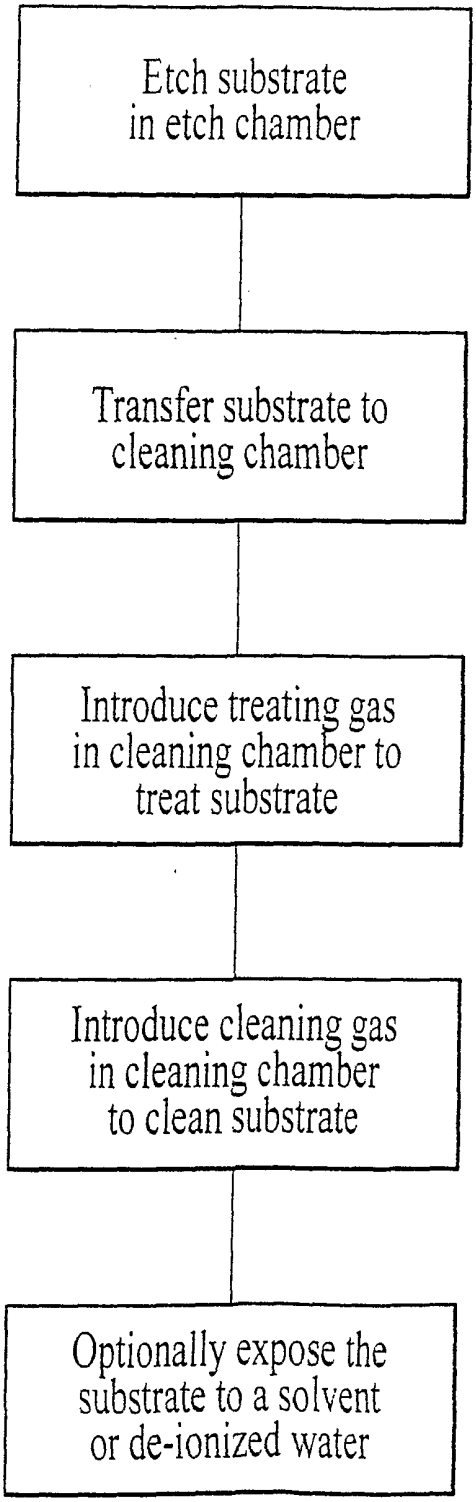

Etch substrate in etch chamber
Transfer substrate to cleaning chamber
Introduce treating gas in cleaning chamber to treat substrate
Introduce cleaning gas in cleaning chamber to clean substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 5B

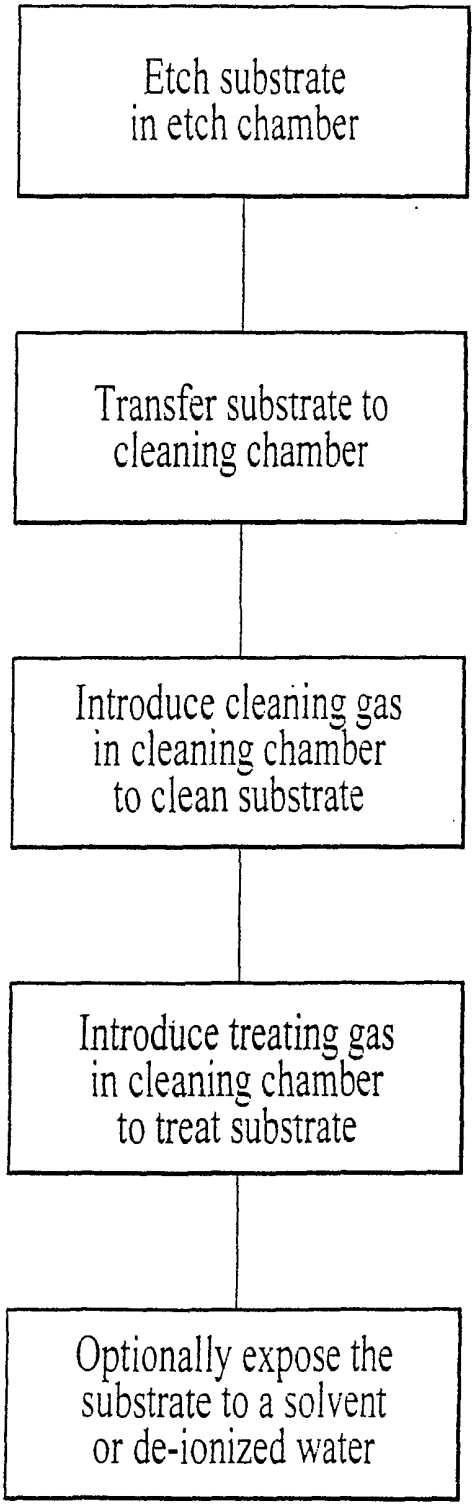

Etch substrate in etch chamber
Transfer substrate to cleaning chamber
Introduce cleaning gas in cleaning chamber to clean substrate
Introduce treating gas in cleaning chamber to treat substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 6A

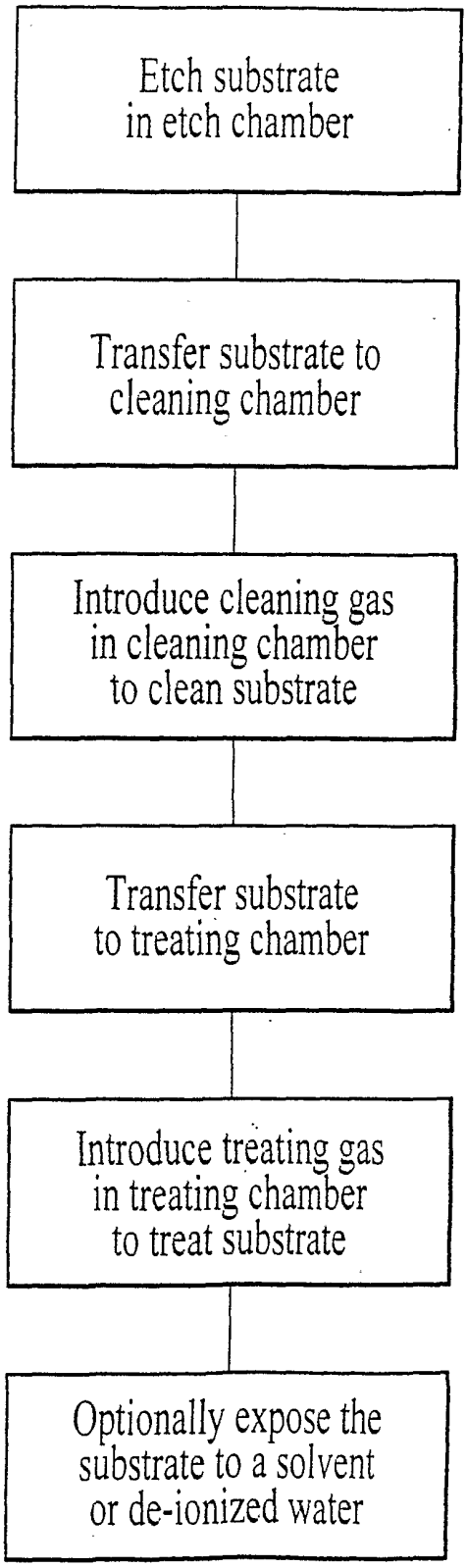

Etch substrate in etch chamber
Transfer substrate to cleaning chamber
Introduce cleaning gas in cleaning chamber to clean substrate
Transfer substrate to treating chamber
Introduce treating gas in treating chamber to treat substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 6B

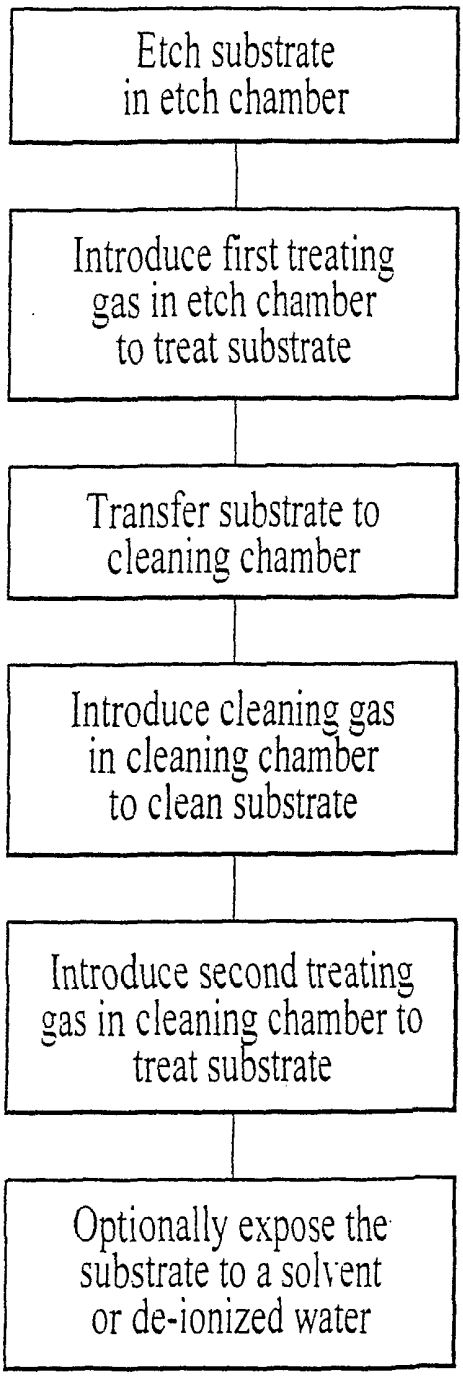

Etch substrate in etch chamber
Introduce first treating gas in etch chamber to treat substrate
Transfer substrate to cleaning chamber
Introduce cleaning gas in cleaning chamber to clean substrate
Introduce second treating gas in cleaning chamber to treat substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 7A

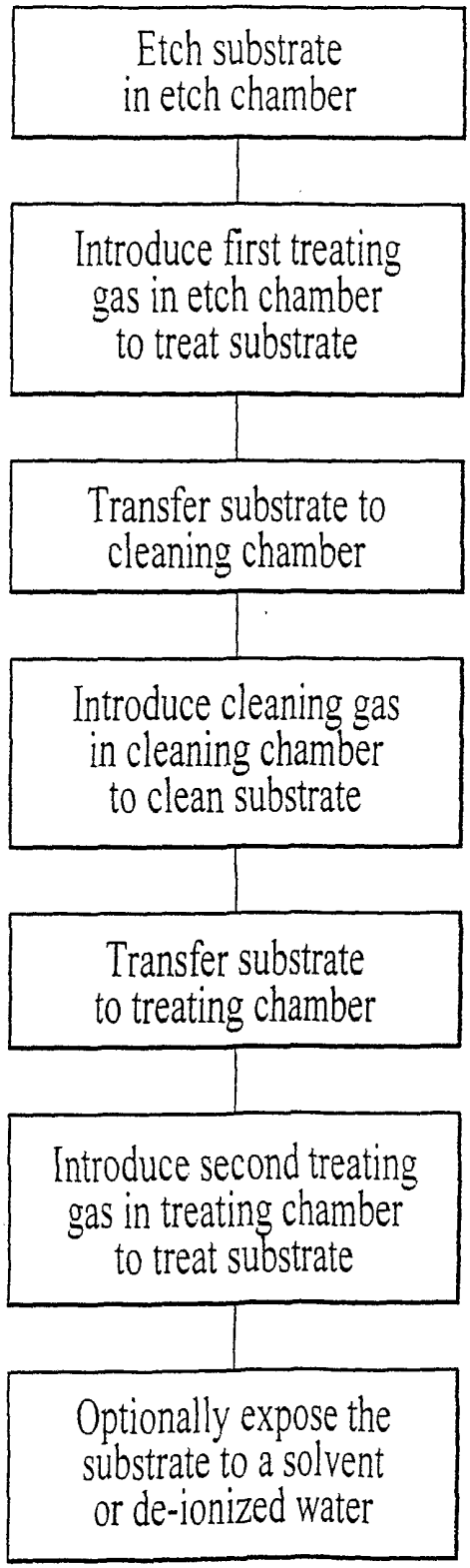

Etch substrate in etch chamber
Introduce first treating gas in etch chamber to treat substrate
Transfer substrate to cleaning chamber
Introduce cleaning gas in cleaning chamber to clean substrate
Transfer substrate to treating chamber
Introduce second treating gas in treating chamber to treat substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 7B

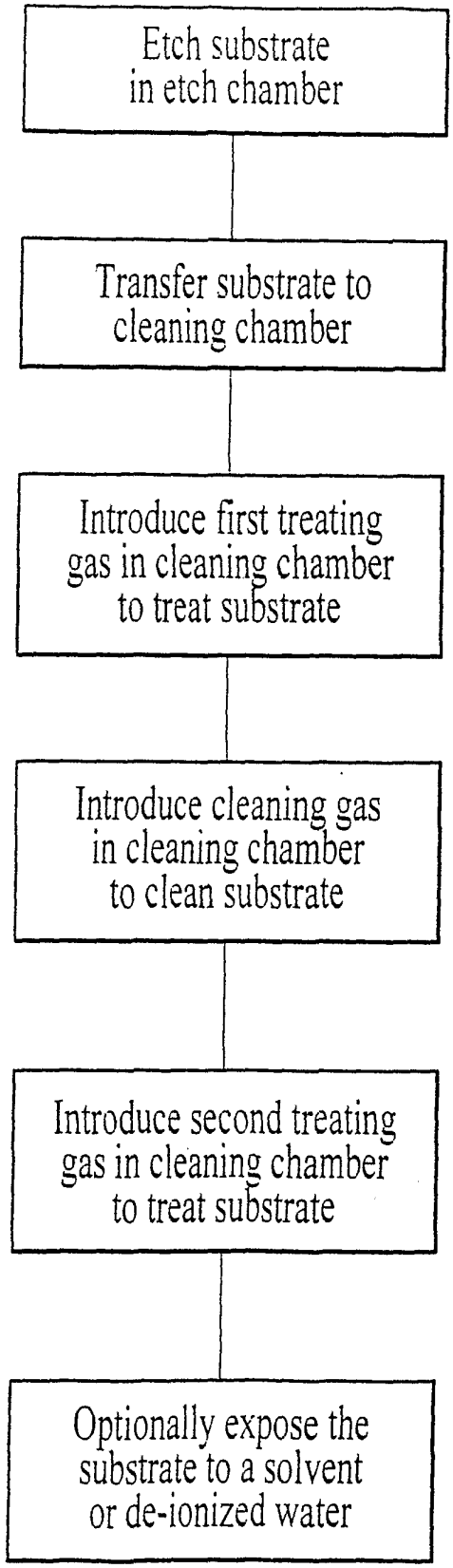

Etch substrate in etch chamber
Transfer substrate to cleaning chamber
Introduce first treating gas in cleaning chamber to treat substrate
Introduce cleaning gas in cleaning chamber to clean substrate
Introduce second treating gas in cleaning chamber to treat substrate
Optionally expose the substrate to a solvent or de-ionized water

FIG. 7C