(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number
WO 01/08209 A1

(51) International Patent Classification[7]: H01L 21/3213

(21) International Application Number: PCT/US00/20320

(22) International Filing Date: 26 July 2000 (26.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/362,924 27 July 1999 (27.07.1999) US

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

(72) Inventors: CHOW, Waiching; 35875 Vivian Place, Fremont, CA 94536 (US). WILLIAMS, Raney; 111 Pacchetti Way, Mountain View, CA 94040 (US). LILL, Thorsten, B.; 880 East Fremont Avenue, #634, Sunnyvale, CA 94087 (US). CHEN, Arthur, Y.; 744 Bodega Court, Fremont, CA 94539 (US).

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

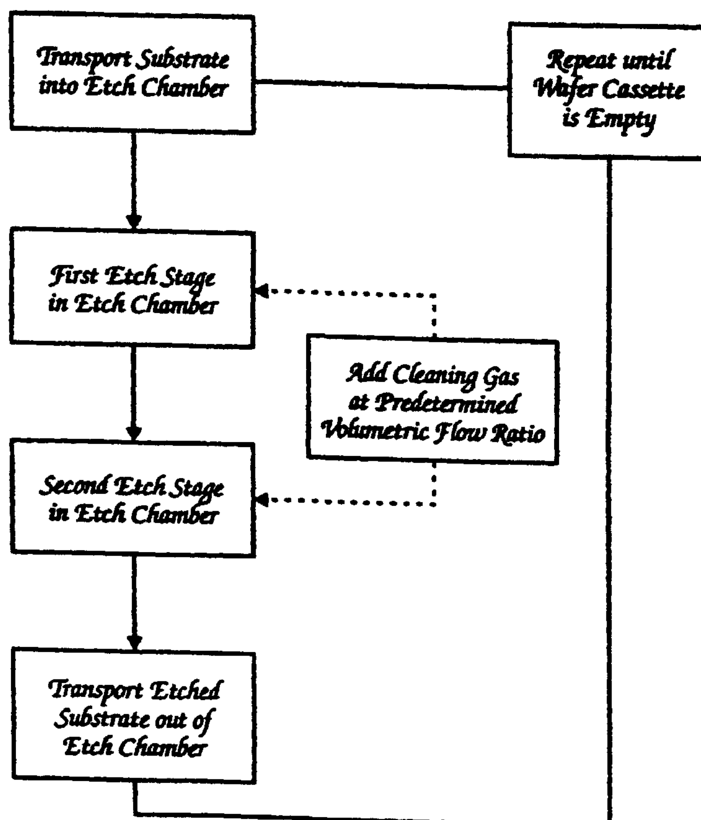
(81) Designated States *(national)*: JP, KR.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MULTIPLE STAGE CLEANING FOR PLASMA ETCHING CHAMBERS



(57) Abstract: A process for etching multiple layers (22, 24) on a substrate (25) in an etching chamber (30) and cleaning a multilayer etchant residue formed on the surface of the walls (45) and components of the etching chamber (30). In multiple etching steps, process gas comprising different compositions of etchant gas is used to etch layers on the substrate (25) thereby depositing a compositionally variant etchant residue inside the chamber (30). In one cleaning step, a first cleaning gas is added to the process gas to clean a first residue or to suppress deposition of the first residue onto the chamber surfaces. In a second cleaning step, another residue composition is cleaned off the chamber surfaces using a second cleaning gas composition. The process is particularly advantageous for etching of metal silicides (22) or polysilicon (24) using chlorine or bromine chemistry, whereby fluorides like CF4, NF3 or SF6 are added as first cleaning gas, and oxygen is used as second cleaning gas.

WO 01/08209 A1

MULTIPLE STAGE CLEANING FOR PLASMA ETCHING CHAMBERS

CROSS-REFERENCE

This application is a continuation-in-part of application Serial No. 08/969,122, filed November 12, 1997, which is incorporated herein by reference.

5

BACKGROUND

The present invention relates to a method of cleaning chambers that are used in the processing of substrates.

10

In the manufacture of integrated circuits, materials such as silicon dioxide, silicon nitride, polysilicon, metal, metal silicide, and monocrystalline silicon, that are deposited or otherwise formed on a substrate, are etched in predefined patterns to form gates, vias, contact holes, trenches, and/or interconnect lines. In the
15 etching process, a patterned mask composed of silicon oxide or silicon nitride (hard mask) or photoresist polymer, is formed on the substrate by conventional photolithographic methods. The exposed portions of the underlying material that lie between the features of the patterned mask are etched by capacitive or inductively coupled plasmas of etchant gas. During the etching processes, etchant residue (often
20 referred to as a polymer) deposits on the walls and other component surfaces inside the etching chamber. The composition of the etchant residue (residue from the etch process) depends upon the chemical composition of vaporized species of etchant gas, the material being etched, and the mask layer on the substrate. For example, when tungsten silicide, polysilicon or other silicon-containing layers are etched, silicon-
25 containing gaseous species are vaporized or sputtered from the substrate; similarly, etching of metal layers results in vaporization of metal species. In addition, the mask layer on the substrate is also partially vaporized by the etchant gas to form gaseous hydrocarbon or oxygen species. The vaporized and gaseous species condense to form etchant residue comprising polymeric byproducts composed of hydrocarbon species
30 from the resist; gaseous elements such as fluorine, chlorine, oxygen, or nitrogen; and elemental silicon or metal species depending on the composition of the substrate

being etched. The polymeric byproducts deposit as thin layers of etchant residue on the walls and components in the chamber. The composition of the etchant residue typically varies considerably across the chamber surface depending upon the composition of the localized gaseous environment, the location of gas inlet and exhaust ports, and the geometry of the chamber.

The compositional variant, non-homogeneous, etchant residue formed on the etching chamber surfaces has to be periodically cleaned to prevent contamination of the substrate. Typically, after processing of about 25 wafers, an in-situ plasma "dry-clean" process is performed in an empty etching chamber to clean the chamber. However, the energetic plasma species rapidly erode the chamber walls and chamber components, and it is expensive to replace these parts and components. Also, erosion of the chamber surfaces can result in instability of the etching process from one wafer to another. The relatively thin and compositionally variant etchant residue can also make it difficult to stop the in-situ plasma clean process immediately after all of the etchant residue is removed - which results in erosion of the underlying chamber surfaces. Also, it is difficult to clean-off the chemically hard residue deposited at portions of the chamber surfaces without entirely removing chemically softer residues at other portions of the chamber and eroding the underlying chamber surfaces. For example, the etchant residue formed near the chamber inlet or exhaust often has a higher concentration of etchant gas species than the residue formed near the substrate which typically contains a higher concentration of resist, hard mask, or of the material being etched.

It is difficult to form a cleaning plasma that uniformly etches away the compositionally different variants of etchant residue. Thus after cleaning of about 100 or 300 wafers, the etching chamber is opened to the atmosphere and cleaned in a "wet-cleaning" process, in which an operator uses an acid or solvent to scrub off and dissolve accumulated etchant residue from the chamber walls. To provide consistent chamber properties, after the wet cleaning step, the chamber and its internal surfaces are "seasoned" by pumping down the chamber for an extended period of time, and thereafter, performing a series of runs of the etch process on dummy wafers. The internal chamber surfaces should exhibit consistent chemical surfaces, i.e., surfaces having little or no variations in the concentration, type, or

functionality of surface chemical groups; otherwise, the etching processes performed in the chamber produce varying etching results from one substrate to another. In the pump-down process, the chamber is pumped down to a high vacuum environment for 2 to 3 hours to outgas moisture and other volatile species trapped in the chamber during the wet clean process. Thereafter, the etch process to be performed in the chamber, is run for 10 to 15 minutes on a set of dummy wafers, or until the chamber provides consistent and reproducible etching properties.

In the competitive semiconductor industry, the increased cost per substrate that results from the downtime of the etching chamber during the dry or wet cleaning and seasoning process steps, is undesirable. It typically takes 5 to 10 minutes for each dry cleaning process step, and 2 to 3 hours to complete the wet cleaning processes. Also, the wet cleaning and seasoning process often provide inconsistent and variable etch properties. In particular, because the wet cleaning process is manually performed by an operator, it often varies from one session to another, resulting in variations in chamber surface properties and a low reproducibility of etching processes. Thus it is desirable to have an etching process that can remove or eliminate deposition of etchant residue on the chamber surfaces.

In semiconductor fabrication, yet another type of problem arises in the etching of multiple layers of materials that have similar constituent elements, for example, silicon-containing materials such as tungsten silicide, polysilicon, silicon nitride, and silicon dioxide. With reference to Figures 1a and 1b, a typical multilayer polycide structure on a semiconductor substrate **25** comprises metal silicide layers **22** deposited over doped or undoped polysilicon layers **24**. The polycide layers are formed over silicon dioxide layers **26** and etched to form the etched features **29**. In these multilayer structures, it is difficult to obtain a high etching selectivity ratio for etching the metal silicide layer **22** relative to the overlying resist layer **28** or the underlying polysilicon layer **24**. It is desirable to have a high etching selectivity ratio for etching polycide structures that have a non-planar and highly convoluted topography. At a certain time during the etching process, the thinner metal silicide layer **22** is etched through and etching of the underlying polysilicon layer **24** begins, while the thicker metal silicide layer **22** is still being etched. Thus, it is desirable to etch the metal silicide layer **22** at a faster rate relative to the rate of etching of the

polysilicon layer **24**, for example. The same problem arises in the etching of a mask layer of silicon nitride **32** on a very thin silicon dioxide layer **34**, prior to forming trenches in a substrate comprising silicon **36**, as for example shown in Figures 1c and 1d. The etched trenches **38** are used to isolate active MOSFET devices formed on the
5 substrate. The etching selectivity ratio for etching silicon nitride relative to silicon dioxide has to be very high to stop on the silicon dioxide layer **34** without etching through the layer.

High etching selectivity ratios are obtained using a process gas
10 composition that etches the different silicon-containing materials at significantly different etching rates which depend upon the chemical reactivity of the particular process gas composition with a particular layer. However, etching metal silicide layers with high selectivity to polysilicon, or etching silicon nitride layers with high selectivity to silicon dioxide layers, is particularly difficult because both materials
15 contain elemental silicon and most conventional etchant plasmas etch the silicon containing layers to form gaseous $SiCl_x$ or SiF_x species. Thus, it is difficult for the etchant plasma to chemically distinguish and preferentially etch the metal silicide layer **22** faster than the polysilicon layer **24**, and the silicon nitride layer **32** faster than the silicon dioxide layer **34**. This problem is further exacerbated because the etchant
20 residue formed on the chamber sidewalls also contains silicon dioxide and attempts to remove the etchant residue during the polycide etching process can lower the etching rate or etching selectivity ratio for etching these layers.

Thus it is desirable to have an etch process that reduces formation of
25 etchant residue in the etching chamber. It is also desirable if the etchant or cleaning gases do not to erode the exposed surfaces in the chamber. It is further desirable to have an etching or cleaning process that restores the original chemical reactivity and surface functional groups of the chamber surfaces. It is further desirable for the cleaning process to remove chemically adhered etchant residue layers having variable
30 thickness and variant chemical compositions and reactivity without excessive erosion of underlying chamber surfaces.

SUMMARY

The present invention provides a method of etching a substrate in an etching chamber and cleaning off the etchant residues formed on the chamber surfaces. By surfaces in the chamber it is meant any surface inside the chamber enclosure including the walls of the chamber itself and the surfaces of the components in the chamber, such as the gas distributor, electrostatic chuck, focus ring and other components.

In one aspect, a method of treating a chamber by cleaning etchant residue from the chamber comprises providing a first energized process gas in the chamber to clean the surfaces and then providing a second and different process gas in the chamber to further clean the surfaces.

In another aspect of the invention, a method of etching a substrate in a chamber and cleaning etchant residue from surfaces in the chamber comprises placing the substrate in the chamber and, in a first stage, providing an energized first process gas comprising substrate etching gas and a first cleaning gas. In a second stage, an energized second process gas comprising a second and different cleaning gas is provided.

In another aspect of the invention, a method of etching a substrate in a chamber and cleaning etchant residue from surfaces in the chamber comprises placing the substrate in the chamber, etching a first material on the substrate thereby depositing a first etchant residue on the surfaces in the chamber, etching a second material on the substrate while suppressing deposition of a second etchant residue onto the first etchant residue, the first etchant residue being compositionally different from the second etchant residue, and cleaning the first and second etchant residue deposits formed on the surfaces in the chamber.

In another aspect of the invention, a method of etching a substrate in a chamber and cleaning etchant residue from surfaces in the chamber comprises electrostatically holding the substrate in the chamber, providing a first energized gas comprising an etching gas to etch the substrate and a residue cleaning gas, and

providing a second energized gas in the chamber to clean etchant residue deposited on the surfaces in the chamber and simultaneously remove residual charge accumulated in the substrate.

5 In another aspect of the invention, a method of etching a substrate in a chamber and cleaning residue that forms on surfaces in the chamber comprises placing the substrate in the chamber, etching one or more materials on the substrate using energized gas, at least one composition of the energized gas including an etching gas comprising one or more of Cl_2, N_2, O_2, HBr and He-O_2 and a residue
10 cleaning gas comprising one or more of CF_4, SF_6 and NF_3, and cleaning the residue formed on the surfaces in the chamber using another energized gas comprising oxygen.

In yet another aspect of the invention, a method of etching a substrate
15 in a chamber and cleaning residue formed on surfaces in the chamber, the chamber comprising an electrostatic chuck, and the method comprising transferring a substrate into the chamber and electrostatically holding the substrate on the electrostatic chuck, providing an energized gas in the chamber to etch a mask layer on the substrate thereby forming residue on the surfaces in the chamber, the residue comprising
20 chemical species originating from the mask layer, providing another energized gas comprising etching gas comprising one or more of Cl_2, N_2, O_2, HBr, and He-O_2 and residue cleaning gas comprising one or more of CF_4, SF_6, and NF_3 in the chamber to etch material below the mask layer, and providing an oxygen containing plasma in the chamber to assist in dechucking the substrate and to clean the residue formed on the
25 surfaces in the chamber.

In yet another aspect of the invention, a method of cleaning a chamber to remove residue from surfaces in the chamber comprises providing an energized first process gas in the chamber to clean the surfaces in the chamber, and adjusting the
30 chamber source power to control the amount of residue removed from the surfaces.

DRAWINGS

These and other features, aspects, and advantages of the present invention will be better understood from the following drawings, description and appended claims, which illustrate examples of the invention. While the description and drawings below illustrate exemplary features of the invention, it is to 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.

Figure 1a is a schematic cross-section of a substrate having silicon dioxide, polysilicon, metal silicide and resist layers;

Figure 1b is a schematic cross-section of the substrate of Figure 1a after etching of the metal silicide and polysilicon layers;

Figure 1c is a schematic cross-section of a silicon or polysilicon substrate having a mask layer of silicon nitride;

Figure 1d is a schematic cross-section of the substrate of Figure 1c after etching of trenches in the silicon or polysilicon;

Figure 2 is a sectional schematic side view of an etching apparatus of the present invention;

Figure 3 is a flowchart of the process steps used to etch substrates and simultaneously clean the surfaces of the etching chamber and its components;

Figure 4 is a graph showing the components of a multilayer etchant residue formed on internal surfaces of the chamber by a conventional process in which a substrate comprising a mask layer and underlying silicon-containing layers was etched;

Figure 5 is a graph showing the components of a multilayer etchant residue formed on internal surfaces of the chamber by a process of the present invention in which a substrate comprising a mask layer and underlying silicon-containing layers was etched;

Figure 6 is a graph showing the deposition and removal rate of etchant residue formed on a bare silicon wafer;

Figure 7 is a graph showing the rate of removal of residue having different compositions and thicknesses; and

Figure 8 is a graph showing the rate of removal of residue for increasing plasma source power levels.

DESCRIPTION

An apparatus **20** suitable for etching a substrate **25** according to the present invention, as schematically illustrated in Figure 2, comprises an enclosed process chamber **30** defining a process zone for processing the substrate. A load-lock transfer area (not shown) is maintained at low pressure for holding a cassette of substrates **25**. The particular embodiment of the apparatus **20** shown herein is suitable for processing of semiconductor substrates **25**, is provided only to illustrate the invention, and should not be used to limit the scope of the invention. The enclosed chamber **30** has sidewalls **45** and a bottom wall **50** fabricated from any one of a variety of materials including metals, ceramics, glasses, polymers, and composite materials. The process zone defined in the etching chamber **30** comprises a volume of at least about 10,000 cm^3, and more preferably about 10,000 to about 50,000 cm^3 and is directly above and surrounds the substrate **25**. The chamber comprises a ceiling **55** that is flat or rectangular shaped, arcuate, conical, dome-shaped, or multiradius dome shaped. The ceiling **55** is dome-shaped to provide a uniform distribution of plasma source power across the entire volume of the plasma process zone. The dome-shaped ceiling **55** is further from the substrate center **60** than a flat ceiling, and can reduce dissociated ion recombination losses near the substrate **25** to provide more uniform plasma ion density across the substrate surface than a flat

ceiling. The dome ceiling **55** can be a flattened dome, conical, truncated conical, cylindrical, or other combination of such shapes, that provides a dome shaped surface above the substrate **25**.

5 Process gas is introduced into the chamber **30** through a gas distribution system **65** that includes a process gas supply **70** and a gas flow control system that comprises a conventional computer system **75** operating a gas flow control valve **80**. The gas distribution system **65** can comprise gas outlets **85** located peripherally around the substrate **25** (as shown), or a showerhead mounted on the ceiling of the 10 chamber **30** with outlets therein (not shown). A second gas supply system **200** provides cleaning gas to the chamber **30** via an electronically operated valve **205**. Spent process gas and etchant byproducts are exhausted from the process chamber **30** through an exhaust system **90** (typically including a 1000 liter/sec roughing pump) capable of achieving a minimum pressure of about 10^{-3} mTorr in the chamber **30**. A 15 throttle valve **95** is provided in the exhaust **90** to control the flow of spent process gas and the pressure of process gas in the chamber **30**. An asymmetric pumping channel **100** is used to pump gases out of the chamber **30** to provide a more symmetrical and uniform distribution of gaseous species around the surface **105** of the substrate.

20

A plasma is generated from the process gas introduced into the chamber **30**, using a plasma generator **110** that couples an electromagnetic field into the gas in the process zone of the chamber. Alternatively process gas can be energized or activated in a remote chamber and the energized or activated process gas can be 25 introduced into the chamber **30** from the remote chamber. A suitable plasma generator **110** comprises an inductor antenna **115** consisting of one or more inductor coils having a circular symmetry with a central axis coincident with the longitudinal vertical axis that extends through the center of the process chamber **30** and perpendicular to the plane of the substrate **25**. The inductor antenna **115** comprises 30 solenoid coils having from 1 to 10 turns, and more typically from 2 to 6 turns. The arrangement and number of solenoid coils are selected to provide the desired product of current and antenna turns (d/dt)(N•I) near the ceiling **55** to provide a strong inductive flux linkage with close coupling to the plasma and therefore greater plasma ion density in the plasma zone adjacent to the substrate **25**, as described in

U.S. patent application no. 08/648,254, which is incorporated herein by reference. When the inductor antenna **115** is positioned near the dome ceiling **55**, the ceiling of the chamber **30** comprises dielectric material which is transparent to electromagnetic fields, such as a slab of machined silicon dioxide or tiles of silicon or silicon dioxide
5 bonded to one another to provide a curved shape. The inductor coil **115** wrapped around the sidewall **45** of the process chamber **30** is a multiradius dome-shaped inductor coil having a "flattened" dome shape that provides increased plasma ion density directly over the substrate center **60** because ion density is affected by local ionization near the inductor coil **115**, and a multiradius inductor coil is closer to the
10 substrate center **60** than a hemispherical coil. In another embodiment, the ceiling **55** comprises a multiradius dome having at least a center radius R and a corner radius r, wherein r is less than the center radius R and R/r is from about 2 to about 10. The frequency of the RF voltage applied to the inductor antenna **115** is typically about 50 KHz to about 60 MHz, and more typically about 13.56 MHz; and the power level
15 of RF voltage applied to the antenna is about 100 to about 5000 Watts.

The plasma formed in the plasma zone can also be enhanced using magnetically enhanced reactors, in which a magnetic field generator (not shown), such as a permanent magnet or electromagnetic coils, are used to apply a magnetic
20 field in the plasma zone to increase the density and uniformity of the plasma. The magnetic field comprises a rotating magnetic field with the axis of the field rotating parallel to the plane of the substrate, as described in U.S. Patent No. 4,842,683, issued June 27, 1989, which is incorporated herein by reference. The magnetic field in the chamber should be sufficiently strong to increase the density of the ions formed
25 in the plasma, and sufficiently uniform to reduce charge-up damage to features such as CMOS gates. Generally, the magnetic field as measured on the surface of the substrate is less than about 500 Gauss, more typically from about 10 to about 100 Gauss, and most typically from about 10 Gauss to about 30 Gauss.

30 In addition to the inductor antenna **115**, one or more process electrodes can be used to accelerate or energize the plasma ions in the chamber **30**. The process electrodes include a first electrode forming a wall of the process chamber **30**, such as the ceiling **55** and/or sidewalls **45** of the chamber. The first electrode is capacitively coupled to a second electrode below the substrate **25**. An electrode

voltage supply supplies an RF potential that maintains the first and second electrodes at different electrical potentials relative to one another.

The enclosed chamber **30** comprises one or more ceramic surfaces that serve different functions. For example, in one embodiment, the walls **45, 50, 55** of the process chamber are coated with or made from a ceramic material, such as boron carbide, boron nitride, silicon, silicon oxide, silicon carbide, or silicon nitride, to protect the walls from chemically erosion in particular etchant gas compositions. For example, boron carbide is useful for protecting sidewalls **45** of chambers from erosion in fluorinated gaseous environments. As another example, sapphire (aluminum oxide) gas distribution plates can be used to release process gas into the chamber **30**. When the chamber contains ceramic surfaces, the etchant residues are difficult to remove, because they can react with some of the ceramic surfaces in the chamber **30** (for example, the surface of the monolithic ceramic member **135** which has highly reactive surface functional groups) such as aluminum oxide, aluminum nitride, silicon, and silicon oxide ceramic surfaces. For example, aluminum oxide or nitride surfaces when exposed to oxygen or moisture form $Al\text{-}OH^-$ surface functional groups that chemically react with the etchant residue to form a hard adherent coating on the chamber surfaces or components.

Another ceramic surface useful in the process chamber **30** is that of a monolithic ceramic member **135** having a ceramic receiving surface **140** for receiving a substrate **25** thereon. Suitable ceramic materials include one or more of aluminum oxide, aluminum nitride, boron carbide, boron nitride, silicon, silicon oxide, silicon carbide, silicon nitride, and titanium oxide. The second electrode can be embedded in the ceramic member **135** so that ceramic material completely surrounds the second electrode to form a unitary monolithic ceramic member. The second electrode is fabricated from an electrical conductor metal such as tungsten, tantalum or molybdenum. The embedded second electrode is the conductor to which a "hot" RF potential is applied, with the other electrodes in the chamber **30** maintained at different potentials, including electrical ground or floating potentials, relative to the second electrode. Because it is embedded in the unitary ceramic member **135**, the second electrode does not have to be electrically isolated from the chamber **30** by additional insulator shields, thereby reducing the parasitic capacitance impedance

loads in the chamber **30** that would otherwise result between the second electrode and the grounded chamber walls **45, 50**. An electrostatic chuck **145**, which can be the second electrode, generates an electrostatic charge for electrostatically holding the substrate **25** to the receiving surface **140** of the ceramic member **135** using a DC chucking voltage applied through an electrical conductor inserted through the ceramic member **135** to connect to the electrode **125**.

The first and second electrodes are electrically biased relative to one another by an electrode voltage supply that includes an AC voltage supply for providing a plasma generating RF voltage to the second electrode and a DC voltage supply **165** for providing a chucking voltage to the electrode. The AC voltage supply provides an RF generating voltage having one or more frequencies from 13.56 MHz to 400 KHz to form a capacitively coupled plasma in the chamber **30**. The power level of the RF bias current applied to the electrode is typically from about 50 to about 3000 Watts. A separate DC voltage from the voltage supply **165** is applied to the electrode **125** to form an electrostatic field that holds the substrate **25** to the chuck **145**. The RF power can be coupled to a bridge circuit and an electrical filter to provide DC chucking power to the electrode **125**.

Operation of the etching chamber **30** to etch one or more of the layers on the substrate **25**, and simultaneously clean the etching chamber, will now be described. The substrate **25** comprises, for example, a semiconductor material, such as a silicon or gallium arsenide wafer, with a plurality of layers comprising, for example, an underlayer of silicon dioxide that functions as a gate oxide layer for MOS transistors, and an overlayer of polycide, which is a combination of tungsten silicide, cobalt silicide, and underlying polysilicon layers. The metal silicide layer on the substrate **25** comprises, for example, tungsten, tantalum, titanium, or molybdenum silicides. A polysilicon layer is below the metal silicide layer and over a silicon dioxide layer. A patterned mask layer, such as photoresist, or a silicon dioxide or silicon nitride hard mask, is formed on the substrate **25**. The exposed portions of the substrate between the mask layer are etched to form features, such as for example, contact holes for fabricating gate electrodes for MOS transistors; polycide interconnecting features that are typically used as gate electrodes; and vias which are multilayer metal structures used to electrically connect two or more electrically

conductive layers separated by insulating silicon oxide/nitride layers. In another example, the substrate comprises silicon nitride layers or silicon oxide layers on a silicon (doped or undoped) substrate.

5 To perform the process of the present invention, a substrate **25** is transferred using a robot arm **170** from a load-lock transfer chamber through a slit valve and into the chamber **30**. A lift finger assembly (not shown) has lift fingers that extend through lift finger openings in the chuck **145** to receive or lift the substrate **25** off the chuck **145**. The robot arm **170** places the substrate **25** on the tips of the lift 10 fingers (not shown) that are elevated by the pneumatic lift mechanism **180** to extend about 2 to 5 centimeters above the surface of the chuck **145**. The pneumatic mechanism, under the control of a computer system, lowers the substrate **25** onto the electrostatic chuck **145**, and helium is supplied through apertures **175** in the chuck to control the temperature of the substrate **25**.

15

A process gas comprising etchant gas for etching the substrate is introduced into the chamber **30** through the gas outlet **85**, and the chamber is typically maintained at a pressure ranging from about 0.1 to about 400 mTorr. Suitable etchant gases for etching layers on the substrate **25**, include for example, 20 HCl, BCl_3, HBr, Br_2, Cl_2, CCl_4, $SiCl_4$, SF_6, F, NF_3, HF, CF_3, CF_4, CH_3F, CHF_3, $C_2H_2F_2$, $C_2H_4F_6$, 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 that are being etched. When multiple layers are sequential etched, first, second, third, etc., etchant gas compositions are sequentially 25 introduced into the chamber to etch each particular layer. Referring to Figure 2, a plasma is energized from the etchant gas using the plasma generator **110** by inductively and/or capacitively coupling energy into the chamber **30**. For example, the plasma can be formed by applying an RF source current to the inductor antenna **115** encircling the chamber **30**, and applying an RF bias voltage to the electrodes. The 30 etchant gas ionizes in the applied electric field to form ions and neutrals that etch the layer on the substrate **25** to form volatile gaseous species that are exhausted from the chamber **30**.

The present process allows etching of one or more layers on a substrate **25** and simultaneous cleaning of the plasma etching chamber **30** in which the etching process is performed, without stopping the etching process. In one or more of the etch process stages, a cleaning gas is added to the etchant gas in a volumetric ratio selected so that the etching residue formed in any one of the etching stages; or the residue formed in all of the etching stages is substantially entirely removed during the etching process. The etchant gas comprises one or more of Cl_2, N_2, O_2, HBr, or He-O_2; and the cleaning gas comprises one or more of NF_3, CF_4, or SF_6. It has been discovered that combinations of these gases provide unique and unexpected etching and cleaning properties.

The volumetric flow ratio of cleaning gas to etchant gas is selected to remove the etchant residue generated from processing at least 2000 to at least 3000 substrates **25** without performing a separate cleaning step for cleaning the chamber **30** in between processing of the substrates. A suitable volumetric flow ratio of cleaning gas to etchant gas is from about 1:20 to about 1:1, and more preferably from about 1:10 to about 2:3, and most preferably about 2:3. It has been discovered that at these volumetric flow ratios of cleaning gas to etchant gas, substantially all the etchant residues on the chamber surfaces **45, 50, 55** are removed without eroding the chamber surfaces. In addition, it has been unexpectedly discovered that the chamber surfaces are cleaned and conditioned by the etchant and cleaning gas combination step, without requiring a separate chamber conditioning or seasoning step. The synergism of etching the substrate **25** and simultaneously removing the etching residues from the surfaces in the chamber **30** (without terminating the etching process or requiring separate cleaning or conditioning steps) provides significantly improved process stability from substrate to substrate, and increased process throughput.

In one example of the present process, a substrate **25** comprising metal silicide or silicon (i.e., polycrystalline or monocrystalline silicon), is etched using a plasma of process gas comprising Cl_2, N_2, and CF_4, and optionally O_2, in a volumetric flow ratio selected to remove substantially all the etchant residue formed on the chamber surfaces upon completion of the etching process. The volumetric flow ratio of Cl_2, N_2, and CF_4 is selected to remove substantially all the etchant residue

generated by etching at least 2000 substrates **25** in the chamber **30**, without performing a separate cleaning step for cleaning the chamber. The ratio of the volumetric flow ratio of CF_4 : (Cl_2 + N_2) may be from about 1:20 to about 1:1. In another example, the process uses a process gas comprising Cl_2, N_2, and SF_6, the volumetric flow ratio of SF_6: (Cl_2 + N_2) being from about 1:20 to about 1:1. In yet another example, a suitable process gas comprises Cl_2, N_2, and NF_3, the volumetric flow ratio of NF_3 : (Cl_2 + N_2) being from about 1:20 to about 1:1.

A burst of cleaning gas is introduced into the etching chamber **30** for a short burst of time to treat and condition the chamber surfaces, while the substrate **25** is still being etched by the etchant gas. Process gas comprising etchant gas is introduced into the chamber **30**, and the composition of the process gas is adjusted to the desired etchant gas composition to etch one or more of the different layers of material on a substrate. During the etching process, a short burst of cleaning gas is added to the process gas while the substrate is still being etched. For example, the burst of cleaning gas can be added to the etchant gas used to etch a polysilicon layer (during the main etch of the polysilicon layer) and terminated before the polysilicon overetching step. The burst of activated cleaning gas provides a larger number of highly reactive cleaning species that removes the freshly deposited etchant residues before they can chemically adhere to the chamber surfaces. Also, a first etchant gas composition can generate a first etchant residue that is weakly adhered to the chamber surfaces or that has a chemically soft and reactive composition; however, when second etchant gas is introduced into the chamber, the second etchant gas can react with the first etchant residue and make it a chemically hard sticking residue. In these processes, the short burst of cleaning gas is introduced into the chamber during the first stage of the etch process, to remove the freshly generated etchant residue before it is chemically changed by exposure to another chemical gas composition. A high flow rate burst and quick removal of the cleaning gas from the chamber **30** also reduces the possibility of the cleaning gas combining to form other chemical species that erode the chamber surfaces and components. This mechanism is further aided by the high flow rates of the burst of gas which flush out reaction byproducts from the chamber **30**. The burst of activated cleaning gas may be introduced into the etching chamber at a flow rate F_R equivalent to a rate of at least about 40 to about 200 sccm for an etching chamber **30** having a volume of about 40,000 cm^3 for a time

period of about 5 to about 100 seconds to clean the etchant residue, substantially without eroding the walls **45, 50, 55** and components in the chamber **30**.

After completion of processing, the substrate **25** is dechucked using suitable dechucking means. A pneumatic lifting apparatus **180** raises lift pins through the electrostatic chuck **145** to raise the substrate **25** and a robotic transport arm is inserted between the substrate **25** and the chuck to lift the substrate off the lift pins. Thereafter, the lift pins are retracted into the chuck **145**, and the robotic arm transports the first substrate **25** out of the etching chamber **30** and into a transfer chamber maintained in a vacuum environment.

Multiple Etching Stages

In another aspect of the present process, multiple stages are used to etch multiple layers on the substrate, and the cleaning gas is introduced in at least one of the stages to remove the etchant residue deposited on the chamber surfaces in one or more of the multiple etching steps, as illustrated in Figure 3. This process is useful for etching, for example, polycide structures that comprise multiple layers of tungsten silicide and polysilicon layers or for etching silicon nitride layers or silicon dioxide layers on silicon wafers. Although the present process is illustrated in the context of etching such layers, it should be understood that the process can be used to etch other layers such as metal layers and silicon dioxide layers. Thus, the present process should not be limited to the examples and illustrative methods provided herein.

The multi-stage process comprises a plurality of etching stages. In a first etching stage, a first etchant gas is introduced into the process chamber **30**, and a plasma is formed from the first etchant gas to etch the first layers on the substrate **25** (for example, a tungsten silicide layer). The first or tungsten silicide layer is typically etched using a first etchant process gas comprising chlorine-containing gases, for example a mixture of chlorine and nitrogen, and optionally oxygen. The volumetric flow ratio of chlorine to nitrogen is about 1:3 to about 1:1, and more preferably about 2:3. The pressure in the chamber **30** is maintained at 1 to 10 mTorr,

the inductor coil source power level at 200 to 800 Watts, and the process electrodes R.F. bias power level at 20 to 120 Watts.

In the second etching stage, a second etchant gas is introduced into the chamber **30**, and a plasma is formed to etch the second layers (for example a polysilicon layer below the tungsten silicide layer) after the first layer has completed etching. The second or polysilicon layer can be etched in more than one etching process step, with the etchant gas composition being changed during each etching step. Suitable second etchant gas compositions comprise Cl_2 in a flow rate of from 20 to 120 sccm, HBr at about 80 to 240 sccm, and He-O_2 at about 2 to 10 sccm. The chamber pressure is from about 25 to 200 mTorr. The power level of the source current applied to the inductor antenna **115** is from about 200 to 800 Watts, and the bias RF power level of the voltage applied to the process electrodes , is from about 20 to 120 Watts.

In one or more of the first and second stages, a cleaning gas is added to the etchant gas in a volumetric ratio selected so that the etching residue formed in any one of the stages is substantially entirely removed during the etching process. The etchant residue formed in the first and second stages typically comprises polymeric organic compounds containing halogen, carbon, hydrogen, and oxygen. When silicon-containing layers are being etched, the etchant residue comprises predominantly silicon dioxide compounds formed during etching of both the tungsten silicide and polysilicon layers on the substrate **25**. However, the composition of etchant residue can vary from the first to the second layer, the first etchant residue composed more of W and Si species, and the second etchant residue composed more of Si and O species. Thus the cleaning gas is added to the process gas in the first or second stage, in a volumetric ratio suitable for removing the first etchant residue formed in the first etching stage in which the tungsten silicide layer was etched, as well as the second etchant residue formed during the second etching stage in which the polysilicon layer was etched. It has been discovered that a suitable volumetric flow ratio of cleaning gas to etchant gas is from about 1:10 to about 2:3. For example, to a flow rate of first etchant gas of about 80 sccm Cl_2 and 40 sccm N_2, was added a cleaning gas comprising CF_4 at a flow rate of 80 sccm, to provide a volumetric ratio of cleaning gas to first etchant gas of about 2:3. It has been

discovered that at these volumetric flow ratios of cleaning gas to etchant gas, substantially all the etchant residues on the chamber surfaces (which are formed during the different stages of the etching process) are removed without eroding the chamber surfaces. In addition, it has been unexpectedly discovered that the chamber
5 surfaces are cleaned and conditioned by the etchant and cleaning gas combination, without requiring a separate seasoning or conditioning process step.

The chamber treatment process of the present invention has been found to uniformly remove etchant residues, irrespective of their thickness or chemical
10 composition, during performance of an etching process. Prior art cleaning processes, particularly those performed by an operator, often fail to uniformly clean and remove the etchant residue deposits formed on chamber surfaces. Build-up of etchant deposits on the chamber surfaces, result in flaking off the etchant deposits and contamination of the substrate **25** etched in the chamber. By uniformly removing the
15 etchant residues formed across substantially all of the chamber surfaces, such contamination and resultant reduced substrate **25** yields, are substantially minimized.

The cleaning gas also results in much less erosive damage to the chamber compared to conventional in-situ plasma cleaning steps, because of the
20 reduced energy levels of the plasma in the etching chamber. This was difficult to accomplish in prior art processes, in which high powered plasmas used to remove the residue deposits also resulted in extensive erosion of chamber surfaces and components. By reducing the need to replace chamber components, the cost of operating the chamber **30** and the cost per substrate **25** are significantly reduced.
25 Furthermore, the activated cleaning gas can be used to efficiently clean an chamber **30** in-situ during etching of substrates **25**, rather than stopping processing to wet clean the chamber walls and components, thereby increasing etching throughput and further reducing costs per substrate. The cleaning process is expected to increase chamber lifetimes by a factor of at least 2, and also increase substrate yields by
30 reducing the deposition of flaked-off etchant byproducts onto the substrate.

The cleaning process removes chemically-adhered etchant deposits from the surfaces in the chamber **30**, and restores the original chemical reactivity and surface functional groups of these surfaces, without requiring a chamber conditioning

process after the cleaning process. The cleaning and treatment process is also particularly useful for cleaning etchant residue that is strongly adhered to, or chemically reacted with chamber surfaces. The cleaning gas is effective at treating and reconditioning these ceramic surfaces to provide surface chemistries and surface functional groups that are chemically compatible with the etching process. The conditioned ceramic surfaces provide more reproducible etching properties in the chamber **30**, than that provided by alternative chamber cleaning processes, such as wet cleaning or RIE cleaning processes. The significantly improved reproducibility of etching processes performed in the chamber **30** is highly desirable.

Multiple Cleaning Stages

In one aspect of the present invention, multiple layers of different materials on a substrate **25** are etched in an etching chamber **30**, and the etchant residue formed on the internal surfaces of the etching chamber are removed or cleaned by a multiple step cleaning process. The multiple layers may be etched utilizing the chamber of Figure 2 and the etching gas may include for example, HCl, BCl_3, HBr, Br_2, Cl_2, CCl_4, $SiCl_4$, SF_6, F, NF_3, HF, CF_3, CF_4, CH_3F, CHF_3, $C_2H_2F_2$, $C_2H_4F_6$, 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 layers being etched comprise, for example, mask or other hard layers overlying a number of silicon-containing layers - by which it is meant a layer composed of any material containing the element silicon including elemental silicon and all its compounds thereof. The substrate **25** typically comprises a semiconductor material, such as silicon or gallium arsenide wafer, with an exemplary set of layers comprise, for example, an underlayer of silicon dioxide that functions as a gate oxide layer for MOS transistors and a polycide overlayer comprising a combination of metal silicide and silicon-containing layers. The metal silicide layer comprises, for example, tungsten, tantalum, titanium, or molybdenum silicide. A mask layer comprising photoresist or hard mask such as, for example, silicon dioxide or silicon nitride, is formed on the substrate **25**. In the etching process, the mask layer is etched in the etching chamber **30**, then the metal silicide layer is etched in the same chamber, thereafter a main and overetch etch step for etching polysilicon is also performed in the same chamber. A conventional process sequence for etching the multiple layers includes a mask etching step, a tungsten silicide etching step, and main and

overetching steps for etching the polysilicon layer, as illustrated in Table 1. These process steps are followed by a dechucking step in which a plasma of nitrogen (which is non-reactive to the multi-layer residue deposit) is used to assist in dechucking the substrate from the electrostatic chuck. The nitrogen based plasma provides opposite
5 charges, for example an electronegative charge, which neutralize the electrostatic charge formed on the substrate allowing the substrate to be easily removed from the chuck.

TABLE 1

10

Process Step	Pressure (mTorr)	Source Power (Watts)	Bias Power (Watts)	Process Gas Composition (sccm)
Etch Si_3N_4 mask	4	950	300	45 CF_4/130 He/ 20 CH_2F_2
WSi_x	5	300	100	50 Cl_2
Polysilicon ME	4	270	40	20 Cl_2/90 HBr/4 He-O_2
Polysilicon OE	50	500	80	50 HBr/3 He-O_2

15

It has been discovered that when a multiple step etching process is performed in a single chamber, such as the exemplary process described above, the
20 etchant residue formed on the chamber walls and surfaces is especially difficult to remove by conventional etch cleaning processes. The processing of multiple layers of material sequentially in a single chamber, such as etching of an overlying hard mask layer followed by etching of an underlying polycide layer, results in formation of an etchant residue comprising multi-layers or having a sandwich-type structure, on the
25 internal surfaces of the chamber. For example, Figure 4 illustrates the compositional profile of the sandwich-type residue that is deposited onto surfaces of chamber walls and components by such an etching process. In this example, the substrate comprised a silicon wafer containing a 1000 Å gate oxide layer, 1000 Å polysilicon layer, 1200 Å tungsten silicide layer, a 2400 Å silicon nitride mask layer, and an
30 overlying 8000 Å I-line photoresist layer. During the nitride mask etch step **301** a relatively large amount of a fluorocarbon based polymer residue **310** is deposited on the chamber surfaces. During subsequent steps for etching other silicon-containing

layers, for example the metal silicide etching step **302**, polysilicon main etching step **303**, and the polysilicon over-etching step **304**, a layer of silicon dioxide **320** is deposited over the fluorocarbon based polymer deposit **310** This layer of silicon dioxide **320** (100-200 A) prevents the cleaning gas from reaching or chemically
5 attacking the underlying polymer residue **310**. As a result, the multi-step etching process creates a multilayer residue that is difficult to remove by conventional cleaning processes. Additionally, the sandwich-type multilayer deposit is prone to flaking and depositing contaminants on the substrate during the etching process, especially because the coefficient of thermal expansion of each of the layers can often
10 differ widely from one another. In the conventional process, a sandwich-type deposit was formed on the internal surfaces of the chamber typically had a total thickness of from about 0 to about 10 microns.

It has been further discovered that a multiple step etching and cleaning
15 process is more effective at removing the multi-layer residue from the internal surfaces of the chamber **30**. The multiple step cleaning process comprises multiple cleaning stages, each cleaning stage being tailored to remove one of the layers of the residue. For example, if the residue comprises a first layer of silicon-containing material, such as a layer comprising predominantly silicon dioxide, the first cleaning
20 gas comprises primarily silicon or silicon dioxide removing gases, or gases that suppress the formation of the silicon-containing layer. Thereafter, the second layer of residue, such as a layer of fluorocarbon polymer residue is removed using a second cleaning gas comprising primarily fluorocarbon polymer removing species. The two stage cleaning process is far more effective at providing a clean internal surface of the
25 chamber than a single stage cleaning process.

In the illustrative example provided herein, the process conditions for etching the nitride mask layer, etching the tungsten silicide layer and a first cleaning/residue suppression step, and the main and overetch process steps for
30 etching the polysilicon layer, as well as a second clean step using oxygen containing cleaning gas, are shown in Table 2.

TABLE 2

Process Step	Pressure (mTorr)	Source Power (Watts)	Bias Power (Watts)	Process Gas Composition (sccm)
Etch Si_3N_4 mask	4	950	300	45 CF_4/130 He/ 20 CH_2F_2
WSi_x (clean)	4	600	60	80 Cl_2/80 CF_4/40 N_2
Polysilicon ME	4	270	40	20 Cl_2/90 HBr/4 He-O_2
Polysilicon OE	50	500	80	50 HBr/3 He-O_2
O_2 cleaning	15	500		95 O_2

The silicon nitride layer was first etched through to form a patterned hard mask layer using an overlying photoresist layer. For purposes of example and without intent to limit the invention, the exemplary process utilizes a plasma of 45 sccm CF_4, 130 sccm He, and 20 sccm CH_2F_2 to etch the mask layer, for example a nitride-containing mask layer, in a process chamber at 4 mTorr pressure with a source power of 950 Watts and a bias power of 300 Watts.

Thereafter, an energized gas comprising a combination of etching gas and first cleaning gas was used to both etch a layer on the substrate, such as the metal silicide layer, and suppress the deposition of the silicon dioxide containing etchant residue on the chamber surfaces. The cleaning gas is added to the etchant gas in a volumetric flow ratio selected to suppress the deposition of silicon dioxide onto the polymer deposit formed by the earlier etching stage in which the mask layer comprising silicon nitride is etched. It has been found that the silicon dioxide residue deposited during subsequent etching steps is sufficiently thin to allow a subsequent cleaning stage to remove both the remaining silicon dioxide containing material as well as the fluorocarbon material of the remaining residue. This combination of a silicon-containing layer etch process step in which formation of a silicon dioxide containing residue is suppressed and a subsequent second cleaning step results in an unexpectedly clean chamber where substantially all the residue, and in some cases all of the residue is removed upon completion of the etch process.

The metal silicide layer can be etched with an etching gas comprising one or more of Cl_2, N_2, O_2, HBr, and He-O_2, and more preferably Cl_2 and N_2. The cleaning gas can comprise one or more of CF_4, SF_6, and NF_3, and more preferably CF_4. The volumetric flow ratio of etching gas to cleaning gas is selected to adequately etch
5 the desired features in the layer and to suppress the deposition of silicon dioxide **320** onto the deposition of residue from the mask etch **310**. The etching gas to cleaning gas volumetric flow ratio is about 1:1 to about 1:20, and is more preferably about 3:2. In a particular composition the process gas comprises 80 sccm Cl_2, 80 sccm CF_4, and 40 sccm N_2. The source power is from about 200 and about 800 Watts,
10 and is more preferably about 600 Watts. The bias power is from about 20 Watts to about 120 Watts, and is more preferably about 60 Watts. The pressure in the chamber is from about 1 mTorr to about 50 mTorr and more preferably is about 4 mTorr.

15 Thereafter, the polysilicon layer is etched in two stages including a main etching stage and an overetching stage. The main etching stage is performed using a plasma of process gas comprising 20 sccm Cl_2, 90 sccm HBr, and 4 sccm He-O_2; a pressure of 4 mTorr, 270 Watts source power, and 40 Watts bias power. The over etch is performed using a process gas comprising 50 sccm HBr and 3 sccm He-O_2 and
20 optionally Cl_2 in a chamber maintained at a pressure of 50 mTorr and 500 Watts source power.

In the present example, it has been further discovered that an oxygen containing plasma can be used to remove the remaining silicon dioxide containing and
25 fluorocarbon based polymer residue **310** remaining on the walls and surfaces of the chamber. The oxygen plasma cleaning step is performed after etching or otherwise processing the last residue creating layer on the substrate, such as the polysilicon over-etching step. In this step an oxygen-containing gas, such as an oxygen species generating gas, oxygen or ozone is introduced into the chamber, and a plasma is
30 sustained by applying a current at a power level of 500 Watts to the inductor coil. The oxygen flow is maintained at about 95 sccm and at a gas pressure of 15 mTorr. The oxygen plasma cleans off substantially all the residue remaining on the chamber surfaces including a relatively thin layer of silicon dioxide residue. The removal of the underlying polymer deposit **310** is much more difficult if the deposit is covered by and

partially protected from the cleaning gas by a thick overlying layer of silicon dioxide residue **320**. Additionally, the oxygen plasma also serves to remove residual charge in the chamber to dechuck the substrate when the substrate is electrostatically held on an electrode in the chamber by providing an opposite charge, for example an
5 electronegative charge.

The cleaning gas used to clean the residue from the walls and surfaces of the chamber can also comprise other gas compositions that clean a combination of the fluorocarbon polymer residue **310** and silicon dioxide containing residue **320**. For
10 example, the cleaning gas can also comprise oxygen at a pressure from about 1 mTorr to about 100 mTorr in a plasma sustained at a source power from about 200 Watts to about 1000 Watts. In another example, the process gas comprises 95 sccm O_2 at 15 mTorr pressure and the plasma is formed at a 500 Watts source power level.

15 Figure 5 is a schematic graph illustrating the compositional profile of the etchant residue that is deposited on the walls of the chamber by the method of the present invention during the process steps of etching of the nitride mask **351**, the metal silicide etch **352**, the polysilicon layer main etch **353**, the polysilicon over etch **354**, and the oxygen gas cleaning step. The data in Figure 5 was obtained using the
20 same type of substrate as that used for the data in Figure 4. Comparing Figures 4 and 5, it is apparent that the present process significantly improves on the former process by eliminating a 600-700 A thick residue that was previously formed on the chamber surfaces after substrate processing. While the mask layer etch step **351** continues to produce a fluorocarbon based polymer residue **310** that deposits on the
25 surfaces in the chamber; the metal silicide etch step **352** has been discovered to deposit little or no silicon dioxide **320** over the polymer deposit **310**. The subsequent steps **353, 354** deposit a much thinner silicon dioxide layer **320** than the conventional process. This thinner layer of silicon dioxide **320** allows the cleaning gas to attack the polymer deposit **310** and clean the chamber. When the substrate processing is
30 complete, a substantially clean chamber awaits further use, and the chamber can often be re-used without any further manual cleaning of its internal surfaces.

Referring to Figure 5, it can be seen that, as before, the majority of the passivating layer depositions occurred during the etching of the silicon nitride mask

layer on the substrate. This occurs because the overlying resist layer is substantially etched away from the surface of the substrate in addition to the etching of the apertures through the silicon nitride layer, which contributes silicon and nitrogen species into the environment. The combination of etch resist, silicon, and nitrogen form the polymer deposition on the surfaces in the chamber. Thereafter, in the WSi_x etching step in which a cleaning gas is added to maintain the chamber clean, a net reduction in the deposition thickness of the passivating layer results due to removal of the passivating layer by the fluorinated CF_4 gas. During the main and overetching steps for etching the polysilicon layer, the thickness of the deposition layer is made substantially constant; however, towards the end of the polysilicon overetching step, a net thickness of silicon oxide is being deposited. Although a small amount of silicon oxide is deposited to form the sandwiched layer, this amount is much smaller than the amount deposited in the prior art process by a factor of over about 2.

In another illustrative example, provided to further test and understand the effectiveness of a multiple step cleaning process, Figure 6 shows both the deposition and removal rate of a residue layer formed on the surface of a bare silicon wafer. The residue layer was formed by exposing the substrate to a process gas comprising 45 sccm CF_4, 130 sccm He, 20 sccm CH_2F_2, a bias power of 350 Watts, and a cathode temperature of 65°C. It is seen that the residue deposition is relatively constant and from about 75 to 125 Å per minute. The polymer residue deposited on the bare silicon wafer was thereafter removed by the following process conditions: an oxygen flow rate of 95 sccm, a gas pressure of 15 mTorr, a source power of 500 Watts, no bias power, and a 65°C cathode temperature. The removal rate as shown in the graph was much higher, on the order of 350 Å/minute. The much higher efficiency of the oxygen containing cleaning step - as compared to the rate of deposition of the residue - indicates that the residue can be rapidly and efficiently removed by the present process and without excessively reducing the down-time of the substrate processing apparatus.

In Figure 7, the rate of removal of multi-layer residue comprising layers with different compositions and thicknesses is shown. In these examples, a residue comprising compositionally different layers was formed on a specimen. The residue on specimen 1 was composed simply of polymer with no silicon dioxide thereon. The

residue on specimen 2 comprised a layer of polymer residue and a 130 Å overlying layer of silicon dioxide containing residue. Specimen 3 had a 385 Å thickness of silicon oxide on a polymer residue layer. Finally, specimen 4 had no silicon oxide deposition, but simply a 40 Å thickness layer of polymer residue. It is seen that the specimens 1 and 4 which had only polymer residue were removed at a much higher rate of 350 Å to 400 Å relative to the residues containing silicon dioxide, namely specimens 2 and 3. In fact, the rate of removal of the residue deposited on specimens 2 and 3 ranged from 50 Å to about 350 Å. Thus, removal of the silicon oxide layer (specimens 1 and 4) increases the rate of removal of the polymer residue by approximately 6 to 8 times, which is a significantly and unexpectedly higher rate of removal. It is also seen that reducing the thickness of silicon dioxide containing residue formed over the polymer residue – from about 385 Å to about 130 Å – resulted in a net change in the average rate of removal of the residue from about 100 Å/min to 200 Å per minute, or twice as fast. This provided a significant improvement in the rate of removal of the residue which was wholly unexpected.

In yet another example, Figure 8 shows the rate of removal of residue for increasing power levels applied to the inductor coil. In this example, the process conditions included an oxygen flow rate of 95 sccm, a pressure of 15 mTorr, a variable amount of source power, 0 Watts bias power, and a cathode wall temperature of 65°C. It is seen that as the source power is increased from 400 Watts to about 750 to 800 Watts, the rate of removing residue remains constant at about 320 Å/minute. However, at a source power level of from about 800 to about 900 Watts, the rate of residue removal is significantly improved and increases from 350 Å to 1200 Å/minute. Thus, it has also been discovered in another aspect of the invention, that the source power level should be maintained at a high level. The selected source power level depends upon the composition of the process gas, the gas pressure, and is typically at least about 700 Watts. Residue removal rates exceeding about 600 Å/minute have been obtained at these power levels.

A quartz crystal microbalance (QCM) was used to determine the amounts of etchant residue being deposited onto the chamber surfaces during the etching process. The quartz crystal microbalance comprises a piezoelectric plate that changes in capacitance when a film of etchant residue is deposited thereon as

described in U.S. Patent Application Serial Number 09/116,621, the disclosure of which is incorporated herein by reference In making the presently disclosed measurements, the microbalance was mounted on an internal surface of the process chamber and its leads were connected to a computer outside the process chamber.

5

The present invention has been described with reference to certain versions thereof; however, other versions are possible. For example, the treatment and cleaning process of the present invention can be used for treating chambers for other applications, as would be apparent to one of ordinary skill. For example, the

10 process can be applied, as would be apparent to one of ordinary skill in the art, to treat sputtering chambers, ion implantation chambers, or deposition chambers, or in combination with other cleaning processes. Therefore, the spirit and scope of the appended claims should not be limited to the description of the versions contained herein.

15

What is claimed is:

1. A method of treating a chamber to remove residue from surfaces in the chamber, the method comprising the steps of:

5 (a) providing an energized first process gas in the chamber to treat the surfaces in the chamber; and

(b) providing an energized second process gas in the chamber to further treat the surfaces in the chamber, the second process gas being different than the first process gas.

10

2. A method according to claim 1 wherein the first process gas comprises a fluorinated gas.

3. A method according to claim 2 wherein the fluorinated gas
15 comprises one or more of CF_4, SF_6 and NF_3.

4. A method according to claim 1 wherein the second process gas comprises an oxygen containing gas.

20 5. A method according to claim 4 wherein the oxygen containing gas consists essentially of oxygen.

6. A method according to claim 1 wherein the treating of the chamber comprises cleaning the chamber.

25

7. A method of etching a substrate in a chamber and cleaning etchant residue formed on surfaces in the chamber, the method comprising the steps of:

(a) placing the substrate in the chamber;

30 (b) in a first stage, providing an energized first process gas in the chamber, the first process gas comprising a substrate etching gas and a first cleaning gas; and

(c) in a second stage, providing an energized second process gas in the chamber, the second process gas comprising a second cleaning gas that is different from the first cleaning gas.

5 8. A method according to claim 7 wherein the first cleaning gas comprises a fluorinated gas.

9. A method according to claim 8 wherein the fluorinated gas comprises one or more of CF_4, SF_6 and NF_3.

10

10. A method according to claim 7 wherein the second cleaning gas comprises an oxygen containing gas.

11. A method according to claim 10 wherein the oxygen containing 15 gas consists essentially of oxygen.

12. A method according to claim 7 wherein the substrate etching gas comprises a gas capable of etching a metal silicide layer on the substrate.

20 13. A method according to claim 7 wherein the substrate etching gas comprises one or more of Cl_2, N_2, O_2, HBr and He-O_2.

14. A method according to claim 7 wherein the volumetric flow ratio of substrate etching gas to first cleaning gas is from about 1:1 to about 20:1.

25

15. A method according to claim 7 wherein the energized second process gas is provided in the chamber while the substrate is in the chamber.

16. A method according to claim 7 wherein in step (a), the substrate 30 is electrostatically held on an electrostatic chuck in the chamber, and in step (c) comprises providing an electronegative plasma of second process gas.

17. A method according to claim 7 wherein in the second stage, the chamber pressure is maintained at from about 1 mTorr to about 10mTorr.

18. A method according to claim 7 wherein in the second stage, the ratio of source power to bias power is from about 5:3 to about 40:1.

19. A method of etching a substrate in a chamber and cleaning
5 etchant residue from surfaces in the chamber, the method comprising the steps of:

(a) placing the substrate in the chamber;

(b) etching a first material on the substrate thereby depositing a first etchant residue on the surfaces in the chamber;

(c) etching a second material on the substrate while
10 suppressing deposition of a second etchant residue onto the first etchant residue, the first etchant residue being compositionally different from the second etchant residue; and

(d) cleaning the first and second etchant residue deposits formed on the surfaces in the chamber.

15

20. A method according to claim 19 wherein etching the first material comprises the step of providing an energized first gas in the chamber.

21. A method according to claim 20 wherein etching the second
20 material comprises the step of providing an energized second gas in the chamber.

22. A method according to claim 21 wherein the first gas comprises a first cleaning gas and the second gas comprises a second cleaning gas.

25 23. A method according to claim 22 wherein the first cleaning gas comprises a fluorinated gas.

24. A method according to claim 23 wherein the fluorinated gas comprises one or more of CF_4, SF_6 and NF_3.

30

25. A method according to claim 22 wherein the second cleaning gas comprises an oxygen containing gas.

26. A method according to claim 25 wherein the oxygen containing gas consists essentially of oxygen.

27. A method of etching a substrate in a chamber and cleaning
5 etchant residue from surfaces in the chamber, the method comprising the steps of:

(a) electrostatically holding the substrate in the chamber;

(b) providing a first energized gas in the chamber, the first energized gas comprising an etching gas to etch the substrate and a residue cleaning gas; and

10 (c) providing a second energized gas in the chamber to clean etchant residue deposited on the surfaces in the chamber and símultaneously remove residual charge accumulated in the substrate.

28. A method according to claim 27 wherein the first energized gas
15 comprises a fluorinated gas.

29. A method according to claim 28 wherein the fluorinated gas comprises one or more of CF_4, SF_6 and NF_3.

20 30. A method according to claim 27 wherein the second energized gas comprises an oxygen containing gas.

31. A method according to claim 30 wherein the oxygen containing gas consists essentially of oxygen.

25

32. A method according to claim 27 wherein the etching gas comprises a gas capable of etching a metal silicide layer on the substrate.

33. A method according to claim 27 wherein the etching gas
30 comprises one or more of Cl_2, N_2, O_2, HBr and He-O_2.

34. A method according to claim 27 wherein the volumetric flow ratio of etching gas to residue cleaning gas is from about 1:1 to about 20:1.

35. A method of etching a substrate in a chamber and cleaning residue that forms on surfaces in the chamber, the method comprising the steps of:

(a) placing the substrate in the chamber;

(b) in an etching stage, etching one or more materials on the substrate using energized gas, at least one composition of the energized gas including an etching gas comprising one or more of Cl_2, N_2, O_2, HBr and He-O_2; and a residue cleaning gas comprising one or more of CF_4, SF_6 and NF_3; and

(c) cleaning the residue formed on the surfaces in the chamber using another energized gas comprising oxygen.

36. A method according to claim 35 wherein the volumetric flow ratio of etching gas to residue cleaning gas is from about 1:1 to about 20:1.

37. A method according to claim 35 wherein the energized gas comprising oxygen is provided in the chamber while the substrate is in the chamber.

38. A method according to claim 35 wherein in step (a), the substrate is electrostatically held on an electrostatic chuck in the chamber, and in step (c), the energized gas comprising oxygen comprises a plasma that assists in dechucking the substrate from the electrostatic chuck.

39. A method of etching a substrate in a chamber and cleaning residue formed on surfaces in the chamber, the chamber comprising an electrostatic chuck, and the method comprising the steps of:

(a) transferring a substrate into the chamber and electrostatically holding the substrate on the electrostatic chuck, the substrate comprising a mask layer;

(b) providing an energized gas in the chamber to etch the mask layer on the substrate thereby forming residue on the surfaces in the chamber, the residue comprising chemical species originating from the mask layer;

(c) providing another energized gas in the chamber to etch material below the mask layer, the energized gas comprising etching gas and residue cleaning gas, the etching gas comprising one or more of Cl_2, N_2, O_2, HBr, and He-O_2 and the residue cleaning gas comprising one or more of CF_4, SF_6, and NF_3; and

(d) providing an oxygen containing plasma in the chamber to assist in dechucking the substrate and to clean the residue formed on the surfaces in the chamber.

5 40. A method according to claim 39 wherein the volumetric flow ratio of etching gas to residue cleaning gas is from about 1:1 to about 20:1.

41. A method of cleaning a chamber to remove residue from surfaces in the chamber, the method comprising the steps of:

10 (a) providing an energized first process gas in the chamber to clean the surfaces in the chamber; and

(b) adjusting the chamber source power to control the amount of residue removed from the surfaces.

15 42. A method according to claim 41 wherein step (b) comprises increasing the chamber source power to increase the amount of residue removed from the surfaces.

43. A method according to claim 41 further including the step of
20 maintaining the chamber bias power at substantially zero Watts.

44. A method according to claim 41 wherein the first process gas comprises an oxygen containing gas.

25 45. A method according to claim 43 wherein the oxygen containing gas consists essentially of oxygen.

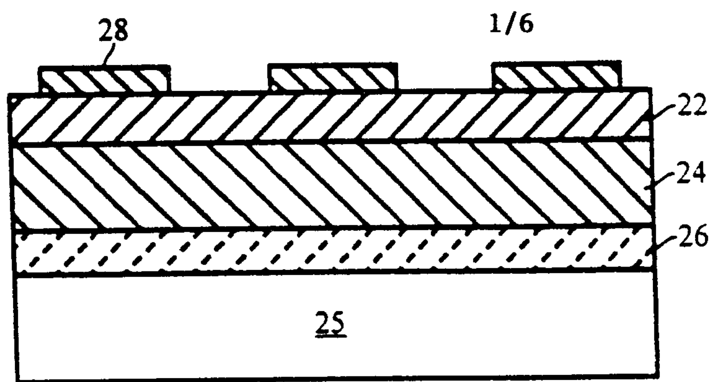


Fig. 1a

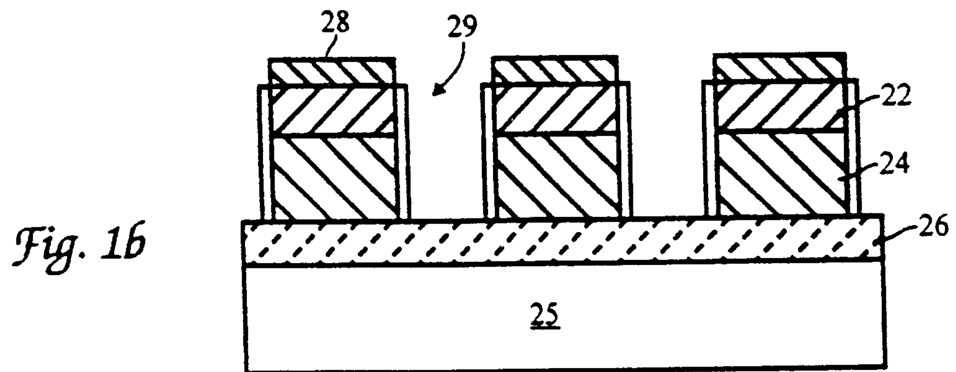


Fig. 1b

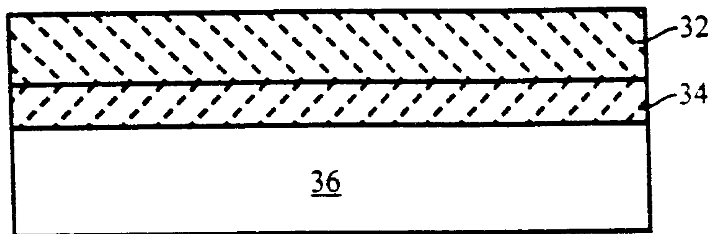


Fig. 1c

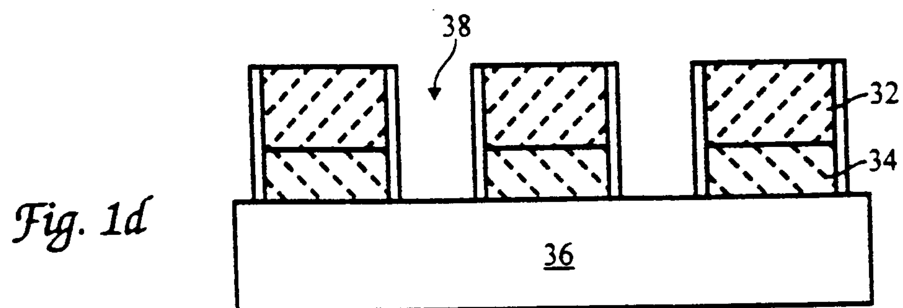


Fig. 1d

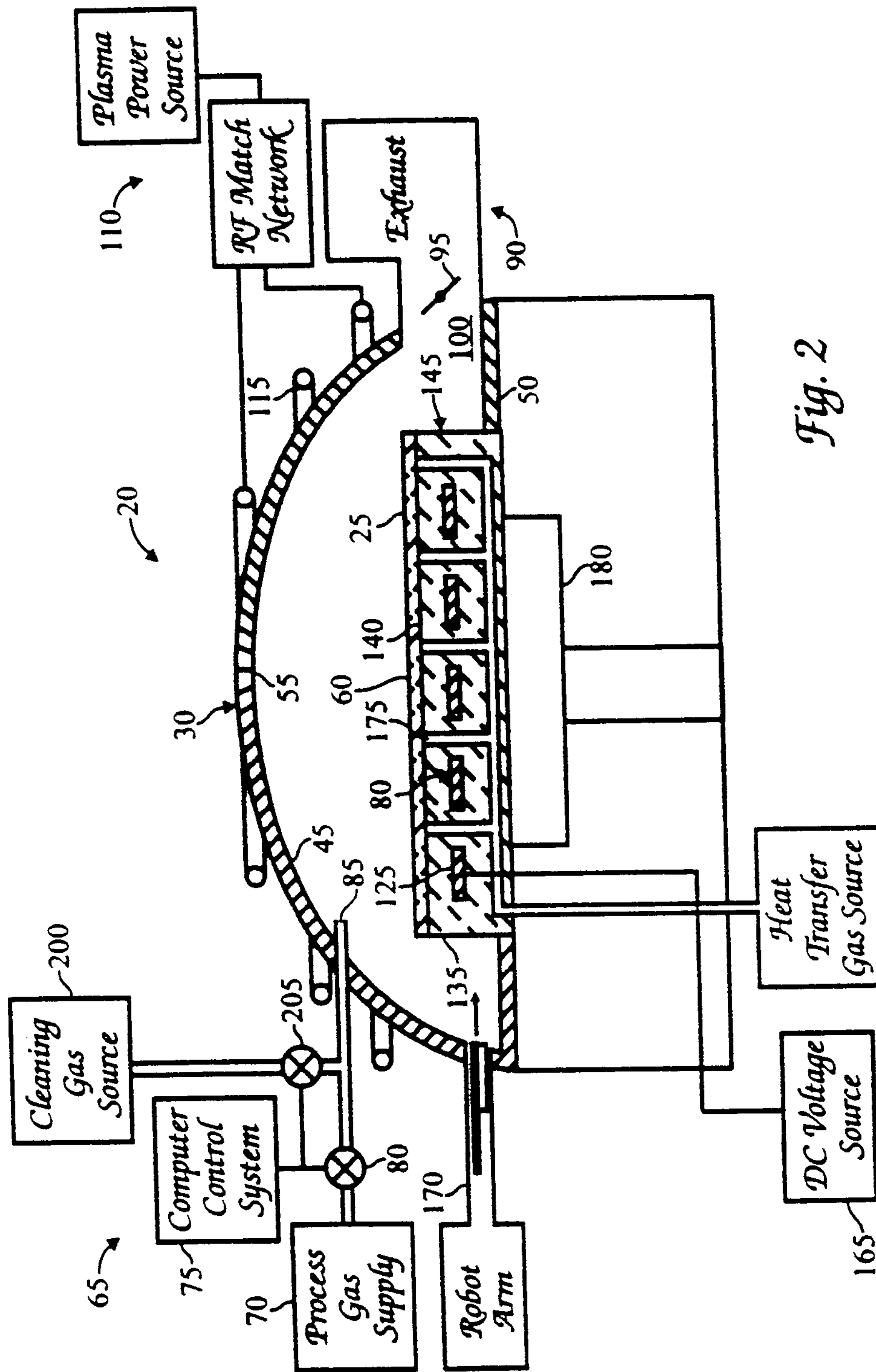


Fig. 2

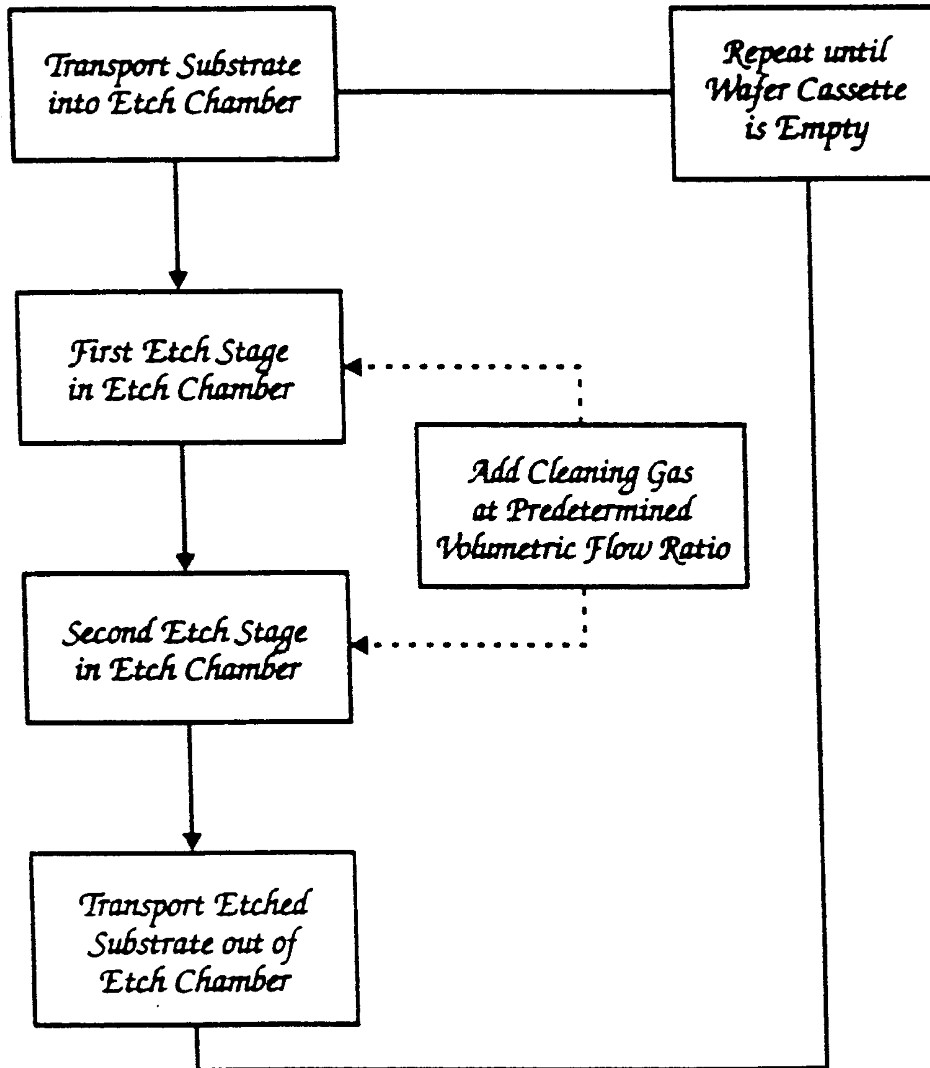


Fig. 3

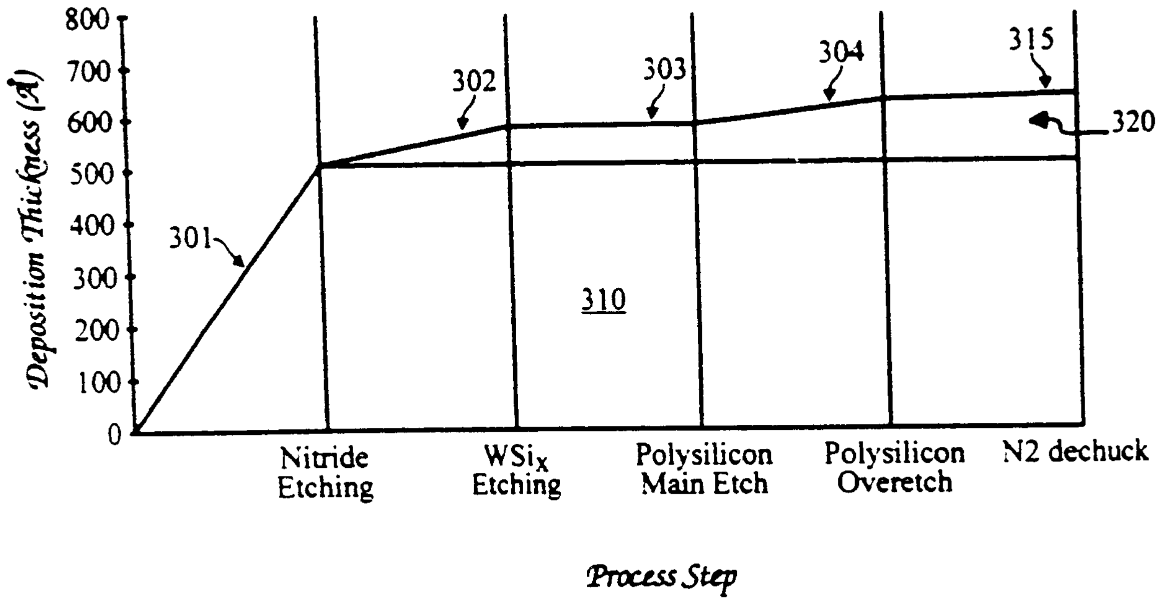


Fig. 4

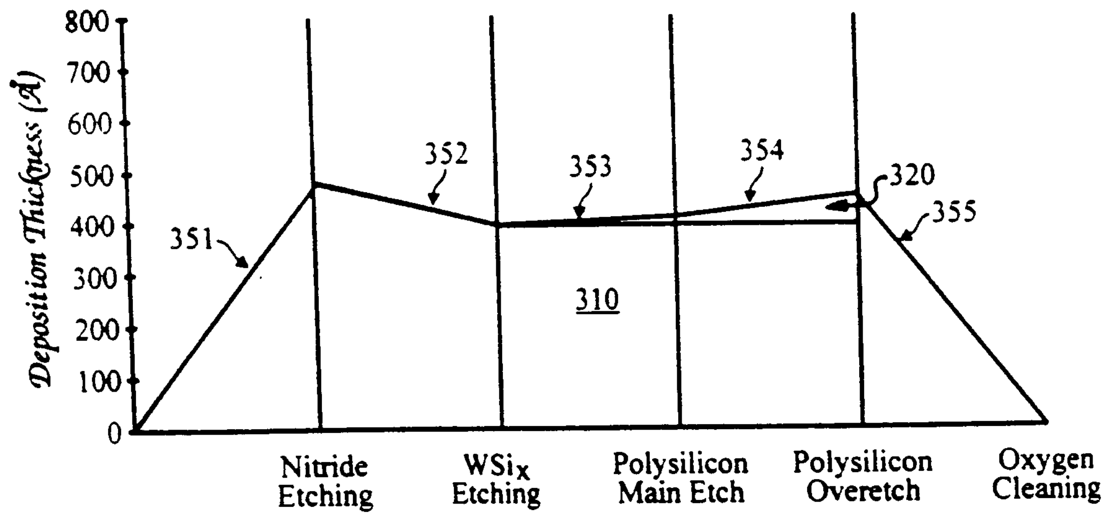


Fig. 5

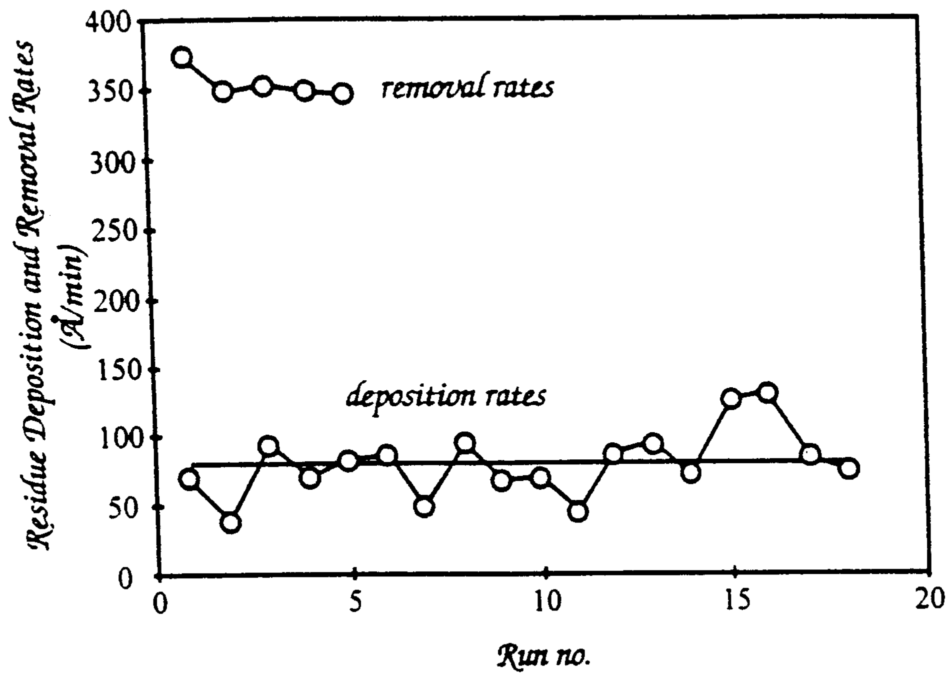


Fig. 6

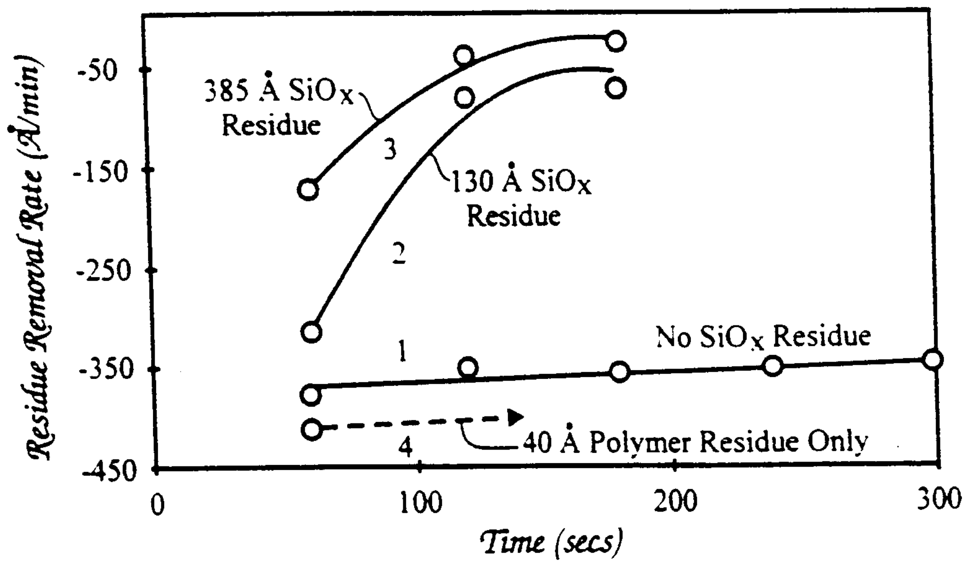


Fig. 7

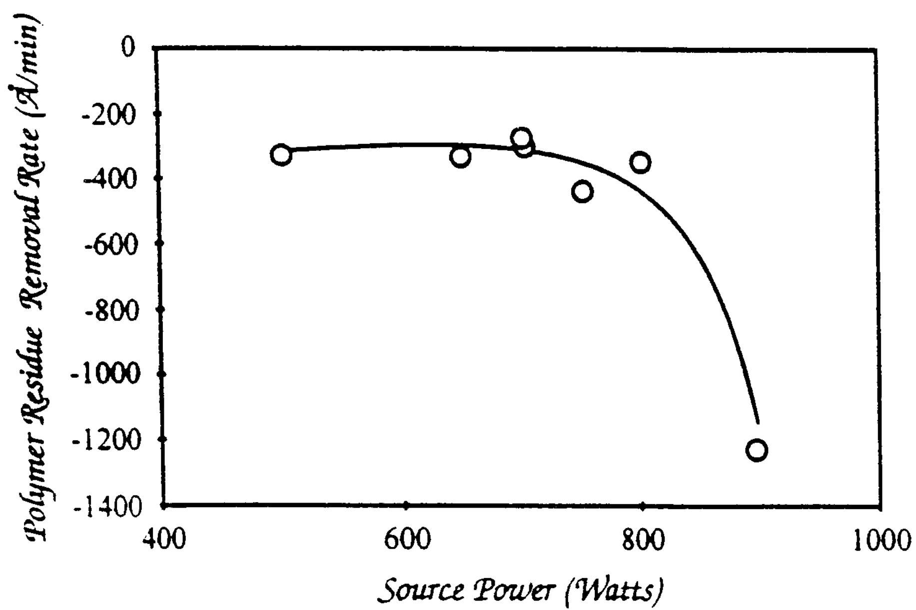


Fig. 8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/20320

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/3213

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01L C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 251 (E-771), 12 June 1989 (1989-06-12) & JP 01 050427 A (HITACHI LTD), 27 February 1989 (1989-02-27) abstract	1-6
X	JP 10 233387 A (DENSO CORP) 2 September 1998 (1998-09-02) -& US 6 090 718 A (SOGA HAJIME ET AL) 18 July 2000 (2000-07-18) column 4, line 52 -column 7, line 24; figures 5,6,8,9	1-4,6, 41,42
X	US 5 700 741 A (LIAO CHIN-CHERNG) 23 December 1997 (1997-12-23) column 4, line 7 -column 10, line 5	41,44,45

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 November 2000	08/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Köpf, C

3

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/20320

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 354 417 A (CHEUNG ERNEST L ET AL) 11 October 1994 (1994-10-11) the whole document ---	7-15, 19-26, 35,39
A	EP 0 709 877 A (HITACHI LTD) 1 May 1996 (1996-05-01) the whole document -----	7,10-13, 15,16, 27, 30-33,39

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/20320

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 01050427 A	27-02-1989	NONE	
JP 10233387 A	02-09-1998	US 6090718 A	18-07-2000
US 5700741 A	23-12-1997	NONE	
US 5354417 A	11-10-1994	EP 0649169 A	19-04-1995
		JP 2915807 B	05-07-1999
		JP 7161701 A	23-06-1995
EP 0709877 A	01-05-1996	JP 8279487 A	22-10-1996
		JP 2948053 B	13-09-1999
		JP 8279486 A	22-10-1996
		US 5681424 A	28-10-1997
		EP 0938134 A	25-08-1999
		WO 9428578 A	08-12-1994