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(54) Title: MONOLAYER FILM MEDIATED PRECISION MATERIAL ETCH

Flow Chart

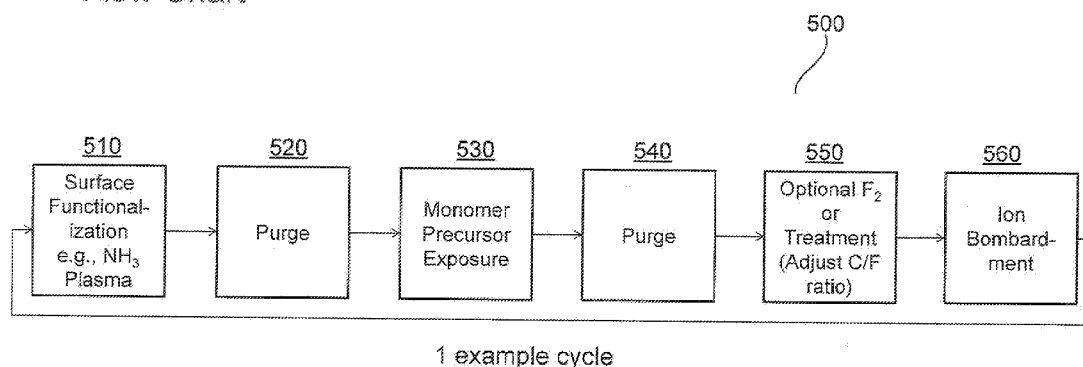


FIG. 5

(57) Abstract: A method of etching is described. The method includes treating at least a portion of a surface exposed on a substrate with an adsorption-promoting agent to alter a functionality of the exposed surface and cause subsequent adsorption of a carbon-containing precursor, and thereafter, adsorbing the organic precursor to the functionalized surface to form a carbon-containing film. Then, at least a portion of the surface of the carbon-containing film is exposed to an ion flux to remove the adsorbed carbon-containing film and at least a portion of the material of the underlying substrate.



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MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
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MONOLAYER FILM MEDIATED PRECISION MATERIAL ETCH

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CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is related to and claims priority to United States Provisional Patent Application serial no. 62/366,529 filed on July 25, 2016, the entire contents of which are herein incorporated by reference.

FIELD OF INVENTION

[0002] The invention relates to a method for etching, and more particularly, a precision etch technique for etching a thin film for electronic device applications.

BACKGROUND OF THE INVENTION

[0003] The present invention relates to a method of manufacturing a semiconductor device such as an integrated circuit and transistors and transistor components for an integrated circuit. In the manufacture of a semiconductor device (especially on the microscopic scale), various fabrication processes are executed such as film-forming depositions, etch mask creation, patterning, material etching and removal, and doping treatments, are performed repeatedly to form desired semiconductor device elements on a substrate. Historically, with microfabrication, transistors have been created in one plane, with wiring/metallization formed above, and have thus been characterized as two-dimensional (2D) circuits or 2D fabrication. Scaling efforts have greatly increased the number of transistors per unit area in 2D circuits, yet scaling efforts are running into greater challenges as scaling enters single digit nanometer semiconductor device fabrication nodes. Semiconductor device fabricators have expressed a desire for three-dimensional (3D) semiconductor devices in which transistors are stacked on top of each other. As

lateral dimensions densify and structures develop vertically, the need for precision material deposition and etch becomes more compelling.

SUMMARY

[0004] Techniques herein pertain to device fabrication using precision etch techniques.

[0005] A method of etching is described. The method includes treating at least a portion of a surface exposed on a substrate with an adsorption-promoting agent to alter a functionality of the exposed surface and cause subsequent adsorption of a carbon-containing precursor, and thereafter, adsorbing the organic precursor to the functionalized surface to form a carbon-containing film. Then, at least a portion of the surface of the carbon-containing film is exposed to an ion flux to remove the adsorbed carbon-containing film and at least a portion of the material of the underlying substrate.

[0006] Of course, the order of discussion of the different steps as described herein has been presented for clarity sake. In general, these steps can be performed in any suitable order. Additionally, although each of the different features, techniques, configurations, etc. herein may be discussed in different places of this disclosure, it is intended that each of the concepts can be executed independently of each other or in combination with each other. Accordingly, the present invention can be embodied and viewed in many different ways.

[0007] Note that this summary section does not specify every embodiment and/or incrementally novel aspect of the present disclosure or claimed invention. Instead, this summary only provides a preliminary discussion of different embodiments and corresponding points of novelty over conventional techniques. For additional details and/or possible perspectives of the invention and embodiments, the reader is directed to the Detailed Description section and corresponding figures of the present disclosure as further discussed below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] In the accompanying drawings:

- [0009] FIG. 1 illustrates a method of conformal adsorption of a thin film on a substrate according to an embodiment;
- [0010] FIG. 2 illustrates a method of non-conformal adsorption of a thin film on a substrate according to an embodiment;
- [0011] FIG. 3 illustrates a method of etching a substrate according to an embodiment;
- [0012] FIG. 4 illustrates a method of etching a substrate according to an embodiment; and
- [0013] FIG. 5 provides a flow chart illustrating a method of etching a substrate according to an embodiment.

DETAILED DESCRIPTION

- [0014] Techniques herein pertain to device fabrication using precision etch techniques. Several instances manifest in semiconductor manufacturing in both front end of line (FEOL, e.g., transistor fabrication) through to the back end of line (BEOL, e.g., interconnect fabrication), where oxide and nitride films (typically silicon-containing, in nature) need to be etched with a high degree of precision. Fluorocarbon based plasmas are used ostensibly because carbon removes the oxygen and fluorine volatilizes silicon. In fact the etch is mediated by a F-C-(O or N)-Si mixing layer as the fluorocarbon forms a film which is checked in its growth by, among other influences, ion bombardment.
- [0015] Absent ion sputtering of the film, it grows potentially in a continuous manner as a thin film. Simply put, it is also the thickness of the film that plays a role in requiring large ion energies from the plasma to etch dielectrics. The ions must penetrate the film to supply energy to the film-virgin substrate interface, where the etching reaction ($\text{SiX} + \text{C} + \text{F} \rightarrow (\text{creates}) \text{volatile products}$, 'X' is an element other than Si) originates. Managing this mixing layer is a major challenge in many fabrication modules, as clogging can result at different feature openings and the film thickness, which may play a role in the selectivity between different films being etched (e.g., nitride and oxide), may be difficult to manage over different feature shapes, distributions or within the feature geometry itself. Self-aligned, high aspect ratio structures and patterning applications all suffer from the integration challenge of

finding the optimal mix of polymerizing, etch precursor ion and energy flux to overcome the myriad of trade-offs that come from uncontrolled polymer growth.

[0016] Atomic layer etching should offer a solution; however, fluorocarbon plasmas deposit fluorocarbon films that are not self-limited. The thickness of the films that would be removed in a subsequent ion bombardment step can only be attempted to be controlled by exposure time and possibly ion energy. Control within a complex structure, through its increasing depth, is difficult as fluorocarbon fluxes change due to shadowing (analogous to ARDE or aspect ratio dependent etch in a continuous process), and are further complicated by iso-dense structural differences. Atomic layer etching of oxide and nitride materials, using fluorocarbon based plasmas, is often referred to as quasi-ALE because it is in fact not ALE as the fluorocarbon film is not self-limited.

[0017] In one embodiment, a carbon-containing film, preferably a monolayer film, is placed on at least a portion of a substrate, including exposed regions of silicon oxide and/or silicon nitride, during an adsorption step. Thereafter, the adsorbed film, including some of the underlying material (e.g., oxide or nitride) is removed by an ion bombardment mediated desorption step (see FIGs. 3 and 5). Organic films or carbon-containing films of prescribed thickness can be deposited using atomic layer deposition. And by doing so, the problem of carbon-containing films of uncontrolled thickness as etch mediating layers in continuous and layer-by-layer etching can be solved.

[0018] In a conformal deposition flow 100 for a substrate having a mask 110 and a material layer 120 (dielectric, e.g.), the atomic layer deposition of a carbon-containing film comprises pre-treating the exposed surface with an adsorption promoting agent 102 to alter the surface functionality of the exposed surface (i.e., “functionalize” the surface) so that a carbon-containing or polymer precursor 104 can chemisorb to the functionalized surface (see FIGs. 1 and 2). Without limitation, approximately one layer of a stoichiometric film is the result. The film may be fluorine-containing or treated with fluorine, e.g., F_2 , a fluorine gas, or non-polymerizing plasma to create a fluorocarbon based layer.

[0019] Following a purge step that evacuates the precursor gases from the chamber, the substrate is exposed to an ion flux, such as the ion flux from an inert plasma (e.g., an argon (Ar) plasma), and ion bombardment at an energy above the etching threshold and below the sputtering threshold is performed. One of such

described cycle constitutes a layer-by-layer removal of dielectric material. A layer may be one or more equivalent molecular layer thicknesses, as required by an application; see FIG. 5 for an exemplary flow chart.

[0020] Furthermore, the ALD deposited film can serve as passivation of the sidewall of a structure being etched (see FIG. 1 and FIG. 4). Excess film may be removed with a flash processing step (i.e., short process time, less than 10 seconds, e.g. an oxygen step, each cycle were it desirable.

[0021] In some embodiments, charged particle bombardment may be used to prepare a surface for film growth (see FIG. 2). When it is desirable to grow a film only on horizontal surfaces, electrons or ions can be used to create dangling bonds to stimulate growth on those surfaces (see FIG. 2). Less flux to the sidewalls or vertical structures allows delayed growth on the sidewalls taking advantage of incubation times or the natural delay of nucleation on un-wettable surfaces.

[0022] Differences in nucleation time between different materials allow one to choose adsorption times to create selectivity between different materials. For example, a full monolayer may be grown on a nitride and less than a monolayer may be grown on an oxide for short adsorption times. Longer adsorption times can be chosen for full coverage of both materials should that be desirable. Selectivity is then achieved through ion energy selection.

[0023] A preferred method for promoting adsorption of the carbon-containing material 204 includes exposing the surface to an ammonia plasma so that the surface is occupied by reactive $-NH_2$ bonds, an adsorption-promoting agent 202. Rendering the surface functionalizable by $-NH_2$ may require pretreatment by a halogen material. However, ion bombardment from an inert gas plasma alone is often sufficient to create the dangling bonds to receive NH_2 radicals. The NH_2 groups on the surface are then reactive with organic material or polymer precursors. This exposure step can be plasma free.

[0024] In other embodiments, the carbon-containing film can be exposed to fluorine to alter the fluorine to carbon ratio in the film. The fluorine exposure may include gas-phase chemistries with or without plasma formation.

[0025] Material removal is then performed during ion bombardment with low and controlled energy ions. The formation of ion flux may be achieved in a 13.56 MHz capacitively coupled plasma (e.g., power ranging from 5-25 W) at a chamber pressure of 100-500 mTorr, or a spatially segregated plasma at high pressure, such

as a surface wave driven microwave source (e.g., power ranging from 1000-2000W) with equivalently low bias power.

[0026] The treating, adsorbing, and exposing steps may be repeated to remove a pre-determined amount of material from the substrate. These steps, and others, may be performed in the same process chamber, or separate chambers. Each process step can include gas-phase chemistry, and be performed at vacuum pressures.

[0027] FIG. 5 illustrates exemplary steps in a process flow 500. The exemplary steps can include (1) a surface functionalization (e.g., ammonia plasma) (510), (2) a purge (520), (3) a monomer precursor exposure (330), (4) a purge (540), (5) an optional fluorine (e.g., F_2 or treatment using C/F with C-to-F ratio adjustment) (550), and (6) an ion bombardment (560).

[0028] In the claims below, any of the dependents limitations can depend from any of the independent claims.

[0029] In the preceding description, specific details have been set forth, such as a particular geometry of a processing system and descriptions of various components and processes used therein. It should be understood, however, that techniques herein may be practiced in other embodiments that depart from these specific details, and that such details are for purposes of explanation and not limitation. Embodiments disclosed herein have been described with reference to the accompanying drawings. Similarly, for purposes of explanation, specific numbers, materials, and configurations have been set forth in order to provide a thorough understanding. Nevertheless, embodiments may be practiced without such specific details. Components having substantially the same functional constructions are denoted by like reference characters, and thus any redundant descriptions may be omitted.

[0030] Various techniques have been described as multiple discrete operations to assist in understanding the various embodiments. The order of description should not be construed as to imply that these operations are necessarily order dependent. Indeed, these operations need not be performed in the order of presentation. Operations described may be performed in a different order than the described embodiment. Various additional operations may be performed and/or described operations may be omitted in additional embodiments.

[0031] “Substrate” or “target substrate” as used herein generically refers to an object being processed in accordance with the invention. The substrate may include any material portion or structure of a device, particularly a semiconductor or other electronics device, and may, for example, be a base substrate structure, such as a semiconductor wafer, reticle, or a layer on or overlying a base substrate structure such as a thin film. Thus, substrate is not limited to any particular base structure, underlying layer or overlying layer, patterned or un-patterned, but rather, is contemplated to include any such layer or base structure, and any combination of layers and/or base structures. The description may reference particular types of substrates, but this is for illustrative purposes only.

[0032] Those skilled in the art will also understand that there can be many variations made to the operations of the techniques explained above while still achieving the same objectives of the invention. Such variations are intended to be covered by the scope of this disclosure. As such, the foregoing descriptions of embodiments of the invention are not intended to be limiting. Rather, any limitations to embodiments of the invention are presented in the following claims.

CLAIMS

1. A method of etching, comprising:
treating at least a portion of a surface exposed on a substrate with an adsorption-promoting agent to alter a functionality of the exposed surface and cause subsequent adsorption of a carbon-containing precursor;
thereafter, adsorbing the carbon-containing precursor to the functionalized surface to form a carbon-containing film; and
exposing at least a portion of the surface of the carbon-containing film to an ion flux to remove the adsorbed carbon-containing film and at least a portion of the material of the underlying substrate.
2. The method of claim 1, wherein the substrate comprises silicon, germanium, or a silicon-germanium alloy.
3. The method of claim 1, wherein the adsorption-promoting agent is NH_2 formed using an ammonia-based plasma.
4. The method of claim 1, further comprising:
pre-treating the surface of the substrate with a pre-treatment charged particle flux prior to treating the surface with the adsorption-promoting agent.
5. The method of claim 4, wherein the pre-treatment charged particle flux includes an ion flux from an inert gas plasma.
6. The method of claim 1, wherein the carbon-containing precursor includes a $-\text{CH}$ containing precursor, or a monomer precursor.
7. The method of claim 1, wherein the material of the underlying substrate being removed includes silicon oxide or silicon nitride.
8. The method of claim 1, further comprising:
exposing the carbon-containing film to a fluorine-containing material to adjust the fluorine to carbon content of the carbon-containing film.

9. The method of claim 1, further comprising:
repeating the treating, adsorbing, and exposing steps to remove multiple layers of material.
10. The method of claim 1, further comprising:
purging the environment following the treating step and preceding the adsorbing step.
11. The method of claim 1, further comprising:
purging the environment following the adsorbing step and preceding the removing step.

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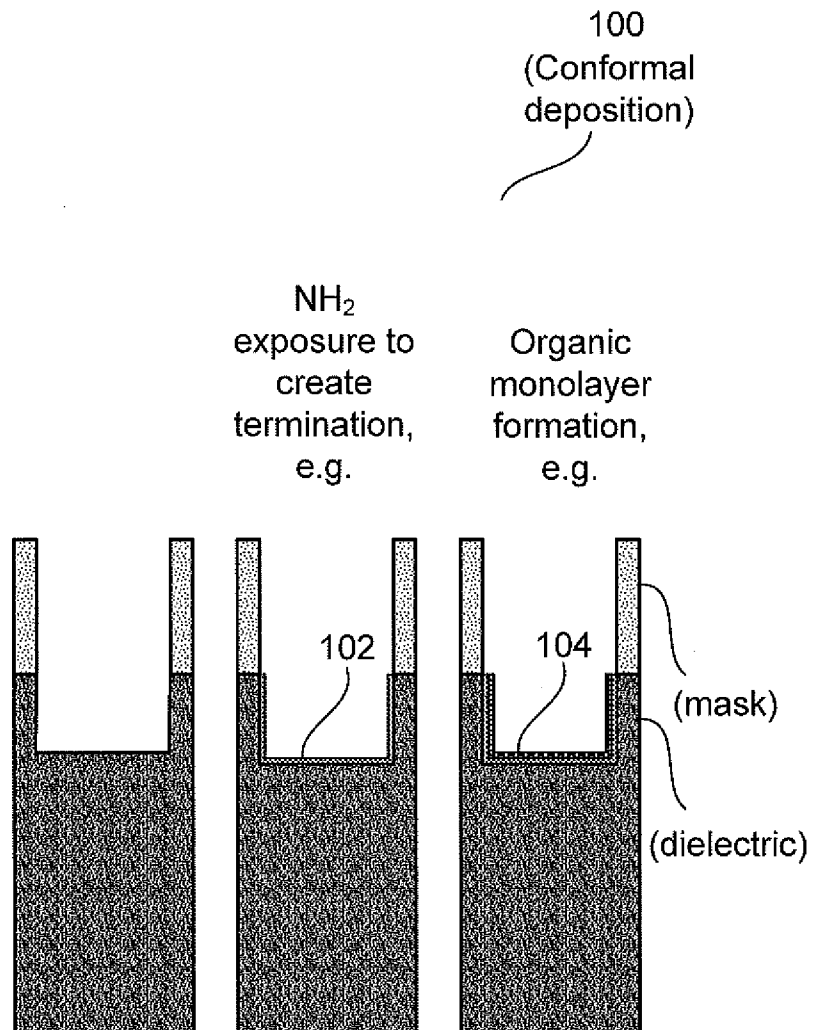


FIG. 1

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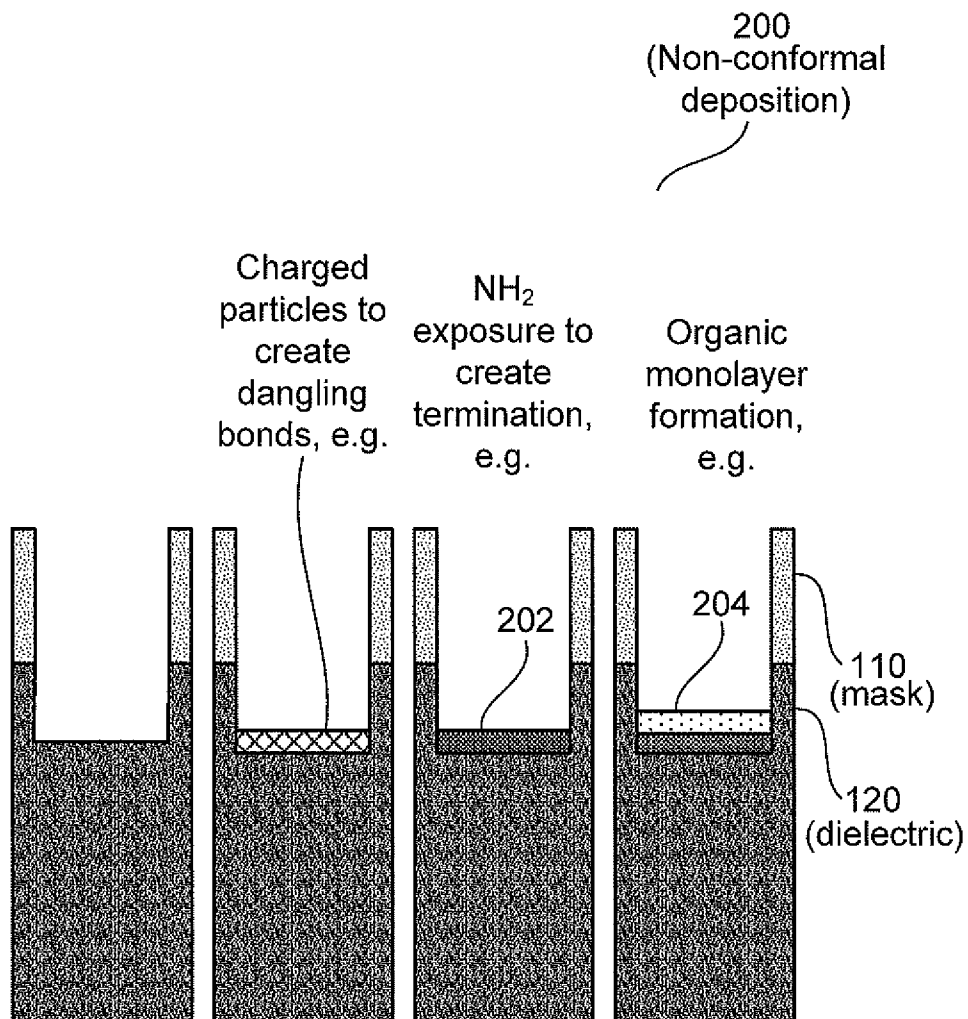
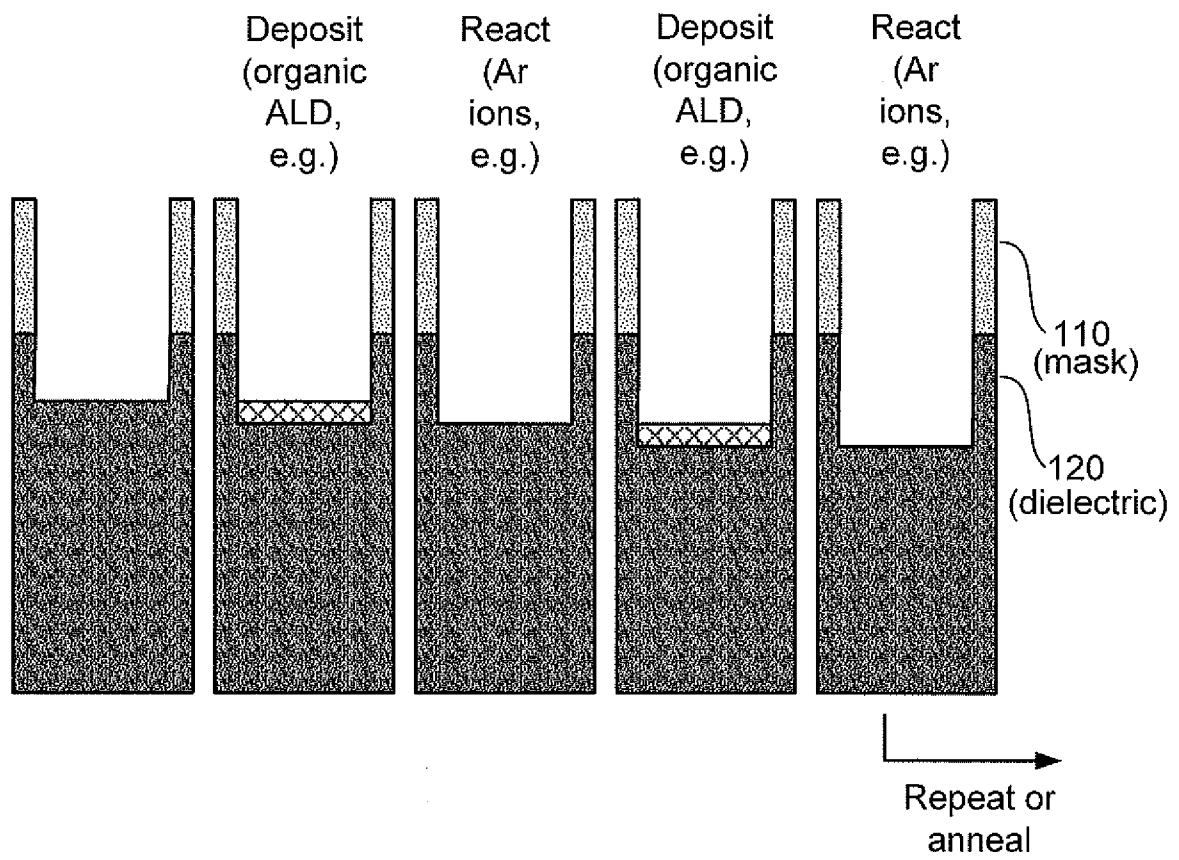


FIG. 2

3/5**FIG. 3**

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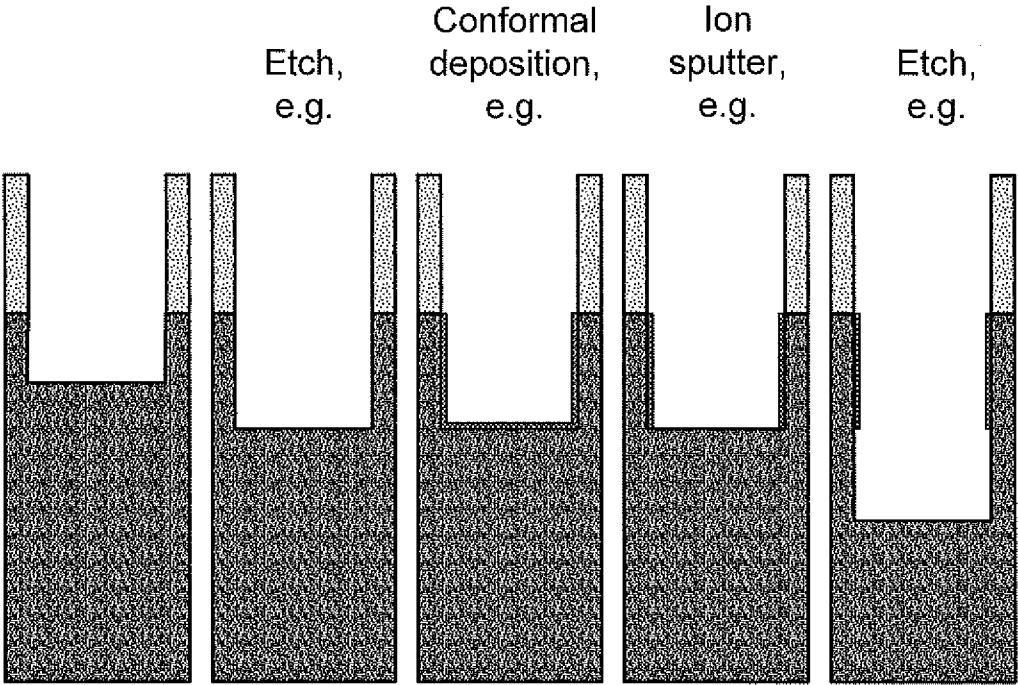


FIG. 4

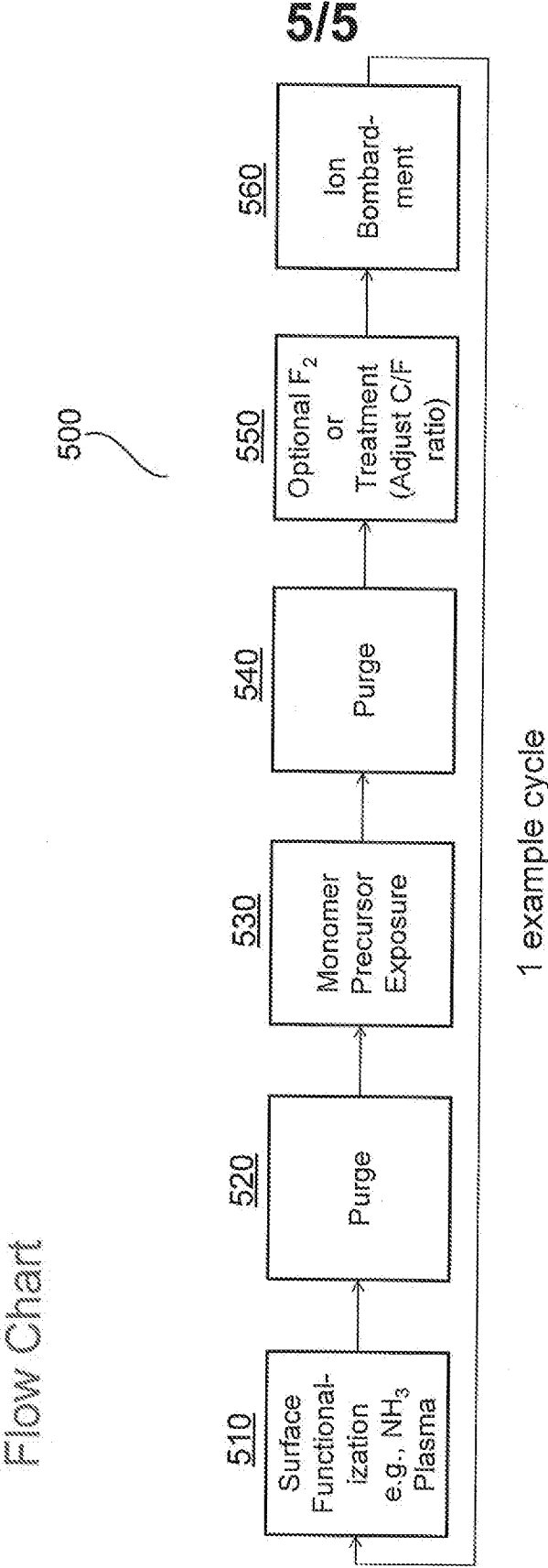


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/043533**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/306(2006.01)i, H01L 21/02(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 21/306; H01L 21/302; H01L 21/469; H01L 21/205; C23C 16/44; H01L 21/31; H01B 19/04; H01J 37/32; H01L 21/02

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: adsorption, etching, fluorine, carbon, ammonia, ion flux, precursor, silicon oxide, silicon nitride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 8435905 B2 (SADAYOSHI HORII et al.) 07 May 2013 See column 3, line 41 - column 7, line 54 and figures 5, 6.	1-11
A	US 7416989 B1 (XINYE LIU et al.) 26 August 2008 See column 7, line 26 - column 14, line 63 and figures 1A-5.	1-11
A	US 2015-0200042 A1 (APPLIED MATERIALS, INC.) 16 July 2015 See paragraphs [0065]-[0104] and figures 2A-4E.	1-11
A	WO 2015-047731 A1 (APPLIED MATERIALS, INC.) 02 April 2015 See paragraphs [0053]-[0071] and figures 3-4E.	1-11
A	KR 10-0297719 B1 (SAMSUNG ELECTRONICS CO., LTD.) 07 August 2001 See the whole document.	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

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"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

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International Application Division

Korean Intellectual Property Office

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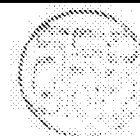


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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/043533

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 8435905 B2	07/05/2013	JP 4813480 B2 KR 10-0960273 B1 KR 10-2008-0012379 A US 2009-0035947 A1 WO 2006-134930 A1	09/11/2011 04/06/2010 11/02/2008 05/02/2009 21/12/2006
US 7416989 B1	26/08/2008	US 8043972 B1	25/10/2011
US 2015-0200042 A1	16/07/2015	TW 201532139 A WO 2015-105673 A1	16/08/2015 16/07/2015
WO 2015-047731 A1	02/04/2015	CN 105518827 A JP 2016-540368 A KR 10-2016-0063378 A TW 201515109 A US 2015-0093891 A1 US 2017-0084486 A1 US 9685371 B2	20/04/2016 22/12/2016 03/06/2016 16/04/2015 02/04/2015 23/03/2017 20/06/2017
KR 10-0297719 B1	07/08/2001	JP 2000-160342 A TW 430863 A US 2002-0048635 A1 US 2003-0003230 A1	13/06/2000 21/04/2001 25/04/2002 02/01/2003