

(51) International Patent Classification:
H01L 21/3065 (2006.01)

(21) International Application Number:

PCT/US2013/076217

(22) International Filing Date:

18 December 2013 (18.12.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/753,677	17 January 2013 (17.01.2013)	US
13/839,948	15 March 2013 (15.03.2013)	US
13/840,206	15 March 2013 (15.03.2013)	US

(71) Applicant: **APPLIED MATERIALS, INC.** [US/US];
3050 Bowers Avenue, Santa Clara, California 95054 (US).(72) Inventors: **WANG, Xikun**; 844 Fife Way, Sunnyvale,
California 94087 (US). **HSU, Ching-Mei**; 25 Olmsted Rd.
#105, Stanford, California 94305 (US). **INGLE, Nitin K.**;
1435 Graywood Drive, San Jose, California 95129 (US).**LI, Zihui**; 1506 Vista Club Cir. #101, Santa Clara, California 95054 (US). **WANG, Anchuan**; 6556 Bollinger Road,
San Jose, California 95129 (US).(74) Agents: **BERNARD, Eugene J.** et al.; Two Embarcadero
Center, Eighth Floor, San Francisco, California 94111
(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, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
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, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,

[Continued on next page]

(54) Title: DRY-ETCH FOR SELECTIVE TUNGSTEN REMOVAL

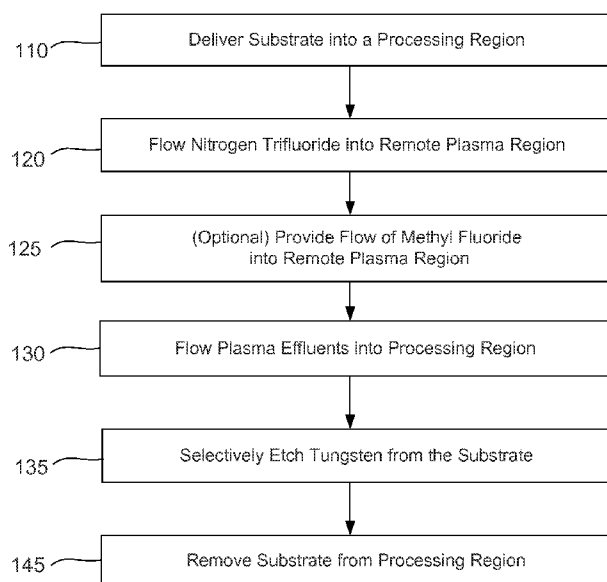


FIG. 1

(57) Abstract: Methods of selectively etching tungsten relative to silicon-containing films (e.g. silicon oxide, silicon carbon nitride and (poly)silicon) as well as tungsten oxide are described. The methods include a remote plasma etch formed from a fluorine-containing precursor and/or hydrogen (H₂). Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents react with the tungsten. The plasma effluents react with exposed surfaces and selectively remove tungsten while very slowly removing other exposed materials. Sequential and simultaneous methods are included to remove thin tungsten oxide which may, for example, result from exposure to the atmosphere.



GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, 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, 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))*

DRY-ETCH FOR SELECTIVE TUNGSTEN REMOVAL**CROSS-REFERENCES TO RELATED APPLICATIONS**

[0001] This application claims priority to U.S. Patent Application Nos. 13/840,206 and 13/839,948, both filed March 15, 2013. USSN 13/840,206 claims the benefit of U.S. Provisional Application No. 61/753,677 by Wang et al, filed January 17, 2013, and titled "DRY-ETCH FOR SELECTIVE TUNGSTEN REMOVAL." This application is also related to U.S. Provisional Application No. 61/732,074 by Kim et al, filed November 30, 2012 and titled "DRY-ETCH FOR SELECTIVE OXIDATION REMOVAL." Each of the above U.S. Applications is incorporated herein in its entirety for all purposes.

BACKGROUND OF THE INVENTION

[0002] Integrated circuits are made possible by processes which produce intricately patterned material layers on substrate surfaces. Producing patterned material on a substrate requires controlled methods for removal of exposed material. Chemical etching is used for a variety of purposes including transferring a pattern in photoresist into underlying layers, thinning layers or thinning lateral dimensions of features already present on the surface. Often it is desirable to have an etch process which etches one material faster than another helping e.g. a pattern transfer process proceed. Such an etch process is said to be selective to the first material. As a result of the diversity of materials, circuits and processes, etch processes have been developed with a selectivity towards a variety of materials. However, there are few options for selectively etching metals.

[0003] Dry etch processes are often desirable for selectively removing material from semiconductor substrates. The desirability stems from the ability to gently remove material from miniature structures with minimal physical disturbance. Dry etch processes also allow the etch rate to be abruptly stopped by removing the gas phase reagents. Some dry-etch processes involve the exposure of a substrate to remote plasma by-products formed from one or more precursors. For example, remote plasma excitation of ammonia and nitrogen trifluoride enables silicon oxide to be selectively removed from a patterned substrate when the plasma effluents are flowed into the substrate processing region. Remote plasma etch processes have recently been developed to selectively remove a variety of dielectrics relative to one another. However, fewer dry-etch processes have been developed to selectively remove metals and their native oxidation.

[0004] Methods are needed to selectively and delicately etch exposed metal surfaces.

BRIEF SUMMARY OF THE INVENTION

[0005] Methods of selectively etching tungsten relative to silicon-containing films (e.g. silicon oxide, silicon carbon nitride and (poly)silicon) as well as tungsten oxide are described. The

methods include a remote plasma etch formed from a fluorine-containing precursor and/or hydrogen (H₂). Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents react with the tungsten. The plasma effluents react with exposed surfaces and selectively remove tungsten while very slowly removing other exposed materials.

- 5 Sequential and simultaneous methods are included to remove thin tungsten oxide which may, for example, result from exposure to the atmosphere.

[0006] Embodiments of the invention include methods of etching a patterned substrate in a substrate processing region of a substrate processing chamber. The patterned substrate has a exposed tungsten region and an exposed second material region. The methods include flowing a
10 fluorine-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a plasma in the plasma region to produce plasma effluents. The methods further include etching the exposed tungsten from the substrate by flowing the plasma effluents into the substrate processing region through through-holes in a showerhead.

[0007] Additional embodiments and features are set forth in part in the description that follows,
15 and in part will become apparent to those skilled in the art upon examination of the specification or may be learned by the practice of the disclosed embodiments. The features and advantages of the disclosed embodiments may be realized and attained by means of the instrumentalities, combinations, and methods described in the specification.

BRIEF DESCRIPTION OF THE DRAWINGS

20 [0008] A further understanding of the nature and advantages of the disclosed embodiments may be realized by reference to the remaining portions of the specification and the drawings.

[0009] FIG. 1 is a flow chart of a tungsten selective etch process according to disclosed embodiments.

[0010] FIG. 2A shows a schematic cross-sectional view of a substrate processing chamber
25 according to the disclosed technology.

[0011] FIG. 2B shows a schematic cross-sectional view of a portion of a substrate processing chamber according to the disclosed technology.

[0012] FIG. 2C shows a bottom plan view of a showerhead according to the disclosed technology.

30 [0013] FIG. 3 shows a top plan view of an exemplary substrate processing system according to the disclosed technology.

[0014] In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Methods of selectively etching tungsten relative to silicon-containing films (e.g. silicon oxide, silicon carbon nitride and (poly)silicon) as well as tungsten oxide are described. The methods include a remote plasma etch formed from a fluorine-containing precursor and/or hydrogen (H_2). Plasma effluents from the remote plasma are flowed into a substrate processing region where the plasma effluents react with the tungsten. The plasma effluents react with exposed surfaces and selectively remove tungsten while very slowly removing other exposed materials. Sequential and simultaneous methods are included to remove thin tungsten oxide which may, for example, result from exposure to the atmosphere.

[0016] An ion suppression element may be included in the etch processes discussed herein in order to achieve high tungsten selectivity. The ion suppression element functions to reduce or eliminate ionically charged species traveling from the plasma generation region to the substrate. Uncharged neutral and radical species may pass through the openings in the ion suppressor to react at the substrate. The ion suppressor helps control the concentration of ionic species in the reaction region at a level that assists the process.

[0017] In accordance with some embodiments of the invention, an ion suppressor as described in the exemplary equipment section may be used to provide radical and/or neutral species for selectively etching substrates. In one embodiment, for example, an ion suppressor is used to provide fluorine-containing plasma effluents to selectively etch tungsten. The ion suppressor may be used to provide a reactive gas having a higher concentration of radicals than ions. Because most of the charged particles of a plasma are filtered or removed by the ion suppressor, the substrate is not necessarily biased during the etch process. Such a process using radicals and other neutral species can reduce plasma damage compared to conventional plasma etch processes that include sputtering and bombardment. Embodiments of the present invention are also advantageous over conventional wet etch processes where surface tension of liquids can cause bending and peeling of small features.

[0018] In order to better understand and appreciate the invention, reference is now made to FIG. 1 which is a flow chart of a tungsten selective etch process according to disclosed embodiments. The tungsten may also have a thin native oxide layer on its surface due to atmospheric exposure. The tungsten may be in the form of a blanket layer on the substrate or it may reside in discrete regions of a patterned substrate surface. In either case, the tungsten forms exposed surfaces of the surface of the substrate. The substrate is then delivered into a processing region (operation 110). A thin layer of tungsten oxide may be present over the otherwise exposed tungsten regions of the substrate prior to delivering the substrate into the processing region. after delivering the substrate to the processing region, for example, by treating exposed regions of tungsten to a reactive oxygen source.

[0019] A flow of nitrogen trifluoride is introduced into a plasma region separate from the processing region (operation 120). Other sources of fluorine may be used to augment or replace the nitrogen trifluoride. In general, a fluorine-containing precursor may be flowed into the plasma region and the fluorine-containing precursor comprises at least one precursor selected from the group consisting of atomic fluorine, diatomic fluorine, bromine trifluoride, chlorine trifluoride, nitrogen trifluoride, hydrogen fluoride, sulfur hexafluoride and xenon difluoride. However, the inventors have observed higher etch rates for all embodiments disclosed herein when using nitrogen trifluoride in the mix of precursors delivered to the remote plasma region. The inventors conjecture that nitrogen trifluoride plasma effluents experience a significantly longer excited lifetime prior to deexcitation and/or recombination. The extended lifetime allows etch species to travel from remote plasma region into the vicinity of the substrate prior to deexcitation/recombination.

[0020] The separate plasma region may be referred to as a remote plasma region herein and may be within a distinct module from the processing chamber or a compartment within the processing chamber. A carbon-and-hydrogen-containing precursor, in this case methyl fluoride (CH_3F) is also flowed into the plasma region (operation 125) where it is simultaneously excited in a plasma along with the nitrogen trifluoride. The flow rate of the atomic hydrogen may be greater than the flow rate of the atomic fluorine in order to maintain a removal rate of tungsten. In this example, fluorine contributions come from both the carbon source and the nitrogen trifluoride. The contribution from each precursor must be considered in order to calculate the H:F atomic flow ratio. Diatomic hydrogen (H_2) may be added as well and is necessary in some instances so that an atomic flow rate ratio greater than H:F=1 is possible.

[0021] The plasma effluents formed in the remote plasma region are then flowed into the substrate processing region (operation 130). Tungsten on the substrate is selectively etched (operation 135) such that tungsten may be removed more rapidly than a variety of other materials. The selective etch disclosed in all examples disclosed herein may etch tungsten significantly faster than one of tungsten oxide, titanium nitride or a silicon-containing material such as silicon (e.g. polysilicon), silicon oxide, silicon nitride or silicon carbon nitride in embodiments of the invention. Such a process may have broad-based utility, but may find clear utility in removing a layer of tungsten gapfill used to fill small high aspect ratio trenches (such as may be used to form a temporary separator between vertically integrated memory sub-elements). The invention may involve maintenance of an atomic flow ratio of fluorine (F) to hydrogen (H) in order achieve high etch selectivity of tungsten. The copresence of fluorine and hydrogen is thought to enable two reactions to proceed: (1) one which consumes hydrogen (from CH_3F) to convert native tungsten oxide to tungsten by shedding moisture through the exhaust system and (2) another reaction which consumes fluorine to remove tungsten in the form of exhausted tungsten hexafluoride (WF_6). Maintaining an atomic flow ratio (H:F) greater than 1:1, the inventors have found that the collective process is highly selective of tungsten over a variety of other materials including tungsten oxide, despite being capable of removing a thin native tungsten oxide. The reactive chemical species and any process effluents are removed from the substrate processing region and then the substrate is removed from the processing region (operation 145).

[0022] In disclosed embodiments, an atomic gas flow ratio (H:F) greater than or about 1:1, greater than or about 2:1 or greater than or about 3:1. An atomic gas flow ratio (H:F) less than or about 15:1, less than or about 12:1, less than or about 10:1 or less than or about 7:1 is used, in embodiments of the invention, to achieve favorable selectivities. The inventors have also found that selective dry etches described herein can achieve favorable selectivities without any hydrogen component when not native oxide is present on a tungsten surface. The etch selectivity (tungsten:secondary material other than tungsten) of the processes disclosed herein may be greater than or about 10:1, greater than or about 20:1, greater than or about 50:1, or greater than or about 100:1 for materials other than in embodiments of the invention. The inventors have found that the processes disclosed herein display etch selectivities of tungsten relative to a variety of specific materials. The etch selectivity of tungsten relative to (poly)silicon may be greater than or about 100:1, greater than or about 150:1, greater than or about 200:1 or greater than or about 250:1 in disclosed embodiments. The etch selectivity of tungsten relative to silicon oxide may be greater than or about 15:1, greater than or about 25:1, greater than or about 30:1 or greater than or about 40:1 in embodiments of the invention. The etch selectivity of tungsten relative to silicon carbon

nitride may be greater than or about 3:1, greater than or about 5:1, greater than or about 7:1 or greater than or about 10:1 in embodiments of the invention. The etch selectivity of tungsten relative to tungsten oxide may be greater than or about 10:1, greater than or about 20:1, greater than or about 50:1 or greater than or about 100:1 in embodiments of the invention.

5 **[0023]** The flows of the fluorine-containing precursor and the carbon-and-hydrogen-containing precursor may further include one or more relatively inert gases such as He, N₂, Ar. The inert gas can be used to improve plasma stability, process uniformity and the like. Argon is helpful, as an additive, to promote the formation of a stable plasma. Process uniformity is generally increased when helium is included. These additives are present in embodiments throughout this
10 specification. Flow rates and ratios of the different gases may be used to control etch rates and etch selectivity.

[0024] In disclosed embodiments, the fluorine-containing gas (e.g. NF₃) is supplied at a flow rate of between about 25 sccm (standard cubic centimeters per minute) and 400 sccm, CH₃F at a flow rate of between about 50 sccm and 600 sccm, He at a flow rate of between about 0 slm (standard
15 liters per minute) and 3 slm, and Ar at a flow rate of between about 0 slm and 3 slm. One of ordinary skill in the art would recognize that other gases and/or flows may be used depending on a number of factors including processing chamber configuration, substrate size, geometry and layout of features being etched, and the like. Inclusion of a flow of hydrogen (H₂) into the remote plasma region can lessen the flow rate requirement for methyl fluoride. The inventors have also found that
20 flowing a combination of hydrogen (H₂) and carbon tetrafluoride (CF₄) is a productive replacement of CH₃F, CH₂F₂ or CHF₃ as well as precursors of the general form C_xH_yF_z, in other words partially fluorinated hydrocarbons. Therefore, a carbon-and-hydrogen-containing precursor, as recited herein, includes a flow of a hydrogen-containing precursor and carbon-containing precursor into the remote plasma region in disclosed embodiments.

25 **[0025]** The method also includes applying energy to the fluorine-containing precursor and the carbon-and-hydrogen-containing precursor (CH₃F) while they are in the remote plasma region to generate the plasma effluents. As would be appreciated by one of ordinary skill in the art, the plasma may include a number of charged and neutral species including radicals and ions. The plasma may be generated using known techniques (e.g., radio frequency excitations, capacitively-
30 coupled power, inductively coupled power, and the like). In an embodiment, the energy is applied using a capacitively-coupled plasma unit. The remote plasma source power may be between about 40 watts and about 500 watts, between about 75 watts and about 400 watts, between about 150 watts and about 350 watts, or between about 200 watts and about 300 watts in embodiments of

the invention. The narrowest RF power embodiment optimizes the selective removal of tungsten relative to a variety of other exposed materials including silicon carbon nitride. The pressure in the remote plasma region may be such that the pressure in the substrate processing region ends up between about 0.01 Torr and about 50 Torr or between about 0.1 Torr and about 5 Torr in disclosed
5 embodiments. The capacitively-coupled plasma unit may be disposed remote from a gas reaction region of the processing chamber. For example, the capacitively-coupled plasma unit and the plasma generation region may be separated from the gas reaction region by a showerhead.

[0026] The temperature of the substrate during this first example may be between about -30°C and about 400°C in general. In embodiments, the temperature of the substrate during the dry etches
10 described in this section may be greater than or about -30°C, greater than or about -10°C, greater than or about 10°C, or greater than or about 25°C. The substrate temperatures may be less than or about 400°C, less than or about 350°C, less than or about 250°C in disclosed embodiments. The etch rate of tungsten was found to rise with increased substrate temperature (from about 10°C up through 100°C) but using lower temperatures was helpful for achieving high selectivities by
15 suppressing, for example, the etch rate of tungsten oxide.

[0027] An additional step may be included (prior to operations 120-135) by providing a flow of hydrogen (H₂) to the remote plasma region. The plasma effluents produced from the excited molecular hydrogen (H₂) has been found by the inventors to remove, presumably, the oxygen from the native tungsten oxide. The net effect was that this additional step exposed a predominantly
20 tungsten region to the further processing depicted in FIG. 1. The addition of a fluorine-containing precursor to the remote plasma region during this step is optional, in part, because of the thinness of native oxides formed when tungsten is exposed to atmosphere.

[0028] Additional process parameters are disclosed in the course of describing an exemplary processing chamber and system.

25 Exemplary Processing System

[0029] FIG. 2A shows a cross-sectional view of an exemplary substrate processing chamber 1001 with partitioned plasma generation regions within the processing chamber. During film etching, e.g., titanium nitride, tantalum nitride, tungsten, silicon, polysilicon, silicon oxide, silicon nitride, silicon oxynitride, silicon oxycarbide, etc., a process gas may be flowed into chamber
30 plasma region 1015 through a gas inlet assembly 1005. A remote plasma system (RPS) 1002 may optionally be included in the system, and may process a first gas which then travels through gas inlet assembly 1005. The inlet assembly 1005 may include two or more distinct gas supply channels where the second channel (not shown) may bypass the RPS 1002, if included.

Accordingly, in disclosed embodiments the precursor gases may be delivered to the processing chamber in an unexcited state. In another example, the first channel provided through the RPS may be used for the process gas and the second channel bypassing the RPS may be used for a treatment gas in disclosed embodiments. The process gas may be excited within the RPS 1002 prior to entering the chamber plasma region 1015. Accordingly, the fluorine-containing precursor as discussed above, for example, may pass through RPS 1002 or bypass the RPS unit in disclosed embodiments. Various other examples encompassed by this arrangement will be similarly understood.

[0030] A cooling plate 1003, faceplate 1017, ion suppressor 1023, showerhead 1025, and a substrate support 1065 (also known as a pedestal), having a substrate 1055 disposed thereon, are shown and may each be included according to disclosed embodiments. The pedestal 1065 may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. This configuration may allow the substrate 1055 temperature to be cooled or heated to maintain relatively low temperatures, such as between about -20°C to about 200°C, or therebetween. The heat exchange fluid may comprise ethylene glycol and/or water. The wafer support platter of the pedestal 1065, which may comprise aluminum, ceramic, or a combination thereof, may also be resistively heated in order to achieve relatively high temperatures, such as from up to or about 100°C to above or about 1100°C, using an embedded resistive heater element. The heating element may be formed within the pedestal as one or more loops, and an outer portion of the heater element may run adjacent to a perimeter of the support platter, while an inner portion runs on the path of a concentric circle having a smaller radius. The wiring to the heater element may pass through the stem of the pedestal 1065, which may be further configured to rotate.

[0031] The faceplate 1017 may be pyramidal, conical, or of another similar structure with a narrow top portion expanding to a wide bottom portion. The faceplate 1017 may additionally be flat as shown and include a plurality of through-channels used to distribute process gases. Plasma generating gases and/or plasma excited species, depending on use of the RPS 1002, may pass through a plurality of holes, shown in FIG. 2B, in faceplate 1017 for a more uniform delivery into the chamber plasma region 1015.

[0032] Exemplary configurations may include having the gas inlet assembly 1005 open into a gas supply region 1058 partitioned from the chamber plasma region 1015 by faceplate 1017 so that the gases/species flow through the holes in the faceplate 1017 into the chamber plasma region 1015. Structural and operational features may be selected to prevent significant backflow of plasma from the chamber plasma region 1015 back into the supply region 1058, gas inlet assembly 1005, and

fluid supply system 1010. The structural features may include the selection of dimensions and cross-sectional geometries of the apertures in faceplate 1017 to deactivate back-streaming plasma. The operational features may include maintaining a pressure difference between the gas supply region 1058 and chamber plasma region 1015 that maintains a unidirectional flow of plasma
5 through the showerhead 1025. The faceplate 1017, or a conductive top portion of the chamber, and showerhead 1025 are shown with an insulating ring 1020 located between the features, which allows an AC potential to be applied to the faceplate 1017 relative to showerhead 1025 and/or ion suppressor 1023. The insulating ring 1020 may be positioned between the faceplate 1017 and the showerhead 1025 and/or ion suppressor 1023 enabling a capacitively coupled plasma (CCP) to be
10 formed in the first plasma region. A baffle (not shown) may additionally be located in the chamber plasma region 1015, or otherwise coupled with gas inlet assembly 1005, to affect the flow of fluid into the region through gas inlet assembly 1005.

[0033] The ion suppressor 1023 may comprise a plate or other geometry that defines a plurality of apertures throughout the structure that are configured to suppress the migration of ionically-
15 charged species out of chamber plasma region 1015 while allowing uncharged neutral or radical species to pass through the ion suppressor 1023 into an activated gas delivery region between the suppressor and the showerhead. In disclosed embodiments, the ion suppressor 1023 may comprise a perforated plate with a variety of aperture configurations. These uncharged species may include highly reactive species that are transported with less reactive carrier gas through the apertures. As
20 noted above, the migration of ionic species through the holes may be reduced, and in some instances completely suppressed. Controlling the amount of ionic species passing through the ion suppressor 1023 may provide increased control over the gas mixture brought into contact with the underlying wafer substrate, which in turn may increase control of the deposition and/or etch characteristics of the gas mixture. For example, adjustments in the ion concentration of the gas
25 mixture can significantly alter its etch selectivity, e.g., W:WO_x etch ratios, W:SiCN etch ratios, etc. In alternative embodiments in which deposition is performed, it can also shift the balance of conformal-to-flowable style depositions for dielectric materials.

[0034] The plurality of holes in the ion suppressor 1023 may be configured to control the passage of the activated gas, i.e., the ionic, radical, and/or neutral species, through the ion suppressor 1023.
30 For example, the aspect ratio of the holes, or the hole diameter to length, and/or the geometry of the holes may be controlled so that the flow of ionically-charged species in the activated gas passing through the ion suppressor 1023 is reduced. The holes in the ion suppressor 1023 may include a tapered portion that faces chamber plasma region 1015, and a cylindrical portion that faces the showerhead 1025. The cylindrical portion may be shaped and dimensioned to control the flow of

ionic species passing to the showerhead 1025. An adjustable electrical bias may also be applied to the ion suppressor 1023 as an additional means to control the flow of ionic species through the suppressor.

[0035] The ion suppression element 1023 may function to reduce or eliminate the amount of

5 ionically charged species traveling from the plasma generation region to the substrate. Uncharged neutral and radical species may still pass through the openings in the ion suppressor to react with the substrate. It should be noted that the complete elimination of ionically charged species in the reaction region surrounding the substrate is not always the desired goal. In many instances, ionic species are required to reach the substrate in order to perform the etch and/or deposition process.

10 In these instances, the ion suppressor may help to control the concentration of ionic species in the reaction region at a level that assists the process.

[0036] Showerhead 1025 in combination with ion suppressor 1023 may allow a plasma present in chamber plasma region 1015 to avoid directly exciting gases in substrate processing region

1033, while still allowing excited species to travel from chamber plasma region 1015 into substrate

15 processing region 1033. In this way, the chamber may be configured to prevent the plasma from contacting a substrate 1055 being etched. This may advantageously protect a variety of intricate structures and films patterned on the substrate, which may be damaged, dislocated, or otherwise warped if directly contacted by a generated plasma. Additionally, when plasma is allowed to

20 increase. Accordingly, if the exposed second material is oxide, this material may be further protected by maintaining the plasma remotely from the substrate.

[0037] The processing system may further include a power supply 1040 electrically coupled with the processing chamber to provide electric power to the faceplate 1017, ion suppressor 1023,

showerhead 1025, and/or pedestal 1065 to generate a plasma in the chamber plasma region 1015 or

25 processing region 1033. The power supply may be configured to deliver an adjustable amount of power to the chamber depending on the process performed. Such a configuration may allow for a tunable plasma to be used in the processes being performed. Unlike a remote plasma unit, which is often presented with on or off functionality, a tunable plasma may be configured to deliver a specific amount of power to chamber plasma region 1015. This in turn may allow development of
30 particular plasma characteristics such that precursors may be dissociated in specific ways to enhance the etching profiles produced by these precursors.

[0038] A plasma may be ignited either in chamber plasma region 1015 above showerhead 1025 or substrate processing region 1033 below showerhead 1025. A plasma may be present in chamber

plasma region 1015 to produce the radical-fluorine precursors from an inflow of the fluorine-containing precursor. An AC voltage typically in the radio frequency (RF) range may be applied between the conductive top portion of the processing chamber, such as faceplate 1017, and showerhead 1025 and/or ion suppressor 1023 to ignite a plasma in chamber plasma region 1015 during deposition. An RF power supply may generate a high RF frequency of 13.56 MHz but may also generate other frequencies alone or in combination with the 13.56 MHz frequency.

[0039] Plasma power can be of a variety of frequencies or a combination of multiple frequencies. In the exemplary processing system the plasma may be provided by RF power delivered to faceplate 1017 relative to ion suppressor 1023 and/or showerhead 1025. The RF power may be between about 10 watts and about 2000 watts, between about 100 watts and about 2000 watts, between about 200 watts and about 1500 watts, or between about 200 watts and about 1000 watts in different embodiments. The RF frequency applied in the exemplary processing system may be low RF frequencies less than about 200 kHz, high RF frequencies between about 10 MHz and about 15 MHz, or microwave frequencies greater than or about 1 GHz in different embodiments. The plasma power may be capacitively-coupled (CCP) or inductively-coupled (ICP) into the remote plasma region.

[0040] Chamber plasma region 1015 (top plasma in figure) may be left at low or no power when a bottom plasma in the substrate processing region 1033 is turned on to, for example, cure a film or clean the interior surfaces bordering substrate processing region 1033. A plasma in substrate processing region 1033 may be ignited by applying an AC voltage between showerhead 1055 and the pedestal 1065 or bottom of the chamber. A cleaning gas may be introduced into substrate processing region 1033 while the plasma is present.

[0041] A fluid, such as a precursor, for example a fluorine-containing precursor, may be flowed into the processing region 1033 by embodiments of the showerhead described herein. Excited species derived from the process gas in chamber plasma region 1015 may travel through apertures in the ion suppressor 1023, and/or showerhead 1025 and react with an additional precursor flowing into the processing region 1033 from a separate portion of the showerhead. Alternatively, if all precursor species are being excited in chamber plasma region 1015, no additional precursors may be flowed through the separate portion of the showerhead. Little or no plasma may be present in the processing region 1033. Excited derivatives of the precursors may combine in the region above the substrate and, on occasion, on the substrate to etch structures or remove species on the substrate in disclosed applications.

[0042] Exciting the fluids in the chamber plasma region 1015 directly, or exciting the fluids in the RPS units 1002, may provide several benefits. The concentration of the excited species derived from the fluids may be increased within the processing region 1033 due to the plasma in the chamber plasma region 1015. This increase may result from the location of the plasma in the chamber plasma region 1015. The processing region 1033 may be located closer to the chamber plasma region 1015 than the remote plasma system (RPS) 1002, leaving less time for the excited species to leave excited states through collisions with other gas molecules, walls of the chamber, and surfaces of the showerhead.

[0043] The uniformity of the concentration of the excited species derived from the process gas may also be increased within the processing region 1033. This may result from the shape of the chamber plasma region 1015, which may be more similar to the shape of the processing region 1033. Excited species created in the RPS 1002 may travel greater distances in order to pass through apertures near the edges of the showerhead 1025 relative to species that pass through apertures near the center of the showerhead 1025. The greater distance may result in a reduced excitation of the excited species and, for example, may result in a slower growth rate near the edge of a substrate. Exciting the fluids in the chamber plasma region 1015 may mitigate this variation for the fluid flowed through RPS 1002, or alternatively bypassed around the RPS unit.

[0044] The processing gases may be excited in chamber plasma region 1015 and may be passed through the showerhead 1025 to the processing region 1033 in the excited state. While a plasma may be generated in the processing region 1033, a plasma may alternatively not be generated in the processing region. In one example, the only excitation of the processing gas or precursors may be from exciting the processing gases in chamber plasma region 1015 to react with one another in the processing region 1033. As previously discussed, this may be to protect the structures patterned on the substrate 1055.

[0045] In addition to the fluid precursors, there may be other gases introduced at varied times for varied purposes, including carrier gases to aid delivery. A treatment gas may be introduced to remove unwanted species from the chamber walls, the substrate, the deposited film and/or the film during deposition. A treatment gas may be excited in a plasma and then used to reduce or remove residual content inside the chamber. In other disclosed embodiments the treatment gas may be used without a plasma. When the treatment gas includes water vapor, the delivery may be achieved using a mass flow meter (MFM), an injection valve, or by commercially available water vapor generators. The treatment gas may be introduced to the processing region 1033, either

through the RPS unit or bypassing the RPS unit, and may further be excited in the first plasma region.

[0046] FIG. 2B shows a detailed view of the features affecting the processing gas distribution through faceplate 1017. As shown in FIG. 2A and FIG. 2B, faceplate 1017, cooling plate 1003, and gas inlet assembly 1005 intersect to define a gas supply region 1058 into which process gases may be delivered from gas inlet 1005. The gases may fill the gas supply region 1058 and flow to chamber plasma region 1015 through apertures 1059 in faceplate 1017. The apertures 1059 may be configured to direct flow in a substantially unidirectional manner such that process gases may flow into processing region 1033, but may be partially or fully prevented from backflow into the gas supply region 1058 after traversing the faceplate 1017.

[0047] The gas distribution assemblies such as showerhead 1025 for use in the processing chamber section 1001 may be referred to as dual channel showerheads (DCSH) and are additionally detailed in the embodiments described in FIG. 2A as well as FIG. 2C herein. The dual channel showerhead may provide for etching processes that allow for separation of etchants outside of the processing region 1033 to provide limited interaction with chamber components and each other prior to being delivered into the processing region.

[0048] The showerhead 1025 may comprise an upper plate 1014 and a lower plate 1016. The plates may be coupled with one another to define a volume 1018 between the plates. The coupling of the plates may be so as to provide first fluid channels 1019 through the upper and lower plates, and second fluid channels 1021 through the lower plate 1016. The formed channels may be configured to provide fluid access from the volume 1018 through the lower plate 1016 via second fluid channels 1021 alone, and the first fluid channels 1019 may be fluidly isolated from the volume 1018 between the plates and the second fluid channels 1021. The volume 1018 may be fluidly accessible through a side of the gas distribution assembly 1025. Although the exemplary system of FIG. 2 includes a dual-channel showerhead, it is understood that alternative distribution assemblies may be utilized that maintain first and second precursors fluidly isolated prior to the processing region 1033. For example, a perforated plate and tubes underneath the plate may be utilized, although other configurations may operate with reduced efficiency or not provide as uniform processing as the dual-channel showerhead as described.

[0049] In the embodiment shown, showerhead 1025 may distribute via first fluid channels 1019 process gases which contain plasma effluents upon excitation by a plasma in chamber plasma region 1015. In embodiments, the process gas introduced into the RPS 1002 and/or chamber plasma region 1015 may contain fluorine, e.g., CF_4 , NF_3 or XeF_2 . The process gas may also

include a carrier gas such as helium, argon, nitrogen (N₂), etc. Plasma effluents may include ionized or neutral derivatives of the process gas and may also be referred to herein as a radical-fluorine precursor referring to the atomic constituent of the process gas introduced.

[0050] FIG. 2C is a bottom view of a showerhead 1025 for use with a processing chamber

5 according to disclosed embodiments. Showerhead 1025 corresponds with the showerhead shown in FIG. 2A. Through-holes 1031, which show a view of first fluid channels 1019, may have a plurality of shapes and configurations in order to control and affect the flow of precursors through the showerhead 1025. Small holes 1027, which show a view of second fluid channels 1021, may be distributed substantially evenly over the surface of the showerhead, even amongst the through-
10 holes 1031, which may help to provide more even mixing of the precursors as they exit the showerhead than other configurations.

[0051] An additional dual channel showerhead, as well as this processing system and chamber, are more fully described in patent application Ser. No. 13/251,714 filed on Oct. 3, 2011, which is hereby incorporated by reference for all purposes to the extent not inconsistent with the claimed
15 features and description herein.

[0052] The chamber plasma region 1015 or a region in an RPS may be referred to as a remote plasma region. In embodiments, the radical precursor, e.g., a radical-fluorine precursor, is created in the remote plasma region and travels into the substrate processing region where it may or may not combine with additional precursors. In embodiments, the additional precursors are excited
20 only by the radical-fluorine precursor. Plasma power may essentially be applied only to the remote plasma region in embodiments to ensure that the radical-fluorine precursor provides the dominant excitation. Nitrogen trifluoride or another fluorine-containing precursor may be flowed into chamber plasma region 1015 at rates between about 25 sccm and about 500 sccm, between about 50 sccm and about 150 sccm, or between about 75 sccm and about 125 sccm in disclosed
25 embodiments. Methyl fluoride or another partially fluorinated hydro-carbon may be flowed with a flowrate that results in an atomic H:F flow rate ratio of greater than, for example, 1:1.

[0053] Combined flow rates of precursors into the chamber may account for 0.05% to about 20% by volume of the overall gas mixture; the remainder being carrier gases. The fluorine-containing precursor may be flowed into the remote plasma region, but the plasma effluents may have the
30 same volumetric flow ratio in embodiments. In the case of the fluorine-containing precursor, a purge or carrier gas may be first initiated into the remote plasma region before the fluorine-containing gas to stabilize the pressure within the remote plasma region.

[0054] Substrate processing region 1033 can be maintained at a variety of pressures during the flow of precursors, any carrier gases, and plasma effluents into substrate processing region 1033. The pressure may be maintained between about 0.1 mTorr and about 100 Torr, between about 1 Torr and about 20 Torr or between about 1 Torr and about 5 Torr in different embodiments.

5 [0055] Embodiments of the deposition systems may be incorporated into larger fabrication systems for producing integrated circuit chips. FIG. 3 shows one such processing system 1101 of deposition, etching, baking, and curing chambers according to disclosed embodiments. In the figure, a pair of front opening unified pods (load lock chambers 1102) supply substrates of a variety of sizes that are received by robotic arms 1104 and placed into a low pressure holding area
10 1106 before being placed into one of the substrate processing chambers 1108a-f. A second robotic arm 1110 may be used to transport the substrate wafers from the holding area 1106 to the substrate processing chambers 1108a-f and back. Each substrate processing chamber 1108a-f, can be outfitted to perform a number of substrate processing operations including the dry etch processes described herein in addition to cyclical layer deposition (CLD), atomic layer deposition (ALD),
15 chemical vapor deposition (CVD), physical vapor deposition (PVD), etch, pre-clean, degas, orientation, and other substrate processes.

[0056] The substrate processing chambers 1108a-f may include one or more system components for depositing, annealing, curing and/or etching a dielectric film on the substrate wafer. In one configuration, two pairs of the processing chamber, e.g., 1108c-d and 1108e-f, may be used to
20 deposit dielectric material on the substrate, and the third pair of processing chambers, e.g., 1108a-b, may be used to etch the deposited dielectric. In another configuration, all three pairs of chambers, e.g., 1108a-f, may be configured to etch a dielectric film on the substrate. Any one or more of the processes described may be carried out in chamber(s) separated from the fabrication system shown in different embodiments.

25 [0057] In the preceding description, for the purposes of explanation, numerous details have been set forth in order to provide an understanding of various embodiments of the present invention. It will be apparent to one skilled in the art, however, that certain embodiments may be practiced without some of these details, or with additional details.

[0058] As used herein "substrate" may be a support substrate with or without layers formed
30 thereon. The patterned substrate may be an insulator or a semiconductor of a variety of doping concentrations and profiles and may, for example, be a semiconductor substrate of the type used in the manufacture of integrated circuits. Exposed "silicon" of the patterned substrate is predominantly Si but may include minority concentrations of other elemental constituents such as

nitrogen, oxygen, hydrogen, carbon and the like. Exposed "tungsten" of the patterned substrate is predominantly W but may include minority concentrations of other elemental constituents such as nitrogen, oxygen, hydrogen, carbon and the like. Of course, "exposed tungsten" may consist of only tungsten. Exposed "silicon nitride" of the patterned substrate is predominantly Si_3N_4 but may include minority concentrations of other elemental constituents such as oxygen, hydrogen, carbon and the like. "Exposed silicon nitride" may consist only of silicon and nitrogen. Exposed "silicon oxide" of the patterned substrate is predominantly SiO_2 but may include minority concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. In some embodiments, silicon oxide films etched using the methods disclosed herein consist of silicon and oxygen. "Tungsten oxide" is predominantly tungsten and oxygen but may include minority concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. Tungsten oxide may consist of tungsten and oxygen. "Titanium nitride" is predominantly titanium and nitrogen but may include minority concentrations of other elemental constituents such as nitrogen, hydrogen, carbon and the like. Titanium nitride may consist of titanium and nitrogen.

[0059] The term "precursor" is used to refer to any process gas which takes part in a reaction to either remove material from or deposit material onto a surface. "Plasma effluents" describe gas exiting from the chamber plasma region and entering the substrate processing region. Plasma effluents are in an "excited state" wherein at least some of the gas molecules are in vibrationally-excited, dissociated and/or ionized states. A "radical precursor" is used to describe plasma effluents (a gas in an excited state which is exiting a plasma) which participate in a reaction to either remove material from or deposit material on a surface. "Radical-fluorine" (or "radical-hydrogen") are radical precursors which contain fluorine (or hydrogen) but may contain other elemental constituents. The phrase "inert gas" refers to any gas which does not form chemical bonds when etching or being incorporated into a film. Exemplary inert gases include noble gases but may include other gases so long as no chemical bonds are formed when (typically) trace amounts are trapped in a film.

[0060] The terms "gap" and "trench" are used throughout with no implication that the etched geometry has a large horizontal aspect ratio. Viewed from above the surface, trenches may appear circular, oval, polygonal, rectangular, or a variety of other shapes. A trench may be in the shape of a moat around an island of material. The term "via" is used to refer to a low aspect ratio trench (as viewed from above) which may or may not be filled with metal to form a vertical electrical connection. As used herein, a conformal etch process refers to a generally uniform removal of material on a surface in the same shape as the surface, i.e., the surface of the etched layer and the pre-etch surface are generally parallel. A person having ordinary skill in the art will recognize that

the etched interface likely cannot be 100% conformal and thus the term "generally" allows for acceptable tolerances.

[0061] Having disclosed several embodiments, it will be recognized by those of skill in the art that various modifications, alternative constructions, and equivalents may be used without departing from the spirit of the disclosed embodiments. Additionally, a number of well known processes and elements have not been described in order to avoid unnecessarily obscuring the present invention. Accordingly, the above description should not be taken as limiting the scope of the invention.

[0062] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limits of that range is also specifically disclosed. Each smaller range between any stated value or intervening value in a stated range and any other stated or intervening value in that stated range is encompassed. The upper and lower limits of these smaller ranges may independently be included or excluded in the range, and each range where either, neither or both limits are included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included.

[0063] As used herein and in the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a process" includes a plurality of such processes and reference to "the dielectric material" includes reference to one or more dielectric materials and equivalents thereof known to those skilled in the art, and so forth.

[0064] Also, the words "comprise," "comprising," "include," "including," and "includes" when used in this specification and in the following claims are intended to specify the presence of stated features, integers, components, or steps, but they do not preclude the presence or addition of one or more other features, integers, components, steps, acts, or groups.

WHAT IS CLAIMED IS:

1. A method of etching a patterned substrate in a substrate processing region of a substrate processing chamber, wherein the patterned substrate has a exposed tungsten region and an exposed second material region, the method comprising:

flowing a fluorine-containing precursor into a remote plasma region fluidly coupled to the substrate processing region while forming a plasma in the plasma region to produce plasma effluents; and

etching the exposed tungsten from the substrate by flowing the plasma effluents into the substrate processing region through through-holes in a showerhead.

2. The method of claim 1 wherein the exposed tungsten region has a thickness of at least 5 nm.

3. The method of claim 1 wherein the exposed tungsten region consists of tungsten.

4. The method of claim 1 wherein etching the exposed tungsten region comprises etching the exposed tungsten region comprises etching tungsten with a tungsten etch rate greater than ten times the etch rate of the exposed second material region.

5. The method of claim 1 wherein the operation of etching the tungsten comprises etching tungsten faster than silicon by a ratio of about 100:1 or more, faster than silicon oxide by a ratio of about 15:1 or more, faster than silicon carbon nitride by a ratio of about 3:1 or more or faster than tungsten oxide by a ratio of about 10:1 or more.

6. The method of claim 1 wherein the fluorine-containing precursor comprises nitrogen trifluoride.

7. The method of claim 1 wherein the fluorine-containing precursor comprises a partially fluorinated hydrocarbon.

8. The method of claim 1 wherein the fluorine-containing precursor comprises methyl fluoride.

9. The method of claim 1 further comprising a pretreatment step which occurs prior to etching the exposed tungsten region, wherein the pretreatment step comprises flowing hydrogen (H₂) into the remote plasma region and flowing the produced plasma effluents into the

substrate processing region to remove a thin tungsten oxide layer overlying a near-surface tungsten region to create the exposed tungsten region.

10. The method of claim 1 wherein the fluorine-containing precursor comprises carbon tetrafluoride.

11. The method of claim 1 wherein flowing a fluorine-containing precursor and hydrogen (H₂) results in an atomic flow ratio (H:F) of greater than 1:1 entering the substrate processing region.

12. The method of claim 1 wherein flowing a fluorine-containing precursor and hydrogen (H₂) results in an atomic flow ratio (H:F) of less than 15:1 entering the substrate processing region.

13. The method of claim 1 wherein a pressure within the substrate processing region is between about 0.01 Torr and about 50 Torr during the etching operation.

14. The method of claim 1 wherein forming a plasma in the plasma region to produce plasma effluents comprises applying RF power between about 10 watts and about 400 watts to the plasma region.

15. The method of claim 1 wherein a temperature of the substrate is greater than or about -30°C and less than or about 400°C during the etching operation.

1/5

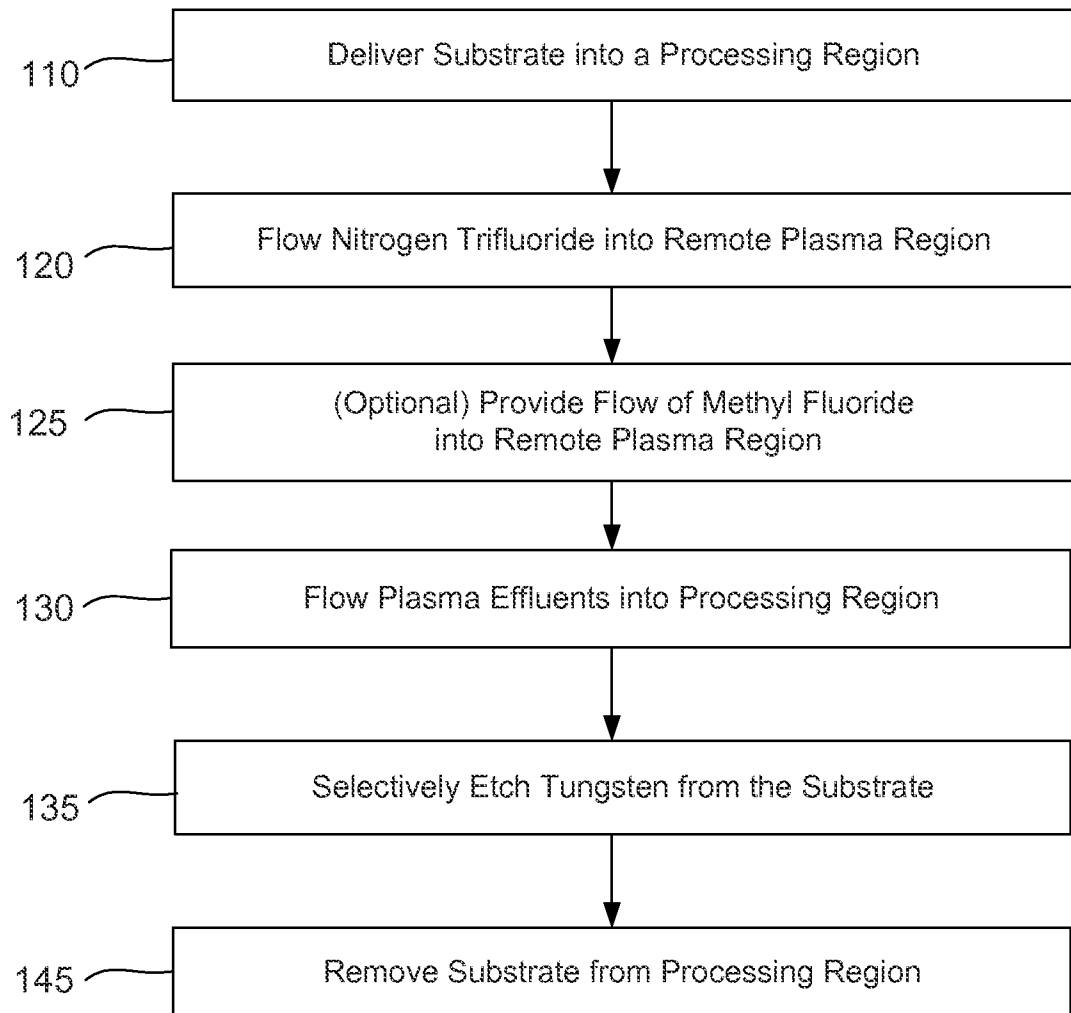
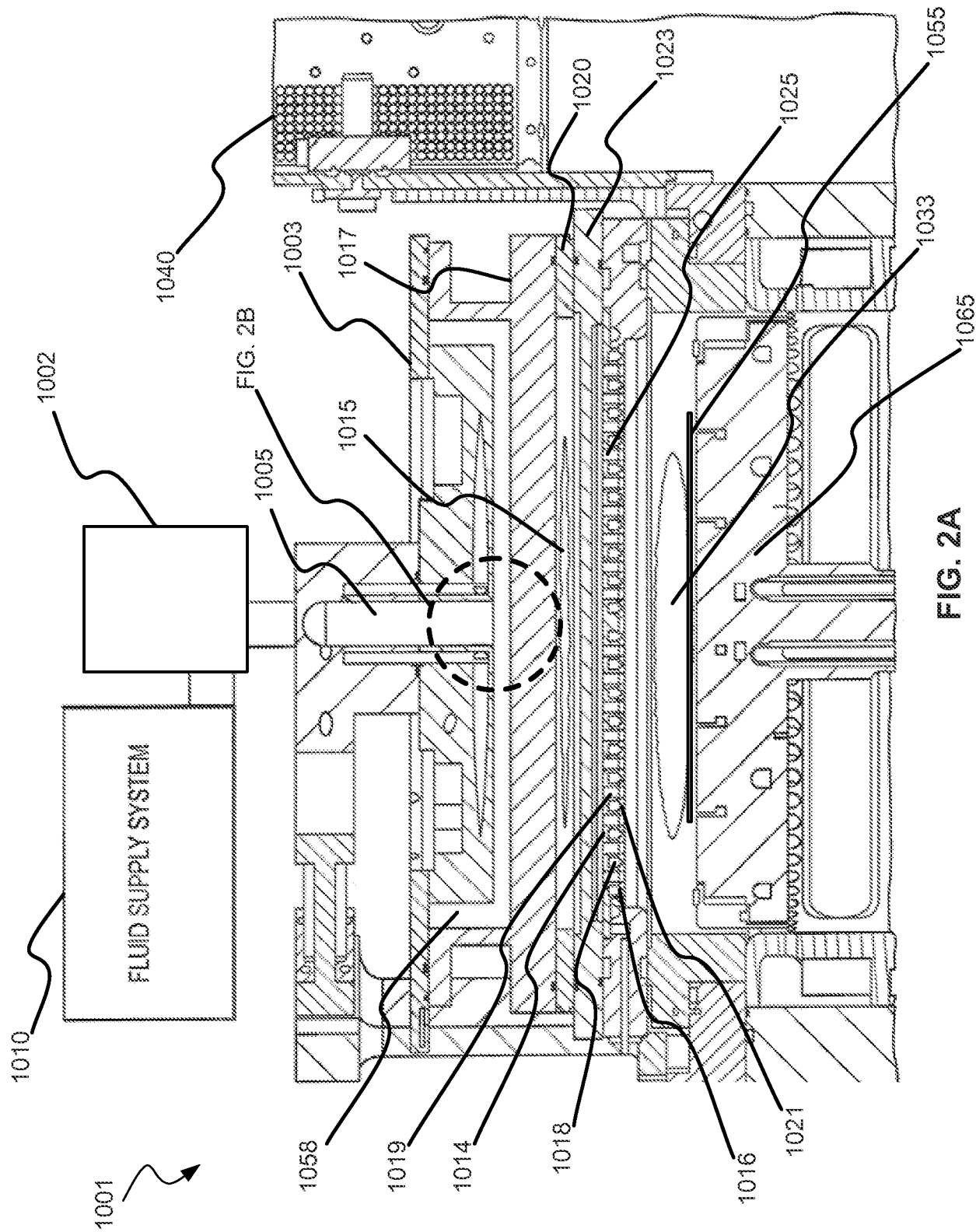


FIG. 1



3/5

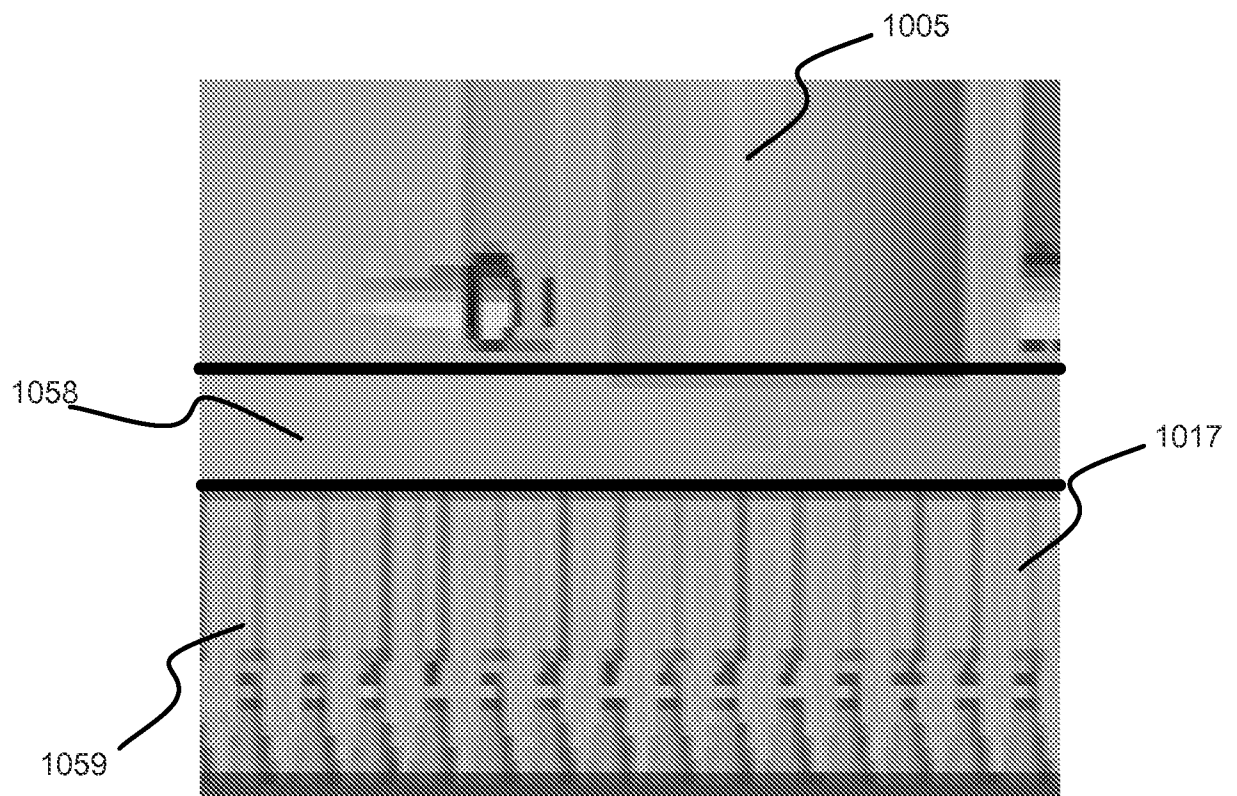


FIG. 2B

4/5

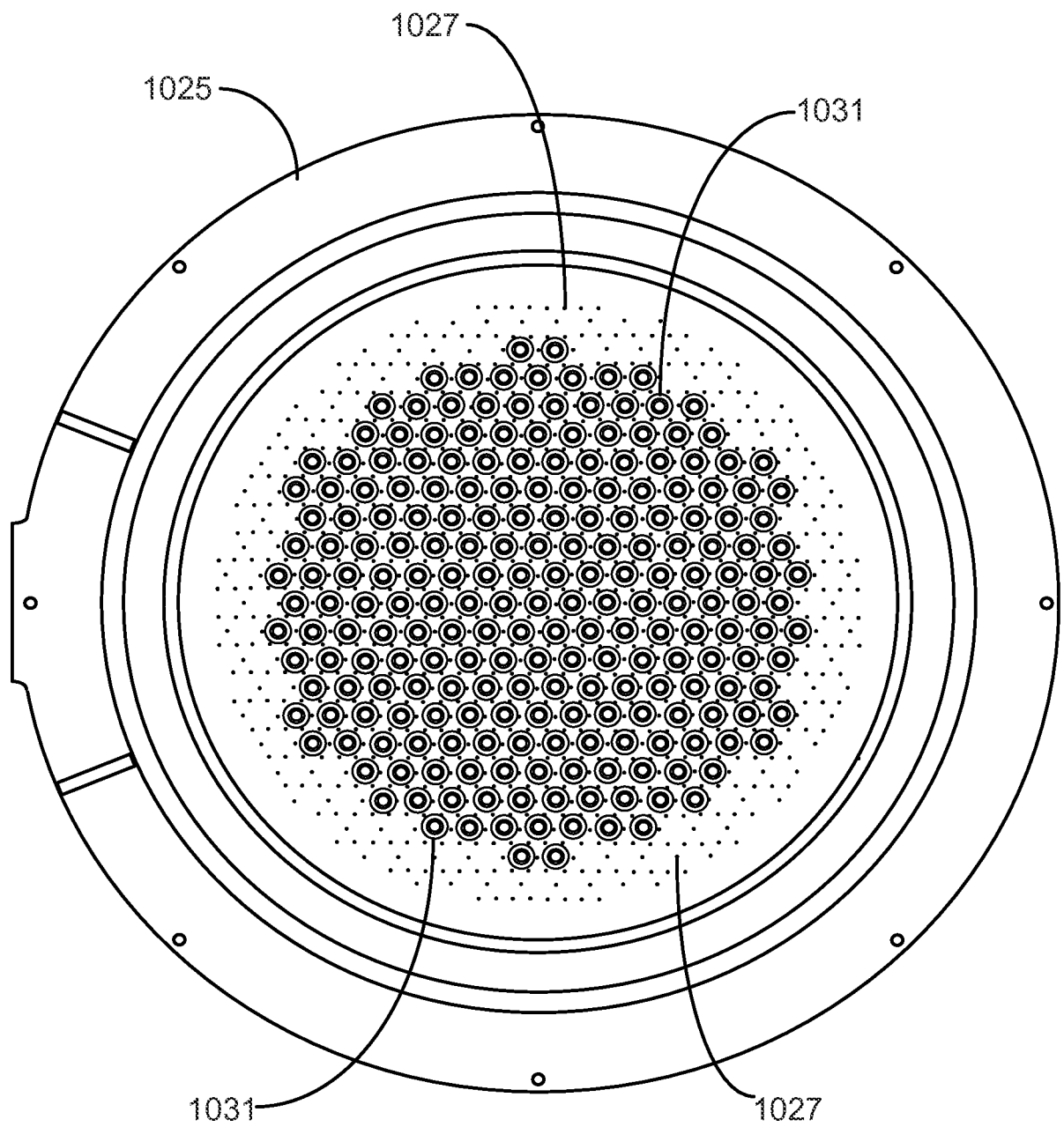


FIG. 2C

5/5

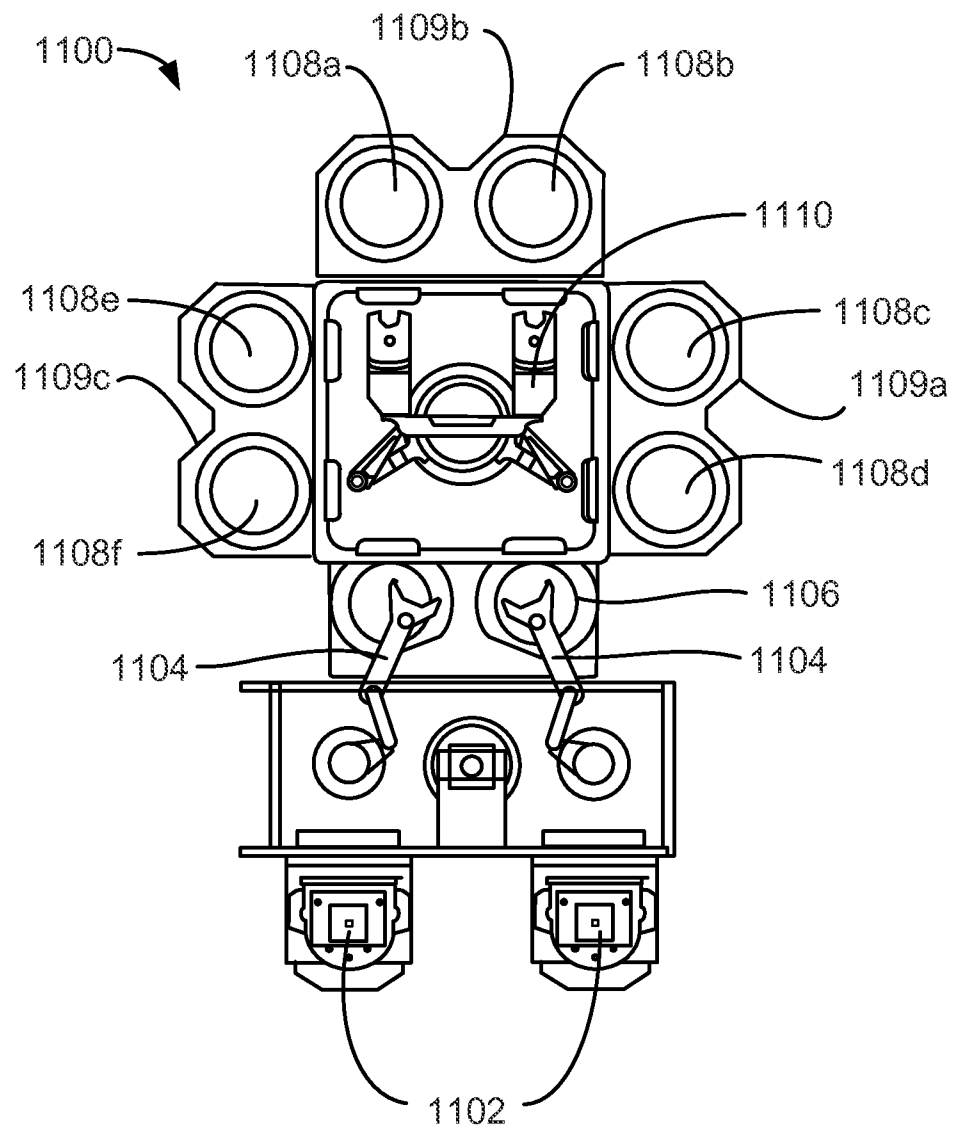


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/076217**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/3065(2006.01)i**

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

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
H01L 21/3065; H05H 1/24; C23F 1/00; C23F 1/02; B44C 1/22; C23C 16/00Documentation 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 modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: remote, plasma, tungsten, etch, fluorine, ion, suppressor**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0238103 A1 (ZHANG JINGCHUN et al.) 20 September 2012 See abstract; paragraphs [0025]-[0075]; and figures 4-5	1-8, 10-15
Y		9
Y	US 2009-0017227 A1 (XINYU FU et al.) 15 January 2009 See abstract; paragraph [0033]; and claims 1, 10.	9
A	US 2012-0211462 A1 (JINGCHUN ZHANG et al.) 23 August 2012 See abstract; paragraphs [0030]-[0035], [0045]-[0054]; claim 1; and figures 1, 4A-5.	1-15
A	US 2006-0000805 A1 (VALENTIN N. TODOROW et al.) 05 January 2006 See abstract; paragraphs [0022], [0030]-[0039]; claims 21-27; and figures 1-3.	1-15

☐ 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

"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

25 April 2014 (25.04.2014)

Date of mailing of the international search report

28 April 2014 (28.04.2014)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

KIM, Young Jin

Telephone No. +042 481 5771



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/076217

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0238103 A1	20/09/2012	CN 103430288 A KR 10-2014-0016938 A TW 201243941 A WO 2012-125654 A2 WO 2012-125654 A3	04/12/2013 10/02/2014 01/11/2012 20/09/2012 27/12/2012
US 2009-0017227 A1	15/01/2009	US 2011-300720 A1 US 8021514 B2 US 8580354 B2	08/12/2011 20/09/2011 12/11/2013
US 2012-0211462 A1	23/08/2012	CN 103380485 A TW 201248720 A WO 2012-115750 A2 WO 2012-115750 A3	30/10/2013 01/12/2012 30/08/2012 15/11/2012
US 2006-0000805 A1	05/01/2006	CN 102280341 A CN 1716530 A CN 1716530 B CN 1716530 C0 KR 10-0859313 B1 KR 10-2006-0048674 A TW 290963 B US 2013-118687 A1 US 8349128 B2	14/12/2011 04/01/2006 17/08/2011 04/01/2006 19/09/2008 18/05/2006 11/12/2007 16/05/2013 08/01/2013