



(51) International Patent Classification:

H01L 21/3213 (2006.01) H01J 37/32 (2006.01)

H01L 21/67 (2006.01)

(21) International Application Number:

PCT/US2023/014520

(22) International Filing Date:

03 March 2023 (03.03.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/322,535 22 March 2022 (22.03.2022) US

(71) Applicant: LAM RESEARCH CORPORATION

[US/US]; 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US).

(72) Inventors: YANG, Wenbing; c/o Lam Research Corporation,

4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). TAN, Samantha SiamHwa; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). PAN, Yang; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). FAN, Yiwen; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S

CA-1, Fremont, California 94538 (US). BENNET, Alexander Declan; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). BALAN, Arunima Deya; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). PATRICK, Roger; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). VAN CLEEMPOT, Patrick August; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). WITKOWICKI, Derek; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). LI, Baichang; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). LEE, Young Ah; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US). THOMAS, Clint Edward; c/o Lam Research Corporation, 4650 Cushing Parkway, M/S CA-1, Fremont, California 94538 (US).

(74) Agent: LEE, Michael; BEYER LAW GROUP LLP, P.O. Box 51887, Palo Alto, California 94303-1887 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,

(54) Title: FAST ATOMIC LAYER ETCH

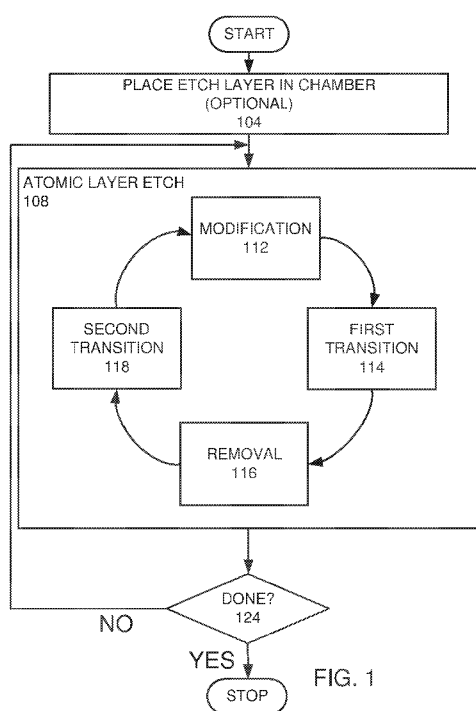


FIG. 1

(57) Abstract: A method for etching an etch layer is provided. The method comprises a plurality of cycles, wherein each cycle, comprises exposing the etch layer to neutral radicals for a time between 10 ms and 600 ms, wherein the neutral radicals are absorbed into the etch layer to form a modified part of the etch layer and exposing the etch layer to bombardment ions for a time between 10 ms and 600 ms, wherein the bombardment ions remove the modified part of the etch layer.

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

FAST ATOMIC LAYER ETCH

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of U.S. Application No. 63/322,535, filed March 22, 2022, which is incorporated herein by reference for all purposes.

5

BACKGROUND

[0002] The background description provided here is for the purpose of generally presenting the context of the present disclosure. Anything described in this background section, and potentially aspects of the written description, are not expressly or impliedly admitted as prior art with respect to the present application.

10

[0003] The disclosure relates to a method of forming semiconductor devices on a semiconductor wafer. More specifically, the disclosure relates to the selective etching of semiconductor devices.

15

[0004] In the formation of semiconductor devices, various layers may be selectively etched. Atomic layer etching may be used to provide an etch with high selectivity. Because an atomic layer etch may remove a monolayer for each cycle, atomic layer etch speed is dependent on the period of each cycle.

20

[0005] Atomic layer etching processes are described in US Patent 10,566,212, entitled “Designer Atomic Layer Etching,” by Kanarik, issued February 18, 2020, US 10,763,083, entitled “High Energy Atomic Layer Etching,” by Yang et al., issued September 1, 2020, US 2021/0005425A1, entitled “Atomic Layer Etching and Smoothing of Refractory Metals and Other High Surface Binding Energy Materials,” by Yang et al., published January 2, 2021, and WO 2020/223152A1, entitled “Atomic Layer Etching for Subtractive Metal Etch,” by Yang et al., published on November 5, 2020, which are all incorporated by references for all purposes.

SUMMARY

25

[0006] To achieve the foregoing and in accordance with the purpose of the present disclosure, a method for etching an etch layer is provided. The method comprises a plurality of cycles, wherein each cycle, comprises exposing the etch layer to neutral radicals for a time between 10 ms and 600 ms, wherein the neutral radicals are absorbed into the etch layer to form a modified part of the etch layer and exposing the etch layer to bombardment ions for a time between 10 ms and 600 ms, wherein the bombardment ions remove the modified part of the etch layer.

30

[0007] In another manifestation, an etching system for etching an etch layer over a substrate, the etching system is provided. A substrate support supports a substrate in a processing chamber. An RF power source provides RF power to etch chamber. A neutral radical source is adapted to provide neutral

radicals in the processing chamber. A bombardment gas source is adapted to provide bombardment gas in the processing chamber. A controller is controllably connected to the RF power source, the neutral radical source, and the bombardment gas source. The controller is configured to expose the etch layer to neutral radicals for a time between 10 ms and 600 ms, wherein the neutral radicals are absorbed into the etch layer to form a modified part of the etch layer and expose the etch layer to bombardment ions for a time between 10 ms and 600 ms, wherein the bombardment ions remove the modified part of the etch layer.

[0008] These and other features of the present disclosure will be described in more detail below in the detailed description and in conjunction with the following figures.

10

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present disclosure is illustrated by way of example, and not by way of limitation, in the figures of the accompanying drawings and in which like reference numerals refer to similar elements and in which:

[0010] FIG. 1 is a high level flow chart according to some embodiments.

15

[0011] FIGS. 2A-C are schematic cross-sectional views of an example stack processed according to some embodiments.

[0012] FIGS. 3A-C are detailed schematic views of an example etch layer processed according to some embodiments.

20

[0013] FIG. 4 is a cross-sectional side view of an example etch layer that has been processed according to an embodiment.

[0014] FIG. 5 is a schematic view of an exemplary plasma processing chamber that may be used in some embodiments.

[0015] FIG. 6 is a schematic view of an example computer system that may be used in practicing some embodiments.

25

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The present disclosure will now be described in detail with reference to a few preferred embodiments thereof as illustrated in the accompanying drawings. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present disclosure. It will be apparent, however, to one skilled in the art, that the present disclosure may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not unnecessarily obscure the present disclosure.

[0017] In the formation of semiconductor devices, various layers may be selectively etched. Atomic layer etching may be used to provide an etch with high selectivity. In an atomic layer etch (ALE), a cyclical process is provided. The cyclical process may have a first step of modifying part of an etch layer and a second step of removing the modified part of the etch layer. Such an ALE may use a self-limiting process to modify part of the etch layer. The self-limiting process may modify a few monolayers of the etch layer forming a self-limiting layer. In such a case, the removing of the modified part of the etch layer may remove just a monolayer of the etch layer. As a result, many cycles are needed in order to etch a substantial part of the etch layer. Each cycle may be more than 12 seconds long. As a result, an ALE process may take a long time in order to etch a substantial part of an etch layer.

[0018] To facilitate understanding, FIG. 1 is a high level flow chart illustrating processes used in some embodiments. As shown, an etch layer over a substrate and under a mask is placed in a processing chamber (step 104). FIG. 2A is a schematic cross-sectional view of an example wafer 204 under an etch layer 208 disposed below a mask 212. In some embodiments, the etch layer 208 is silicon and the photoresist mask 212 is a polymer containing photoresist mask 212. In various embodiments, the photoresist mask may be formed from one or more of extreme ultraviolet (EUV) photoresist, metal-containing photoresist, organometallic photoresist, tin-containing photoresist, tin-oxide containing photoresist, and organotin photoresist. In other embodiments, the mask may not be made of a photoresist material. FIG. 3A is a schematic view of an enlarged section of an exposed portion of the etch layer 208 showing atoms 304 therein.

[0019] The etch layer 208 is etched using an atomic layer etch (step 108). The atomic layer etch (step 108) is a cyclical process where in each cycle an exposed surface of the etch layer 208 is modified (step 112). The modification gas is transformed into neutral radicals. The neutral radicals may be created by forming a plasma from the modification gas. In some embodiments, the plasma is formed by providing more than 2000 Watts of RF power at 13.56 megahertz (MHz). In some embodiments, a pressure of between 10 mTorr and 500 mTorr is provided. For example, a pressure of about 35 mTorr may be provided. A higher pressure increases the number of ions that are transformed into neutral radicals. An electric charge may be used to repel ions from the etch layer 208. In some embodiments where a bias is provided, the bias may be less than 50 eV. In other embodiments, a bias may not be provided during the surface modification (step 112). If a bias is provided, the bias may either be pulsed or continuous. If a pulsed bias is provided, the pulsed bias may have a duty cycle of greater than 10% in order to decrease the time needed for the surface modification (step 112). The duty cycle may be adjusted to increase

neutral radicals and decrease ions. In some embodiments, this surface modification (step 112) is provided for less than 0.5 seconds (s). In some embodiments, the surface modification is provided for a time between 10 milliseconds (ms) and 600 ms. In other embodiments, the surface modification is provided for a time between 50 ms and 300 ms. In various embodiments, various methods may be used to suppress ions from reaching the etch layer 208. In some
5 embodiments, the flux of neutral radicals near the exposed etch layer is greater than 10^{18} neutral radicals per centimeters (cm) square per second s ($/\text{cm}^2\text{s}$). In various embodiments, the flux of the neutral radicals is between about 10^{17} to 10^{20} neutral radicals $/\text{cm}^2\text{s}$. A higher flux of neutral radicals helps to reduce the time needed for the modification step. The higher flux of neutral
10 radicals can be provided by using one or more of higher pressure, higher RF power, and/or a higher flow rate, as well as possibly other factors.

[0020] FIG. 2B is a schematic cross-sectional view of an example wafer 204 under the etch layer 208 disposed below the mask 212 after an exposed portion of the etch layer 208 has been modified. The modified portion is schematically illustrated by the shaded regions 216. The
15 shaded regions 216 are not drawn to scale in order to facilitate understanding since, in this example, a few atomic layers are modified. In various embodiments, from about 1 to 30 atomic or molecular layers are modified. FIG. 3B is a schematic view of an enlarged section of an exposed portion of the etch layer 208 after part of the exposed portion of the etch layer 208 has been modified. Some of the neutral radical atoms 308 form bonds with exposed atoms 304.

[0021] After the modification (step 112), a first transition is provided (step 114). The first transition removes the modification gas and provides a bombardment gas (also called a removal gas). In some embodiments, the bombardment gas comprises argon (Ar). In some embodiments, the first transition is accomplished in less than 0.5 s. In various embodiments, the first transition is accomplished in the range of 1 ms to 500 ms. In some embodiments, the first transition is
25 accomplished in the range of 0.2 s to 0.5 s.

[0022] After the first transition (step 114), a removal step is provided (step 116). In some embodiments, the bombardment gas is provided at a pressure of about 20 mTorr. In various embodiments, the pressure is 1 mTorr to 25 mTorr. In some embodiments, the pressure of the modification gas is at least 10 mTorr more than the pressure of the bombardment gas. In some
30 embodiments, the bombardment gas can be transformed into a plasma by providing more than 500 Watts of RF power at 13.56 MHz. In some embodiments, a bias is in the range of 200 eV to 2000 eV. In various embodiments, the bias is greater than 700 eV. In some embodiments, the bias voltage during the removal step is at least 10 times the bias voltage during the modification

step. In some embodiments, this removal step (step 116) is provided for less than 0.5 s. In some
embodiments, the removal step is provided for a time between 10 ms to 600 ms. In other
embodiments, the removal step is provided for a time between 10 ms and 300 ms. In other
embodiments, the removal step is provided for a time between 10 ms and 50 ms. In some
5 embodiments, the removal step is provided for a time of less than 25 ms. In some embodiments,
the bias power is provided as a continuous wave. In embodiments with a continuous wave, the
removal step (step 116) may be for 20 ms in some examples. In some embodiments, the bias
power may be pulsed. In pulsed embodiments, an exemplary pulsed RF bias power may be
provided at a pulsed frequency of 100 Hz, the RF bias power has a 10% duty cycle during the
10 removal step. In such pulsed embodiments with a 10% duty cycle, the removal step (step 116) is
about 200 ms. In various embodiments, the pulsed bias has a duty cycle between 10% and
100%. In other embodiments, the pulsed bias has a duty cycle between 40% and 100%. A
continuous wave bias for 20 ms can provide the same results as a pulsed bias at a 10% duty
cycle for 200 ms if other parameters are the same. Therefore, an embodiment using a continuous
15 bias during the removal step (step 116) for 20 ms can provide the same removal as a pulsed bias
process with a 10% duty cycle for 200 ms. In order to provide a short removal step, bias
ramping times must be short. In some embodiments, the bias may be ramped in less than 100
ms. In some embodiments, the bias can be ramped 0.1 ms to 10 ms. In some embodiments, the
flux of bombardment ions near the modified layer is greater than 10^{17} ions /cm²s. In some
20 embodiments, the flux of the ions is between about 10^{17} to 10^{21} ions /cm²s. The higher flux and
higher energy ion bombardment reduces the time needed for the removal step.

[0023] FIG. 2C is a schematic cross-sectional view of a wafer 204 under the etch layer 208
disposed below the mask 212 after the removal step (step 116). The modified portion has been
removed. FIG. 3C is a schematic view of an enlarged section of an exposed portion of the etch
25 layer 208 during the removal step. Ions 312 bombard the etch layer causing modified atoms 304
bound with neutral radical atoms 308 to be removed.

[0024] After the removal step (step 116), a second transition is provided (step 118). The
second transition removes the bombardment gas and provides the modification gas. In some
embodiments, the second transition is accomplished less than 0.5 s. In various embodiments, the
30 second transition is accomplished in the range of 1 ms to 500 ms. In some embodiments, the first
transition is accomplished in the range of 0.2 s to 0.5 s.

[0025] The cycle of the steps of modification (step 112), first transition (step 114), removal (step 116), and second transition (step 118) is repeated a plurality of times until features are etched to a desired depth. In some embodiments, 70 Å is etched at each cycle.

[0026] Some embodiments are able to increase etch speeds by more than ten times over prior art ALE processes. The use of one or more of neutral radicals, faster transition times, the use of continuous wave or high duty cycle bias, and/or a greater ion flux during bombardment enable such faster embodiments. In an example, each cycle is about could be less than 35 ms. In some embodiments, each cycle is between about 20 ms and 1500 ms. In other embodiments, each cycle is between about 30 ms and 1000 ms.

[0027] FIG. 4 is a cross-sectional side view of an etch layer 208 that has been etched according to some embodiments. It should be noted that the depth of the narrow features is about equal to the depth of the wide features. In addition, the bottom of the wide feature is relatively flat. In addition, much of the patterned photoresist mask 212 remains, indicating that the etch is highly selective.

[0028] It has been found that the combination of using neutral radicals, with a high flux and low bias provides a monolayer in less than 0.5 s. The time for absorption of the neutral radicals in forming the monolayer may be modeled accordingly in the relationship:

$$t \sim (1 - e^{-k_N J_N t}) \quad (1).$$

This relationship shows how time t is related to a reaction coefficient for the neutral radical (k_N) and neutral radical flux (J_N). In some embodiments, the coefficient for neutral radicals is greater than the coefficient for ions. Some embodiments may have a flux of neutral radicals in the range between about 10^{17} to 10^{21} neutral radicals /cm²s.

[0029] It has been found that the combination of using higher energy ions and a high flux allows the removal of the modified monolayer in less than a second. The time for removing the modified layer may be modeled according to the relationship:

$$t \sim (1 - e^{-k J_i Y_i t}) \quad (2).$$

This relationship shows how time t is related to the ion yield (Y_i) and the ion flux (J_i). The ion yield Y_i is a function of ion energy, according to the relationship $Y(\epsilon) \sim \sqrt{\epsilon_i} - \sqrt{\epsilon_{th}}$. Some embodiments have an ion flux in the range of between about 10^{17} to 10^{21} ions /cm²s. Some embodiments provide a bias in the range of 200 eV to 2000 eV in order to provide a desired ion energy.

[0030] In various embodiments, the modification gas is chlorine gas (Cl₂), and the neutral radicals are chlorine neutral radicals. When the modification gas is chlorine gas, in some

embodiments, the etch layer is a silicon etch layer. The silicon etch layer may be a doped silicon. In other embodiments, the etch layer may be other silicon containing etch layers, such as silicon germanium (SiGe), silicon nitride (SiN), or silicon oxide (SiO₂). In other embodiments, the etch layer may be a metal etch layer. The metal etch layer may be ruthenium (Ru), molybdenum (Mo), tungsten (W), tantalum (Ta), or titanium (Ti). In other embodiments, the etch layer may be a metal containing etch layer, such as titanium nitride (TiN) or tantalum nitride (Ta₂N₅). In other embodiments, the etch layer may be a metalloid or metalloid containing layer, such as a germanium (Ge) or germanium containing layer.

[0031] In other embodiments, the modification gas is an oxygen containing gas and the radical neutrals are oxygen atoms. In such embodiments, the mask may be SiO₂ or SiN. When the modification gas is an oxygen containing gas, the etch layer may be a carbon containing layer, such as an amorphous carbon layer that has some hydrogen or pure carbon, or a ruthenium containing layer. In various embodiments, the oxygen containing gas is oxygen gas (O₂), carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂), and water (H₂O). In various embodiments, the modification gas consists essentially of chlorine gas or an oxygen containing gas. In various embodiments, the bombardment gas may comprise Ar, helium (He), neon (Ne), krypton (Kr), and xenon (Xe). In some embodiments, the bombardment gas consists essentially of one or more of Ar, He, Ne, Kr, and Xe. For example, Ar⁺ bombardment ions can be generated from Ar bombardment gas.

[0032] To provide an embodiment of a processing chamber that may be used in some embodiments, FIG. 5 schematically illustrates an example of a plasma processing chamber system 500 that may be used for the plasma processing process. The plasma processing chamber system 500 includes a plasma reactor 502 having a plasma processing confinement chamber 504 therein. A plasma power supply 506, tuned by a plasma matching network 508, supplies power to a transformer coupled plasma (TCP) coil 510 located near a dielectric inductive power window 512 to create a plasma 514 in the plasma processing confinement chamber 504 by providing an inductively coupled power.

[0033] The TCP coil (upper power source) 510 may be configured to produce a uniform diffusion profile within the plasma processing confinement chamber 504. For example, the TCP coil 510 may be configured to generate a toroidal power distribution in the plasma 514. The dielectric inductive power window 512 is provided to separate the TCP coil 510 from the plasma processing confinement chamber 504 while allowing energy to pass from the TCP coil 510 to the plasma processing confinement chamber 504. The TCP coil 510 acts as an electrode for

providing radio frequency (RF) power to the plasma processing confinement chamber 504. A wafer bias voltage power supply 516 tuned by a bias matching network 518 provides power to an electrode 520 to set the bias voltage on the substrate 566. The substrate 566 is supported by the electrode 520 so that the electrode acts as a substrate support. A controller 524 controls the plasma power supply 506 and the wafer bias voltage power supply 516.

[0034] The plasma power supply 506 and the wafer bias voltage power supply 516 may be configured to operate at specific radio frequencies such as, for example, 13.56 megahertz (MHz), 27 MHz, 2 MHz, 60 MHz, 400 kilohertz (kHz), 2.54 gigahertz (GHz), or combinations thereof. Plasma power supply 506 and wafer bias voltage power supply 516 may be appropriately sized to supply a range of powers in order to achieve the desired process performance. For example, in some embodiments, the plasma power supply 506 may supply power in a range of 50 to 5000 Watts, and the wafer bias voltage power supply 516 may supply a bias voltage in a range of 20 to 2000 V. In addition, the TCP coil 510 and/or the electrode 520 may be comprised of two or more sub-coils or sub-electrodes. The sub-coils or sub-electrodes may be powered by a single power supply or powered by multiple power supplies.

[0035] As shown in FIG. 5, the plasma processing chamber system 500 further includes a gas source/gas supply mechanism 530. The gas source 530 is in fluid connection with plasma processing confinement chamber 504 through a gas inlet, such as a gas injector 540. The gas injector 540 may be located in any advantageous location in the plasma processing confinement chamber 504 and may take any form for injecting gas. Preferably, however, the gas inlet may be configured to produce a “tunable” gas injection profile. The tunable gas injection profile allows independent adjustment of the respective flow of the gases to multiple zones in the plasma process confinement chamber 504. More preferably, the gas injector is mounted to the dielectric inductive power window 512. The gas injector may be mounted on, mounted in, or form part of the power window. The process gases and by-products are removed from the plasma process confinement chamber 504 via a pressure control valve 542 and a pump 544. The pressure control valve 542 and pump 544 also serve to maintain a particular pressure within the plasma processing confinement chamber 504. The pressure control valve 542 can maintain a pressure of less than 1 torr during processing. An edge ring 560 is placed around the substrate 566. The gas source/gas supply mechanism 530 is controlled by the controller 524. An example of such a plasma processing chamber system 500 is described in PCT application PCT/US21/31490, entitled Distributed Plasma Source Array, filed on May 10, 2021, which is

incorporated by reference for all purposes. An example of such a plasma processing chamber is the Syndion[®] etch system manufactured by Lam Research Corporation of Fremont, CA.

[0036] FIG. 6 is a high level block diagram showing a computer system 600. The computer system 600 is suitable for implementing a controller 524 used in embodiments. The computer system 600 may have many physical forms ranging from an integrated circuit, a printed circuit board, and a small handheld device up to a huge supercomputer. The computer system 600 includes one or more processors 602, and further can include an electronic display device 604 (for displaying graphics, text, and other data), a main memory 606 (e.g., random access memory (RAM)), storage device 608 (e.g., hard disk drive), removable storage device 610 (e.g., optical disk drive), user interface devices 612 (e.g., keyboards, touch screens, keypads, mice or other pointing devices, etc.), and a communications interface 614 (e.g., wireless network interface). The communications interface 614 allows software and data to be transferred between the computer system 600 and external devices via a link. The system may also include a communications infrastructure 616 (e.g., a communications bus, cross-over bar, or network) to which the aforementioned devices/modules are connected.

[0037] Information transferred via communications interface 614 may be in the form of signals such as electronic, electromagnetic, optical, or other signals capable of being received by communications interface 614, via a communications link that carries signals and may be implemented using wire or cable, fiber optics, a phone line, a cellular phone link, a radio frequency link, and/or other communications channels. With such a communications interface 614, it is contemplated that the one or more processors 602 might receive information from a network, or might output information to the network in the course of performing the above-described method steps. Furthermore, method embodiments may execute solely upon the processors or may execute over a network such as the Internet, in conjunction with remote processors that share a portion of the processing.

[0038] The term “non-transient computer readable medium” is used generally to refer to media such as main memory, secondary memory, removable storage, and storage devices, such as hard disks, flash memory, disk drive memory, CD-ROM, and other forms of persistent memory and shall not be construed to cover transitory subject matter, such as carrier waves or signals. Examples of computer readable code include machine code, such as produced by a compiler, and files containing higher level code that are executed by a computer using an interpreter. Computer readable media may also be computer code transmitted by a computer data signal to a processor.

[0039] In some embodiments, the computer readable media may comprise computer readable code for providing a modification step for less than 0.5 seconds (step 112), computer readable code for providing a first transition from the modification gas to the bombardment gas in less than 0.5 seconds (step 114), computer readable code for providing a removal step for less than 5 0.5 seconds (step 116), and computer readable code for providing a second transition from the bombardment gas to the modification gas in less than 0.5 seconds (step 118).

[0040] In other embodiments, instead of forming the plasma in the reactor where the substrate is located, for the modification step, the plasma may be formed remotely. Radical neutrals may be provided by the remote plasma source. In some embodiments, charged ions are prevented 10 from entering the reactor during the modification step.

[0041] While this disclosure has been described in terms of several preferred embodiments, there are alterations, modifications, permutations, and various substitute equivalents, which fall within the scope of this disclosure. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present disclosure. It is therefore intended 15 that the following appended claims be interpreted as including all such alterations, modifications, permutations, and various substitute equivalents as fall within the true spirit and scope of the present disclosure.

CLAIMS

What is claimed is:

1. A method for etching an etch layer, the method comprising a plurality of cycles, wherein each cycle, comprises:
 - 5 exposing the etch layer to neutral radicals for a time between 10 ms and 600 ms, wherein the neutral radicals are absorbed into the etch layer to form a modified part of the etch layer; and
 - exposing the etch layer to bombardment ions for a time between 10 ms and 600 ms, wherein the bombardment ions remove the modified part of the etch layer.
2. The method, as recited in claim 1, wherein the exposing the etch layer to bombardment
10 ions provides a bias of greater than 700 eV.
3. The method, as recited in claim 1, wherein the neutral radicals have a flux of greater than 10^{17} neutral radicals /cm²s.
4. The method, as recited in claim 1, wherein the bombardment ions have a flux of greater than 10^{17} ions /cm²s.
- 15 5. The method, as recited in claim 1, wherein the exposing the etch layer to bombarding ions is for a time between 10 ms and 250 ms.
6. The method of claim 1, wherein the exposing the etch layer to bombarding ions is for a time between 10 ms and 25 ms.
7. The method, as recited in claim 1, wherein the exposing the etch layer to bombarding
20 ions comprises providing a bias in a range of 200 eV to 2000 eV.
8. The method, as recited in claim 7, wherein the bias is a continuous wave bias.
9. The method, as recited in claim 7, wherein the bias is a pulsed bias.
10. The method, as recited in claim 7, wherein the bias is ramped up in less than 100 ms.
11. The method, as recited in claim 1, further comprising:
 - 25 providing a first transition from a modification gas to a bombardment gas in less than 0.5 seconds, wherein the modification gas transformed to provide the neutral radicals the bombardment gas is transformed into bombardment ions, and wherein the first transition is after the exposing the etch layer to neutral radicals and before exposing the etch layer to bombardment ions; and
 - 30 providing a second transition from the bombardment gas to the modification gas, wherein the second transition is after the exposing the etch layer to the bombardment ions and before exposing the etch layer to neutral radicals.

12. The method, as recited in claim 1, wherein the neutral radicals are chloride atoms or oxygen atoms.
13. The method, as recited in claim 1, wherein the bombardment ions are ions of argon, helium, neon, krypton, and xenon.
- 5 14. The method, as recited in claim 1, wherein the exposing the etch layer to bombardment ions comprises providing an RF power of more than 2000 W.
15. An etching system for etching an etch layer over a substrate, the etching system, comprising:
- a processing chamber;
 - 10 a substrate support for supporting a substrate in the processing chamber;
 - an RF power source for providing RF power to etch chamber;
 - a neutral radical source adapted to provide neutral radicals in the processing chamber;
 - a bombardment gas source adapted to provide bombardment gas in the processing chamber;
 - 15 a controller controllably connected to the RF power source, the neutral radical source, and the bombardment gas source, configured to:
 - a) expose the etch layer to neutral radicals for a time between 10 ms and 600 ms, wherein the neutral radicals are absorbed into the etch layer to form a modified part of the etch layer; and
 - 20 b) expose the etch layer to bombardment ions for a time between 10 ms and 600 ms, wherein the bombardment ions remove the modified part of the etch layer.
16. The etching system, as recited in claim 15, wherein the exposing the etch layer to bombardment ions provides a bias of greater than 700 eV.
17. The etching system, recited in claim 15, wherein the neutral radicals have a flux of
25 greater than 10^{17} neutral radicals /cm²s.
18. The etching system, as recited in claim 15, wherein the bombardment ions have a flux of greater than 10^{17} ions /cm²s.
19. The etching system, as recited in claim 15, wherein the exposing the etch layer to bombarding ions comprises providing a bias in a range of 200 eV to 2000 eV.
- 30 20. The etching system, as recited in claim 19, wherein the bias is a continuous wave bias.
21. The etching system, as recited in claim 19, wherein the bias is a pulsed bias.
22. The etching system, as recited in claim 19, wherein the bias is ramped up in less than 100 ms.

23. The etching system, as recited in claim 15, wherein the controller is further configured to:
provide a first transition from a modification gas to a bombardment gas in less than 0.5
seconds, wherein the modification gas transformed to provide the neutral radicals the
bombardment gas is transformed into bombardment ions, and wherein the first transition is after
5 the exposing the etch layer to neutral radicals and before exposing the etch layer to bombardment
ions; and
provide a second transition from the bombardment gas to the modification gas, wherein
the second transition is after the exposing the etch layer to the bombardment ions and before
exposing the etch layer to neutral radicals.
- 10 24. The etching system, as recited in claim 15, wherein the exposing the etch layer to
bombardment ions comprises providing an RF power of more than 2000 W.

1/7

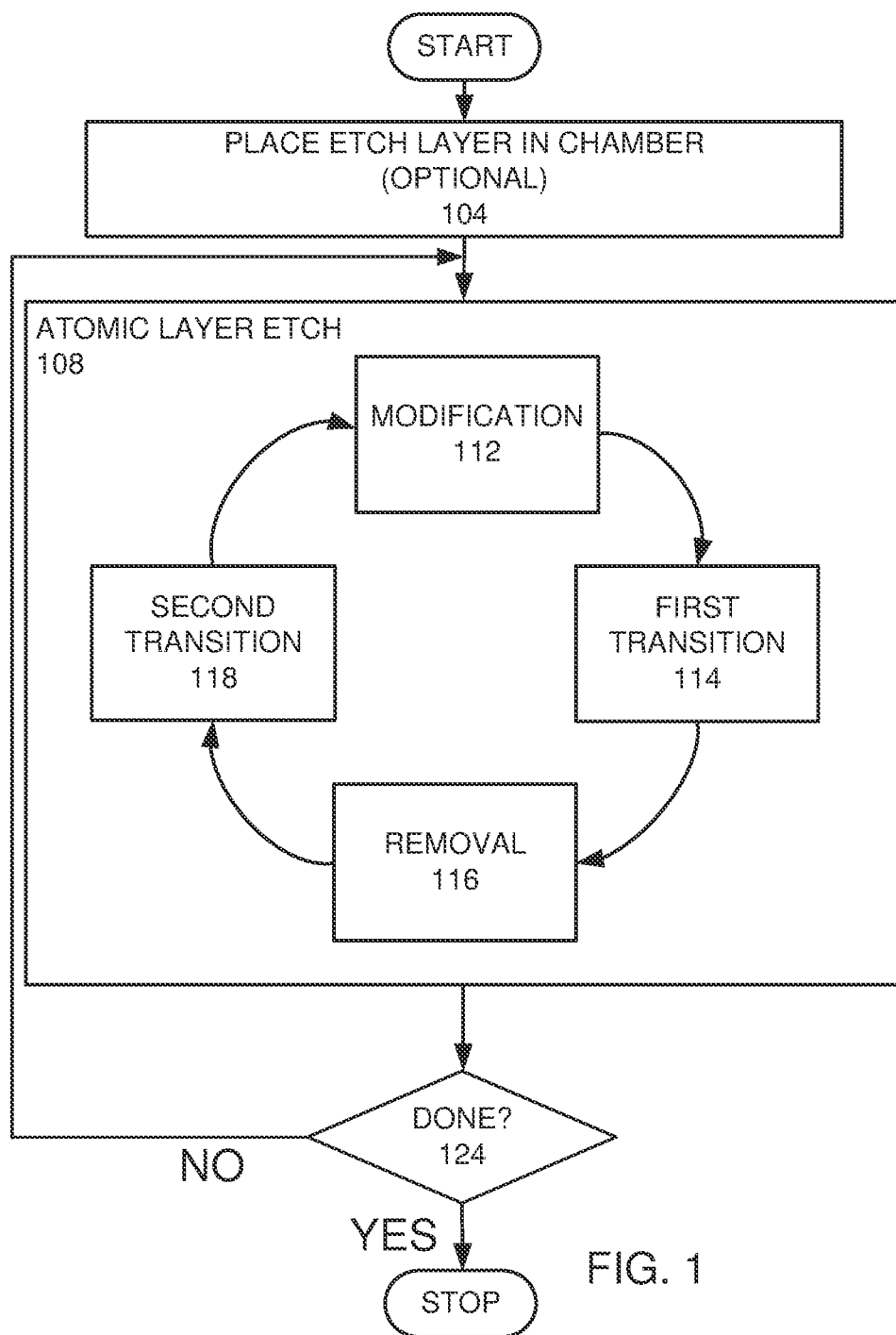


FIG. 1

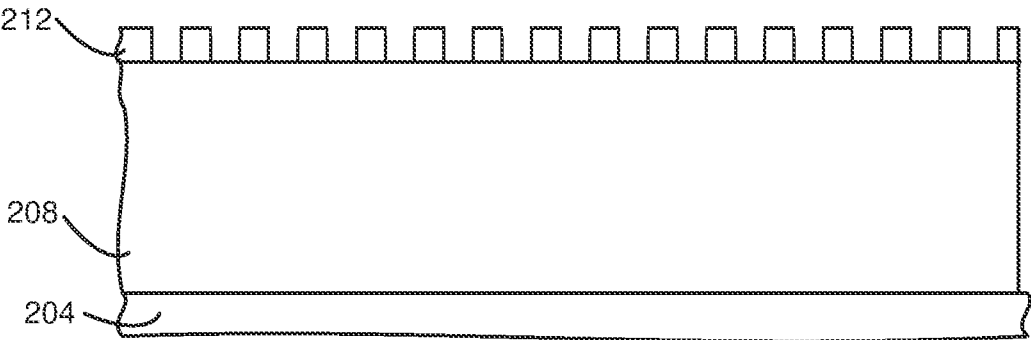


FIG. 2A

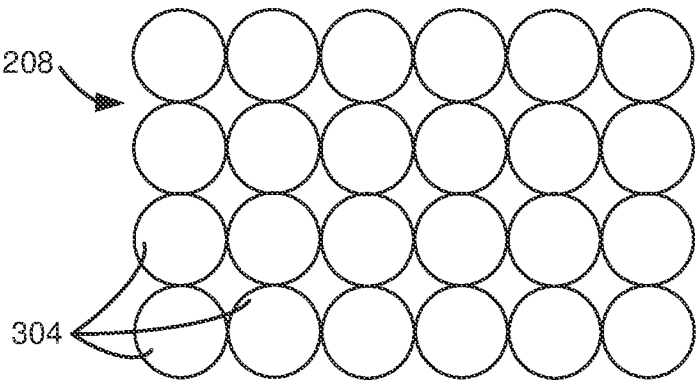


FIG. 3A

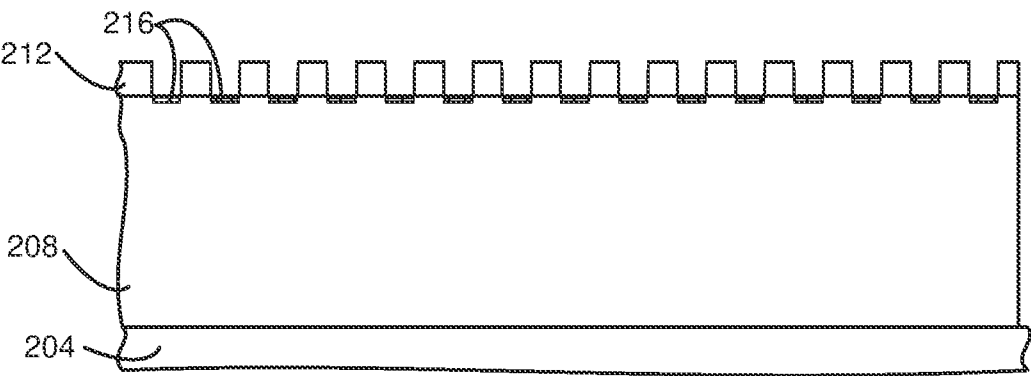


FIG. 2B

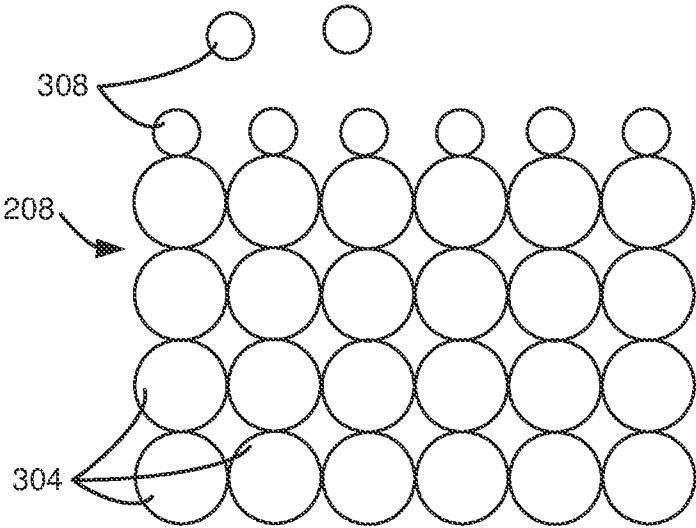


FIG. 3B

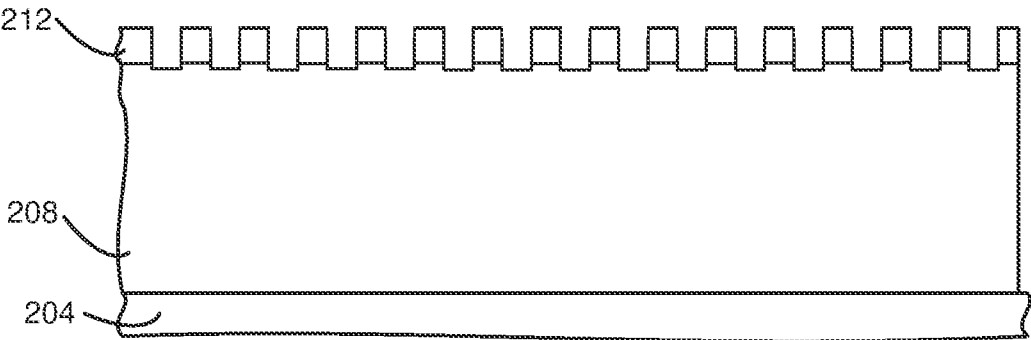


FIG. 2C

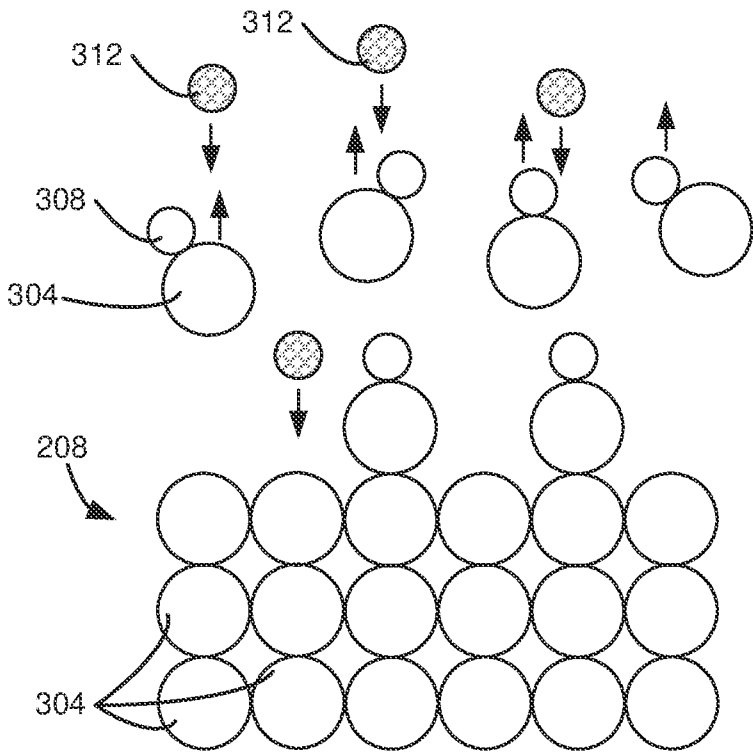


FIG. 3C

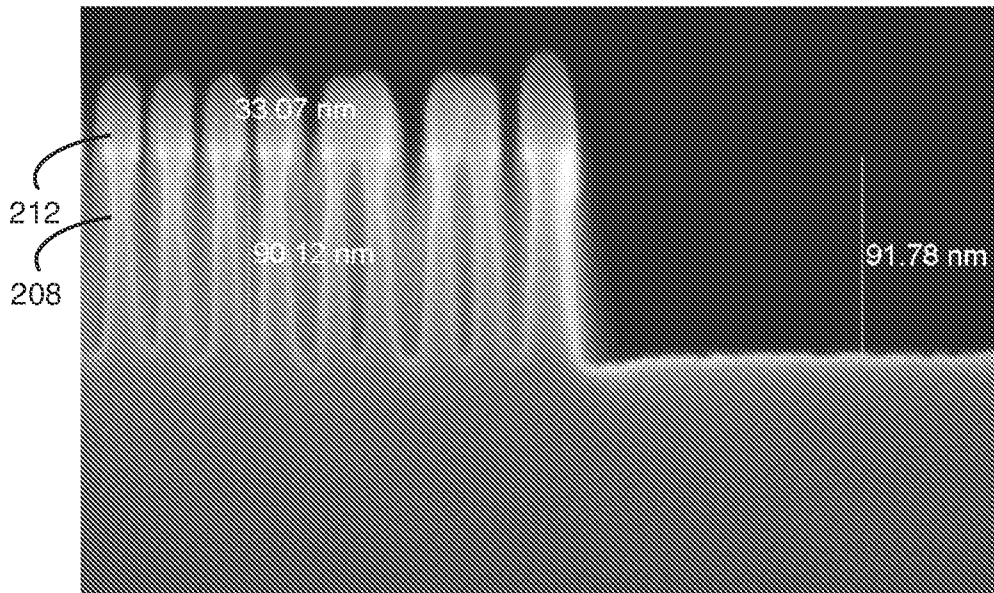


FIG. 4

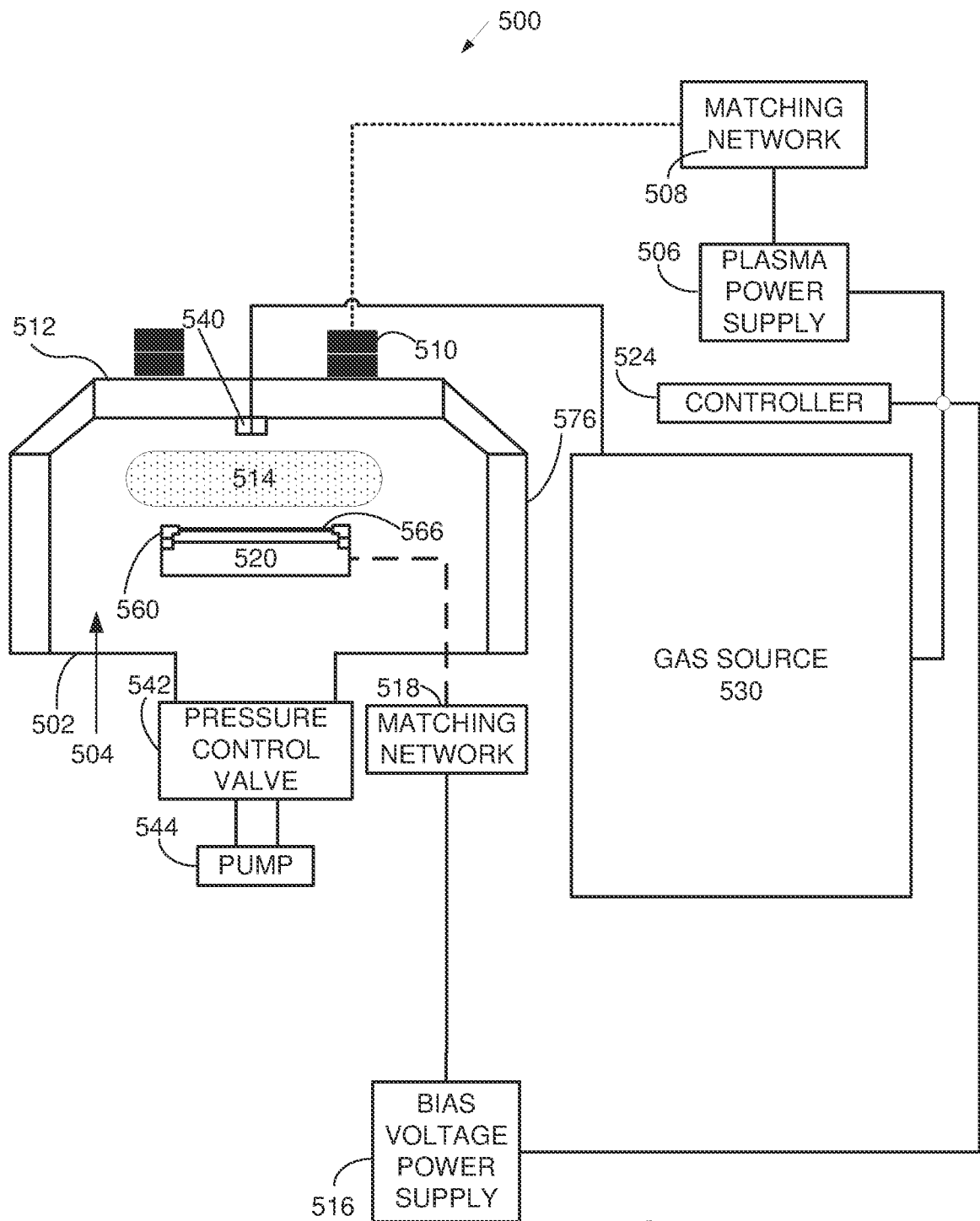


FIG. 5

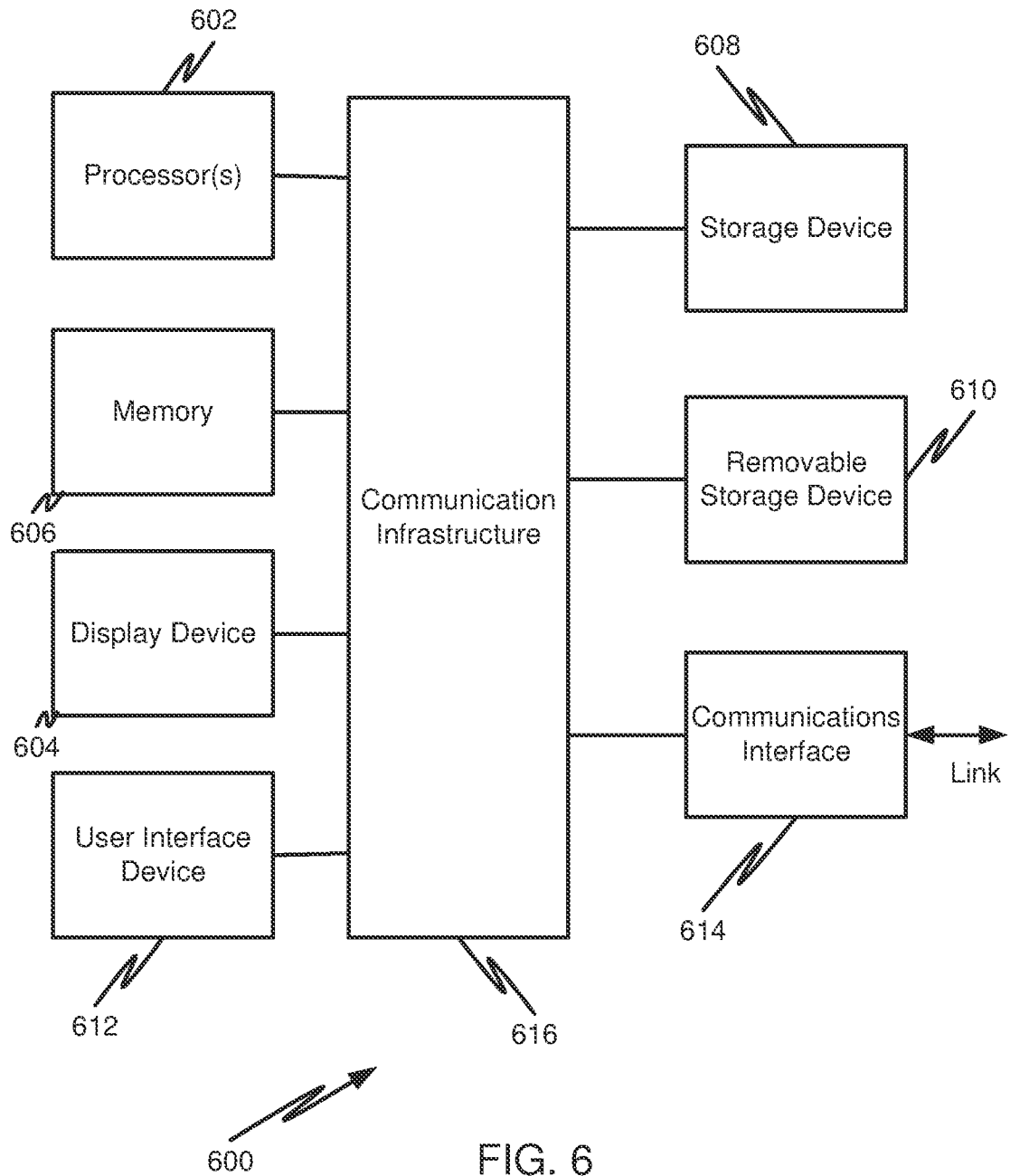


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2023/014520

A. CLASSIFICATION OF SUBJECT MATTER**H01L 21/3213**(2006.01)i; **H01L 21/67**(2006.01)i; **H01J 37/32**(2006.01)i

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)

H01L 21/3213(2006.01); H01J 37/32(2006.01); H01L 21/3065(2006.01); H01L 21/311(2006.01); H01L 21/67(2006.01)

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: ALE (Atomic Layer Etching), neutral radicals, modified part, bombardment ions, time

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
DY	US 2021-0005425 A1 (LAM RESEARCH CORPORATION) 07 January 2021 (2021-01-07) See paragraphs [0032]-[0055] and figure 1.	1-24
Y	US 2021-0366723 A1 (TOKYO ELECTRON LIMITED) 25 November 2021 (2021-11-25) See paragraphs [0008], [0030]-[0054] and figures 1-4D.	1-24
DY	US 10763083 B2 (LAM RESEARCH CORPORATION) 01 September 2020 (2020-09-01) See column 20, lines 29-47 and figure 3A.	2,7-10,16,19-22
A	US 2021-0280433 A1 (LAM RESEARCH CORPORATION) 09 September 2021 (2021-09-09) See paragraphs [0054]-[0072] and figures 1-2.	1-24
A	KR 10-1917304 B1 (BEIJING NAURA MICROELECTRONICS EQUIPMENT CO., LTD.) 12 November 2018 (2018-11-12) See paragraphs [0034]-[0063] and figures 1-4.	1-24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

“D” document cited by the applicant in the international application

“E” earlier application or patent 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

26 June 2023

Date of mailing of the international search report

26 June 2023

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon
35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

PARK, Hye Lyun

Telephone No. +82-42-481-3463

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2023/014520

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2021-0005425	A1	07 January 2021	CN	111937122	A	13 November 2020
				EP	3776636	A1	17 February 2021
				EP	3776636	A4	22 December 2021
				KR	10-2020-0128185	A	11 November 2020
				US	11450513	B2	20 September 2022
				US	2022-0392747	A1	08 December 2022
				WO	2019-190781	A1	03 October 2019
US	2021-0366723	A1	25 November 2021	TW	202213497	A	01 April 2022
				US	11651970	B2	16 May 2023
				WO	2021-236359	A1	25 November 2021
US	10763083	B2	01 September 2020	CN	111448641	A	24 July 2020
				EP	3692567	A1	12 August 2020
				EP	3821457	A4	13 April 2022
				JP	2020-536393	A	10 December 2020
				KR	10-2020-0053623	A	18 May 2020
				TW	201923893	A	16 June 2019
				US	2019-0108982	A1	11 April 2019
				US	2020-0402770	A1	24 December 2020
				WO	2019-070737	A1	11 April 2019
US	2021-0280433	A1	09 September 2021	CN	112424914	A	26 February 2021
				EP	3821457	A1	19 May 2021
				EP	3821457	A4	13 April 2022
				JP	2021-532573	A	25 November 2021
				KR	10-2021-0019121	A	19 February 2021
				TW	202018807	A	16 May 2020
				US	11637022	B2	25 April 2023
				WO	2020-014065	A1	16 January 2020
KR	10-1917304	B1	12 November 2018	CN	105448635	A	30 March 2016
				CN	105448635	B	09 January 2018
				JP	2017-535057	A	24 November 2017
				JP	6454409	B2	16 January 2019
				KR	10-2017-0048468	A	08 May 2017
				SG	11201701159	QA	30 March 2017
				TW	201608662	A	01 March 2016
				TW	I620260	B	01 April 2018
				WO	2016-029817	A1	03 March 2016