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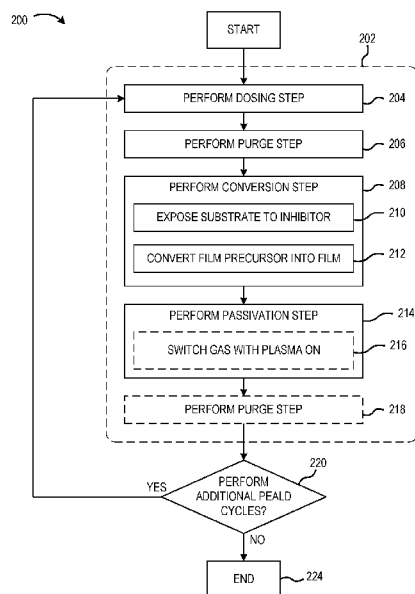


FIG. 2

(57) Abstract: Examples are disclosed that relate to performing plasma-enhanced atomic layer deposition (PEALD) with in-situ passivation, and to protecting a hardmask when performing etching of a gapfill film. One example provides a method including performing a plurality of PEALD cycles to deposit a film into the gap. Each PEALD cycle comprises introducing a film precursor into a processing chamber to adsorb the film precursor to surfaces within the gap, and then purging the chamber. The PEALD cycle further comprises, in a conversion step, forming a plasma using a gas mixture comprising a reactant and an inhibitor to expose the substrate to the inhibitor and convert the film precursor into a film within the gap. The PEALD cycle further comprises, after the conversion step, in a passivation step, exposing the substrate to a plasma comprising a passivation agent to remove at least some of the inhibitor from the surfaces in the gap.

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**ATOMIC LAYER DEPOSITION WITH INHIBITION AND IN-SITU
PASSIVATION, AND HARDMASK PROTECTION DURING ETCHING OF A
GAPFILL FILM**

BACKGROUND

[0001] Electronic device fabrication processes involve many steps of material deposition, patterning, and removal to form integrated circuits on substrates. Various methods can be used to process films of materials to form integrated circuits. For example, atomic layer deposition (ALD) can be used to form a film on a substrate in a layer-by-layer manner. ALD can be used to form highly conformal films on complex substrate topologies.

SUMMARY

[0002] This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter. Furthermore, the claimed subject matter is not limited to implementations that solve any or all disadvantages noted in any part of this disclosure.

[0003] Examples are disclosed that relate to the use of an in-situ passivation step following a conversion step of a plasma-enhance atomic layer deposition (PEALD) cycle. One example provides a method of processing a substrate comprising a gap. The method comprises performing a plurality of plasma-enhanced atomic layer deposition (PEALD) cycles to deposit a film into the gap. Each PEALD cycle of the plurality of PEALD cycles comprises, in a first step, introducing a film precursor into a processing chamber to adsorb the film precursor to surfaces within the gap. The PEALD cycle further comprises purging the processing chamber after the first step. The PEALD cycle further comprises, in a second step, forming a plasma using a gas mixture comprising a reactant and an inhibitor to expose the substrate to the inhibitor, and convert the film precursor into a film within the gap. The PEALD cycle further comprises, after the second step, in a third step, exposing the substrate to a plasma comprising a passivation agent to remove at least some of the inhibitor from the surfaces in the gap.

[0004] In some such examples, the method further comprises performing one or more modified PEALD cycles that omits exposing the substrate to the plasma comprising the passivation agent.

[0005] In some such examples, the method further comprises performing one or more modified PEALD cycles that omits exposing the substrate to the inhibitor in the second step.

[0006] In some such examples, exposing the substrate to the plasma comprising the passivation agent comprises switching gas flow from the gas mixture to the passivation agent while maintaining the plasma.

[0007] In some such examples, the PEALD cycle further comprises purging the processing chamber after performing the third step.

[0008] In some such examples, the second step is performed under conditions configured to deposit the inhibitor into the gap such that a concentration of the inhibitor deposited at a first depth within the gap is greater than a concentration of the inhibitor deposited at a second depth within the gap, the second depth being deeper in the gap than the first depth.

[0009] In some such examples, the film comprises one or more of silicon oxide, silicon oxynitride, silicon oxycarbide, and silicon oxycarbonitride.

[0010] In some such examples, the inhibitor comprises one or more of molecular fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane.

[0011] In some such examples, after performing the plurality of PEALD cycles, the film comprises a fluorine concentration that is less than 4×10^{20} F atoms/cm³.

[0012] In some such examples, the passivation agent comprises one or more of NH₃ and H₂.

[0013] In some such examples, the third step is performed for 0.05 to 0.5 seconds in each PEALD cycle.

[0014] In some such examples, the third step is performed for 0.3 seconds or less in each PEALD cycle.

[0015] In some such examples, the substrate comprises dynamic random access memory shallow trench isolation structures.

[0016] Another examples provides an atomic layer deposition (ALD) tool. The ALD tool comprises a processing chamber. The ALD tool further comprises a substrate

support disposed in the processing chamber. The ALD tool further comprises flow control hardware configured to control flow of a film precursor, an oxidant, an inhibitor, and a passivation agent into the processing chamber. The ALD tool further comprises an exhaust system. The ALD tool further comprises a radiofrequency power source configured to form a plasma in the processing chamber. The ALD tool further comprises a controller configured to control the ALD tool to perform a plurality of plasma-enhanced ALD (PEALD) cycles to process a substrate disposed on the substrate support. The controller is configured to, in a first step of a PEALD cycle, operate the flow control hardware to flow the film precursor into the processing chamber to adsorb the film precursor within a gap on the substrate. The controller is further configured to, in a second step of the PEALD cycle after the first step, operate the exhaust system to purge the processing chamber. The controller is further configured to in a third step of the PEALD cycle after the second step, operate the flow control hardware to flow the oxidant and the inhibitor into the processing chamber, and operate the radiofrequency power source to form a plasma using the oxidant and the inhibitor to expose the substrate to the inhibitor and convert the precursor into a film within the gap. The controller is further configured to, in a fourth step of the PEALD cycle after the third step, operate the flow control hardware to flow the passivation agent into the processing chamber and operate the radiofrequency power source to form a plasma using the passivation agent to remove at least some of the inhibitor from the surfaces in the gap.

[0017] In some such examples, the controller is configured to operate the radiofrequency power source continuously between the third step and the fourth step.

[0018] In some such examples, the inhibitor comprises one or more of molecular fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane and the passivation agent comprises one or more of NH_3 and H_2 .

[0019] In some such examples, the fourth step is performed for 0.3 seconds or less in each PEALD cycle.

[0020] Another example provides a method of processing a substrate comprising a gap. The method comprises performing a plurality of plasma-enhanced atomic layer deposition (PEALD) cycles to deposit a film into the gap. Each PEALD cycle of the plurality of PEALD cycles comprises, in a first step, introducing a film precursor into a processing chamber to adsorb the film precursor to surfaces within the

gap. The PEALD cycle further comprises purging the processing chamber after the first step. The PEALD cycle further comprises, in a second step, supplying radiofrequency power to form a plasma in the processing chamber using a gas mixture comprising a reactant and an inhibitor to expose the substrate to the inhibitor, and convert the precursor into a film within the gap. The PEALD cycle further comprises, after the second step, in a third step, switching gas flow to a passivation agent while supplying the radiofrequency power, thereby forming a plasma comprising the passivation agent to remove at least some of the inhibitor from the surfaces in the gap. The method omits a purge step between PEALD cycles.

[0021] In some such examples the method further comprises performing a modified PEALD cycle that omits exposing the substrate to the plasma comprising the passivation agent.

[0022] In some such examples the inhibitor comprises one or more of molecular fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane and the passivation agent comprises one or more of NH_3 and H_2 .

[0023] Another example provides a method of forming a tapered profile in a film deposited in a gap on a substrate. The substrate comprises a hardmask located on a field region adjacent to the gap. The method comprises performing a plurality of etching cycles. Each etching cycle comprises exposing the substrate to a plasma comprising an etchant and exposing the substrate to a plasma comprising a passivator. The method further comprises performing at least one atomic layer deposition process between a first etching cycle and a second etching cycle at an intermediate point in the plurality of etching cycles to deposit a protective layer that protects the hardmask during the plurality of etching cycles.

[0024] In some such examples the protective layer and the film deposited in the gap are a same material.

[0025] In some such examples the etchant comprises a fluorine-containing etchant and the passivator comprises a hydrogen-containing passivator.

[0026] In some such examples the film deposited in the gap is a silicon oxide-containing film and the hardmask is a silicon nitride-containing hardmask.

[0027] In some such examples performing the at least one atomic layer deposition process comprises performing the at least one atomic layer deposition process every two to fifty etching cycles.

[0028] In some such examples performing the at least one atomic layer deposition process every two to fifty etching cycles comprises a deposition-etch cycle, and wherein an etching process comprises performing from twenty to one hundred deposition-etch cycles.

[0029] In some such examples exposing the substrate to the plasma comprising the passivator comprises exposing the substrate to a hydrogen-containing passivator and an oxygen-containing passivator.

[0030] In some such examples exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate simultaneously to the hydrogen-containing passivator and the oxygen-containing passivator.

[0031] In some such examples exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate sequentially to the hydrogen-containing passivator and the oxygen-containing passivator.

[0032] Another example provides a method of forming a tapered profile in a film deposited in a gap on a substrate. The substrate comprises a hardmask located on a field region adjacent to the gap. The method comprises performing a plurality of etching cycles. Each etching cycle comprises exposing the substrate to a plasma comprising an etchant and exposing the substrate to a plasma comprising a hydrogen-containing passivator and an oxygen-containing passivator.

[0033] In some such examples exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate simultaneously to the hydrogen-containing passivator and the oxygen-containing passivator.

[0034] In some such examples exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate sequentially to the hydrogen-containing passivator and the oxygen-containing passivator.

[0035] In some such examples the etchant comprises a fluorine-containing etchant.

[0036] In some such examples the film deposited in the gap is a silicon oxide-containing film and the hardmask is a silicon nitride-containing hardmask.

[0037] In some such examples the method further comprises performing at least one atomic layer deposition process between a first etching cycle and a second etching cycle at an intermediate point in the plurality of etching cycles to deposit a protective layer that protects the hardmask during the plurality of etching cycles.

[0038] In some such examples the protective layer and the film deposited in the gap are a same material.

[0039] In some such examples performing the at least one atomic layer deposition process comprises performing the at least one atomic layer deposition process every two to fifty etching cycles.

[0040] In some such examples performing the at least one atomic layer deposition process every two to fifty etching cycles comprises a deposition-etch cycle, and wherein an etching process comprises performing from twenty to one hundred deposition-etch cycles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] FIGS. 1A-1F schematically show structures formed on a substrate in an example atomic layer deposition (ALD) gapfill process that results in seam formation and relatively higher buried inhibitor content.

[0042] FIG. 2 shows a flow diagram of an example plasma-enhanced ALD (PEALD) process that includes in-situ passivation.

[0043] FIGS. 3A-3G show example structures formed using the PEALD process of FIG. 2 to perform gapfill while avoiding buildup of residual inhibitor.

[0044] FIG. 4 shows a graph of fluorine inhibitor concentration in films formed using various PEALD methods.

[0045] FIGS. 5A-5B show a flow diagram of an example method for processing a substrate comprising a gap using PEALD cycles with in-situ passivation.

[0046] FIG. 6 schematically shows an example PEALD tool.

[0047] FIG. 7 shows a block diagram of an example computing device.

[0048] FIG. 8A shows an example method of forming a tapered profile in a film deposited in a gap on a substrate.

[0049] FIG. 8B and FIG. 8C schematically show structures formed on substrate while forming a tapered profile according to the method of FIG. 8A.

[0050] FIG. 9A shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a deposition-etch cycle.

[0051] FIG. 9B and FIG. 9C schematically show structures formed on substrate while forming a tapered profile according to the method of FIG. 9A.

[0052] FIG. 10 shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a co-flow passivation-etch cycle.

[0053] FIG. 11 shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a first sequential passivation-etch cycle.

[0054] FIG. 12 shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a second sequential passivation-etch cycle.

[0055] FIG. 13 shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a co-flow passivation deposition-etch cycle.

[0056] FIG. 14 shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a first sequential passivation deposition-etch cycle.

[0057] FIG. 15 shows an example method of forming a tapered profile in a film deposited in a gap on a substrate using a second sequential passivation deposition-etch cycle.

DETAILED DESCRIPTION

[0058] The term “aspect ratio” generally represents a ratio between a depth of a feature and an average width of the feature.

[0059] The term “atomic layer deposition” (ALD) generally represents a process in which a film is formed on a substrate in a layer-by-layer manner. Each layer is deposited using an ALD cycle. An ALD cycle comprises adsorbing a precursor to the substrate in a dose step, purging excess precursor, and then chemically converting the adsorbed precursor to form the film layer in a conversion step. Plasma-enhanced ALD (PEALD) utilizes a plasma of a reactive gas to facilitate the chemical conversion of the adsorbed precursor to the film layer. The terms “growth” and “deposition”, and variants thereof, also can be used to refer to film formation.

[0060] The term “PEALD cycle” generally represents a sequence of processes used to form one layer of a film in a PEALD process.

[0061] The term “ALD tool” generally represents a machine comprising a processing chamber and other hardware configured to perform ALD processing, such as PEALD.

[0062] The term “film precursor” generally represents any material that can be introduced into a processing chamber to form a film on a substrate disposed within the processing chamber. Examples of film precursors include silicon-containing precursors that can be used to form silicon-containing films such as silicon oxide (SiO_2), silicon nitride, silicon carbide, silicon oxynitride, silicon oxycarbide, and silicon oxycarbonitride films.

[0063] The term “gap” generally represents a recessed feature on a substrate.

[0064] The term “gapfill” generally represents a process to deposit a film into a recessed feature on a substrate.

[0065] The term “inhibition” and variants thereof generally represent a process by which a compound can disrupt one or more chemical processes for film growth on a substrate surface, thereby slowing growth of the film.

[0066] The term “inhibitor” generally represents a compound that can be introduced into a processing chamber to adsorb to a substrate surface to inhibit film growth on the substrate surface. The term “inhibitor” is used herein to represent an inhibitor compound introduced into a processing chamber, reactive inhibitor species formed in a plasma, and adsorbed inhibitor on a substrate surface. Example inhibitors include hydrogen (H_2), nitrogen-containing inhibitors, fluorine-containing inhibitors, and carbon-containing inhibitors.

[0067] Examples of nitrogen-containing inhibitors can include nitrogen (N_2), ammonia (NH_3), amines, diamines, and aminoalcohols.

[0068] Examples of fluorine-containing inhibitors can include fluorine (F_2), nitrogen trifluoride (NF_3), sulfur hexafluoride (SF_6), hydrogen fluoride (HF), xenon difluoride (XeF_2), and fluorocarbons ($\text{C}_x\text{H}_y\text{F}_z$) such as tetrafluoromethane (CF_4) or hexafluoroethane (C_2F_6).

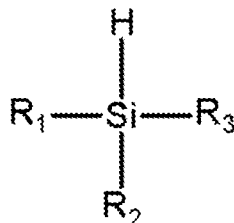
[0069] Examples of carbon-containing inhibitors can include alkanes, alkenes, alkynes, cyclic hydrocarbons, aromatics, alcohols, aldehydes, esters, ethers, ketones, aldehydes, alkyl halides, alkyl amines, and alkyl diamines.

[0070] The term “processing chamber” generally represents an enclosure in which chemical and/or physical processes are performed on substrates.

[0071] The terms “purge” and variants thereof generally represent processes in which unwanted species are removed from a processing chamber.

[0072] The term “showerhead” generally represents a processing chemical outlet comprising a plurality of holes distributed across an area.

[0073] The term “silicon-containing film precursor” generally represents any compound that can be introduced into a processing chamber in a gas phase to form a silicon-containing film on the substrate. Example silicon-containing films include silicon oxide, silicon nitride, silicon oxynitride, silicon carbide, silicon oxycarbide, silicon carbonitride, and silicon oxycarbonitride. Example silicon-containing film precursors for forming silicon-containing films using PEALD can comprise materials having the general structure:



where R₁, R₂ and R₃ can be the same or different substituents. In various examples, R₁, R₂, and R₃ can include silanes, siloxy groups, amines, halides, hydrogen, or organic groups such as alkylamines, alkoxy, alkyl, alkenyl, alkynyl, and cyclic groups (such as aromatic groups).

[0074] Example silicon-containing film precursors include silane and polysilanes (H₃Si-(SiH₂)_n-SiH₃), where n ≥ 0, such as disilane, trisilane, and tetrasilane, and trisilylamine.

[0075] In some examples, the silicon-containing film precursor is an alkoxy silane. Alkoxy silanes that can be used include compounds having a general formula of H_x-Si-(OR)_y, where x = 1-3, x+y = 4 and each R is a substituted or unsubstituted aliphatic or aromatic group; and H_x(RO)_y-Si-Si-(OR)_yH_x, where each R is a substituted or unsubstituted aliphatic or aromatic group. Example alkoxy silanes include tetramethoxysilane (TMOS), diethoxymethylsilane (DEMS), diethoxysilane (DES), dimethoxymethylsilane, dimethoxysilane (DMOS), methyl-diethoxysilane (MDES), methyl-dimethoxysilane (MDMS), t-butoxydisilane, triethoxysilane (TES), and trimethoxysilane (TMS or TriMOS).

[0076] In some examples, the silicon-containing film precursor is a siloxane. Siloxanes include materials having Si-O-Si linkages. Example siloxanes include octamethylcyclotetrasiloxane (OMCTS), octamethoxydodecasiloxane (OMODDS), and tetramethylcyclotetrasiloxane (TMCTS).

[0077] In some examples, the silicon-containing film precursor is an aminosilane. Aminosilanes include materials having a general formula H_x-Si-(NR)_y,

where $x = 1-3$, $x+y = 4$, and R is a substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aromatic group, or hydride group. Example aminosilanes include bisdiethylaminosilane, diisopropylaminosilane, bis(t-butylamino) silane (BTBAS), di-sec-butylaminosilane, and tris(dimethylamino)silane (3DMAS).

[0078] In some examples, the silicon-containing film precursor is a halogen-containing silane. In some examples, a halogen-containing silane can comprise at least one hydrogen atom. Such a silane can have a general formula of SiX_aH_y where $y \geq 1$. Example halosilanes include dichlorosilane (H_2SiCl_2), hexachlorodisilane (Si_2Cl_6), and diiodosilane (H_2SiI_2).

[0079] More specific examples of silicon-containing film precursors include polysilanes ($(\text{Si}_n\text{H}_{2n+2})$, where $n \geq 1$, such as silane, disilane, trisilane, and tetrasilane), trisilylamine, tetraethyl orthosilicate (TEOS), methylsilane, trimethylsilane (3MS), ethylsilane, butasilanes, pentasilanes, octasilanes, heptasilane, hexasilane, cyclobutasilane, cycloheptasilane, cyclohexasilane, cyclooctasilane, cyclopentasilane, 1,4-dioxa-2,3,5,6-tetrasilacyclohexane, triethoxysiloxane (TRIES), and tetraoxymethylcyclotetrasiloxane (TOMCTS).

[0080] An example precursor for providing nitrogen for formation of a silicon nitride film is nitrogen (N_2). An example precursor for providing nitrogen and oxygen for formation of a silicon oxynitride film is N_2O .

[0081] In some examples, an oxidant is used to react with the silicon-containing film precursor. Examples include molecular oxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2), ozone (O_3), carbon dioxide (CO_2), and nitrogen oxides such as nitrous oxide (N_2O).

[0082] The term “substrate” generally represents any object on which a film can be deposited.

[0083] The term “substrate support” generally represents any structure for supporting a substrate in a processing chamber.

[0084] The term “3D DRAM” is an acronym for three-dimensional dynamic random-access memory.

[0085] The term “3D NAND” is an acronym for three-dimensional NOT AND memory, and represents memory architecture based upon NOT AND logic gates.

[0086] As mentioned above, atomic layer deposition (ALD) can be used to fill a gap on a substrate. ALD involves performing one or more deposition cycles to grow a thin film on a substrate surface. Plasma enhanced ALD (PEALD) utilizes a plasma to facilitate deposition of a film. Examples of films that can be deposited by PEALD include oxide films. In an example PEALD oxide film deposition cycle, a film precursor is introduced into a processing chamber in a dose step. The film precursor adsorbs onto a substrate in a self-limiting reaction. Next, the processing chamber is purged to remove excess film precursor. Then, a reactant (such as an oxidant) is introduced to the processing chamber in a conversion step. A plasma is formed by application of radiofrequency power to electrodes within the processing chamber. The plasma forms reactive species from the reactant. The reactive species react with the film precursor to form a layer of the oxide film.

[0087] ALD can be used to fill a gap in a substrate with a material such as a dielectric material. However, it can be challenging to fill a relatively deep and/or high aspect ratio gaps without forming voids in the gap. Voids are caused by film growth fronts converging at a shallower depth in a gap before they converge deeper within the gap, thereby pinching off the gap. This can arise, for example, from substrate surfaces relatively deep within a gap not being fully saturated with adsorbed precursor before performing a conversion step due to the depth and/or high aspect ratio configuration of the gap.

[0088] To avoid void formation, an ALD process can employ an inhibitor to help inhibit film growth on surfaces relatively closer to a gap opening more strongly than surfaces relatively farther from the gap opening. This can help to avoid the above-described pinch-off issue, and thereby fill the gap in a bottom-up manner. FIGS. 1A-1F schematically show structures formed in an example ALD gapfill process that utilizes an inhibitor. In the process of FIGS. 1A-1F, a gap on a substrate is filled with an oxide film using PEALD. Example oxide films include silicon oxide, silicon oxynitride, and silicon oxycarbide.

[0089] First referring to FIG. 1A, substrate 100 comprises a gap 102. Substrate 100 can comprise any suitable material. In a PEALD oxide gapfill process, substrate 100 is positioned in a processing chamber and is exposed to a film precursor gas in a dose step. The film precursor gas diffuses into gap 102 and adsorbs onto substrate surfaces. The processing chamber next is purged. Then, an oxidant is introduced into the plasma chamber in a conversion step. By the application of a plasma, the adsorbed

film precursor reacts with the oxidant to form an oxide film on the surfaces within the gap 102. Repeated cycles of dose steps and conversion steps progressively fill the gap 102. FIG. 1B-1D schematically shows an oxide film 104 formed on substrate 100. Oxide film can represent an intermediate point in a gapfill process to fill gap 102 with a dielectric material. Oxide film 104 is formed using one or more ALD cycles.

[0090] FIG. 1C shows an inhibitor 106 adsorbed to the oxide film 104 in an inhibition step. In this example, the inhibition step is performed before a dose step of a next PEALD cycle. In an example inhibition step, an inhibitor is introduced into the processing chamber, and a plasma is formed in the processing chamber. For example, a fluorine-containing inhibitor (e.g. F_2 , NF_3 , SF_6 , $C_xF_yH_z$) can be introduced into a plasma. The plasma forms reactive inhibitor species from the inhibitor, such as reactive fluorine species. Such species also can etch an oxide film. As such, to avoid etching, a lesser quantity of inhibitor can be introduced into the processing chamber than would be used to etch an oxide film. This allows the reactive inhibitor species to form a surface layer on the substrate, without forming volatile species by further reaction. Inhibition can be performed with every PEALD cycle, or in a desired subset of PEALD cycles in an PEALD process.

[0091] The inhibitor is introduced into the processing chamber in a manner that causes a non-conformal deposition of inhibitor to occur. For example, the inhibitor can be introduced in an amount and for a time insufficient to saturate a surface of the substrate within the gap. This can cause the inhibitor to preferentially adsorb to surfaces inside of the gap closer to an opening of the gap than to surfaces deeper within the gap. As shown in FIG. 1C, a greater amount of inhibitor 106 adsorbs to upper surfaces 108 near the opening of gap 102 than to lower surfaces 110 near the bottom of the gap 102. The depth in the gap to which the inhibitor is adsorbed can be controlled by various processing conditions, as described in more detail below. As a result, the inhibitor has a relatively greater inhibition effect at upper surfaces 108 than on lower surfaces 110.

[0092] Some inhibitor can be consumed during a PEALD cycle. However, an inhibitor that chemisorbs to the substrate, such as a fluorine-based inhibitor or nitrogen-based inhibitor, can at least partially remain on the substrate after performing one or more PEALD cycles. FIG. 1D shows additional layers of oxide film 104 deposited onto substrate 100 and within gap 102. As shown, inhibitor 106 can become trapped under oxide film 104. FIG. 1E schematically shows the result of performing additional PEALD cycles with inhibition to fill gap 102. The process leaves residual inhibitor

embedded within oxide film 104. Residual inhibitor concentration can build up over multiple PEALD cycles. Such residual inhibitor can pose issues with film quality.

[0093] Further, as shown in FIG. 1E, as oxide film 104 fills gap 102, oxide film 104 forms a seam 120. Residual inhibitor in the seam 120 can pose issues seam quality. For example, residual fluorine can lead to weak seam quality by limiting crosslinking in oxide materials. A higher concentration of residual fluorine also can cause reduced film density compared to a lower concentration of residual fluorine. The weak seam quality can cause problems during a subsequent etching step. For example, residual fluorine in seam 120 can lead to relatively higher etch rates in seam 120 than other portions of the film. This can lead to “seam blowout” when etching. In other examples, weak gapfill seam quality can lead to bending of features such as gate structures on the substrate, as the forces exerted on a gate structure from gapfill films on different sides are not balanced. In yet further examples, residual fluorine can degrade electrical performance, such as by causing a relatively high leakage current.

[0094] In an inhibited PEALD process, a passivation step can be performed to remove inhibitor from the substrate. For example, in fluorine-based inhibited PEALD gapfill process, a hydrogen-based plasma passivation step can be used after the PEALD cycles to reduce residual fluorine by forming volatile hydrogen fluoride. An example hydrogen-based passivation step can comprise exposing the substrate to a plasma comprising NH_3 and/or H_2 .

[0095] However, residual inhibitor trapped by overlying layers of film can be difficult to remove by passivation. Further, the passivation step can leave a higher concentration of residual deeper within the gap film that closer to a gap opening removed near the top surface than deeper in the film. FIG. 1F shows some inhibitor 106 removed from oxide film 104 as a result of passivation. However, the concentration of inhibitor 106 deeper in gap 102 remains relatively high. This can pose issues described above, such as poor seam quality and degraded electrical performance.

[0096] Accordingly, examples are disclosed that relate to performing PEALD cycles with in-situ passivation. The term “in-situ” passivation refers to a passivation step that is performed within a PEALD cycle, rather than performed after completion of an ALD process. Briefly, a substrate is processed within a processing chamber of an ALD tool by performing a plurality of PEALD cycles sequentially. A PEALD cycle comprises a dosing step to adsorb film precursor on a substrate and within a gap on the substrate. Then, a purge is performed to remove excess film precursor from the

processing chamber. The PEALD cycle further comprises a conversion step in which a reactant and inhibitor are introduced into the processing chamber. A radiofrequency plasma is formed to expose the substrate to the inhibitor and convert the film precursor into the film. In a passivation step of the PEALD cycle, a plasma is formed using a passivation agent to remove at least some of the inhibitor from the substrate. The passivation step is performed after the conversion step to remove residual inhibitor in each PEALD cycle. By performing passivation after each PEALD cycle, the disclosed examples can help reduce buildup of inhibitor.

[0097] Performing in-situ passivation further can help to reduce processing times. In some examples, a total passivation time budget can be reduced by 60% or more with similar fluorine residual levels compared to examples that include post-deposition passivation. This can help increase throughput. Further, fluorine residual levels can be reduced by 50% or more with a similar passivation time budget compared to examples that include post-deposition passivation. In some examples, both fluorine residuals and passivation time can be reduced. Thus, the disclosed examples can help achieve faster throughput and/or reduced residual passivation concentrations in deposited films.

[0098] Further, in-situ passivation can be performed while avoiding purge steps and/or preparation steps, such as gas line loading. PEALD processes can include a purge step after the conversion step to help separate film precursor from reactant. As the in-situ passivation step omits the reactant, the in-situ passivation step can serve as a purge step between the conversion step and the dosing step of the next PEALD cycle. As such, a separate purge step can be omitted. Further, in some examples, gas line loading (e.g., charging a gas line with a film precursor) can be performed during the in-situ passivation step. By avoiding steps such as gas line loading and purge steps, the disclosed examples can further reduce processing time and improve throughput.

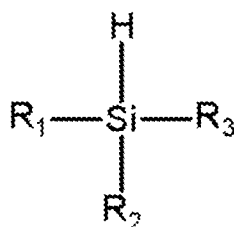
[0099] In some examples, a duration of an in-situ passivation step can be controlled to achieve a desired seam density. For example, a relatively longer duration in-situ passivation step can be used to densify the seam more than a relatively shorter in-situ passivation step. This can help produce a higher quality gapfill with better etch resistance in the seam compared to other examples. By increasing the density of the seam and reducing residual inhibitor concentrations, the disclosed examples can produce oxide films suitable for use in dynamic random-access memory (DRAM)

applications. For example, the disclosed PEALD processes can be used to form shallow trench isolation (STI) regions within an array of DRAM structures.

[00100] Additionally, the disclosed examples can provide a more controllable gapfill process compared to other examples that omit in-situ passivation. This is because inhibitor can build up on the film during PEALD cycles and affect deposition rates in subsequent cycles. This can cause uneven gapfill in some examples. Uneven gapfill can lead to bending of features extending from a substrate surface (e.g., spacers or “fins” between gaps). By performing PEALD cycles with in-situ passivation, such issues can be avoided. By avoiding bending of such features, the disclosed examples can provide better performance in certain applications, such as 2-dimensional DRAM STI structures.

[00101] FIG. 2 shows a flow diagram of an example method 200 for processing a substrate. Method 200 comprises performing PEALD cycles 202 that include in-situ passivation. In some examples, one or more modified PEALD cycles can be performed before, or after, the plurality of sequential PEALD cycles 202. In such examples, a modified PEALD cycle can omit one or more steps, such as omitting a passivation step. PEALD processing is performed using a PEALD tool comprising a processing chamber. Examples of PEALD tools are described in more detail below with regard to FIG. 6.

[00102] PEALD cycle 202 comprises performing a dosing step 204. In dosing step 204, a film precursor is introduced into the processing chamber to adsorb film precursor to surfaces within a gap on the substrate. Any suitable film precursor can be used. Examples include silicon-containing film precursors for forming silicon-containing films. Example silicon-containing films include silicon oxide, silicon nitride, silicon oxynitride, silicon carbide, silicon oxycarbide, silicon carbonitride, and silicon oxycarbonitride. Example silicon-containing film precursors for forming silicon-containing films using PEALD can comprise materials having the general structure:



where R_1 , R_2 and R_3 can be the same or different substituents. In various examples, R_1 , R_2 , and R_3 can include silanes, siloxy groups, amines, halides, hydrogen, or organic groups such as alkylamines, alkoxy, alkyl, alkenyl, alkynyl, and cyclic groups (such as aromatic groups).

[00103] Example silicon-containing film precursors include silane and polysilanes ($H_3Si-(SiH_2)_n-SiH_3$), where $n \geq 0$, such as disilane, trisilane, and tetrasilane, and trisilylamine.

[00104] In some examples, the silicon-containing film precursor is an alkoxysilane. Alkoxysilanes that can be used include compounds having a general formula of $H_x-Si-(OR)_y$, where $x = 1-3$, $x+y = 4$ and each R is a substituted or unsubstituted aliphatic or aromatic group; and $H_x(RO)_y-Si-Si-(OR)_yH_x$, where each R is a substituted or unsubstituted aliphatic or aromatic group. Example alkoxysilanes include tetramethoxysilane (TMOS), diethoxymethylsilane (DEMS), diethoxysilane (DES), dimethoxymethylsilane, dimethoxysilane (DMOS), methyl-diethoxysilane (MDES), methyl-dimethoxysilane (MDMS), t-butoxydisilane, triethoxysilane (TES), and trimethoxysilane (TMS or TriMOS).

[00105] In some examples, the silicon-containing film precursor is a siloxane. Siloxanes include materials having Si-O-Si linkages. Example siloxanes include octamethylcyclotetrasiloxane (OMCTS), octamethoxydodecasiloxane (OMODDS), and tetramethylcyclotetrasiloxane (TMCTS).

[00106] In some examples, the silicon-containing film precursor is an aminosilane. Aminosilanes include materials having a general formula $H_x-Si-(NR)_y$, where $x = 1-3$, $x+y = 4$, and R is a substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aromatic group, or hydride group. Example aminosilanes include bisdiethylaminosilane, diisopropylaminosilane, bis(t-butylamino) silane (BTBAS), di-sec-butylaminosilane, and tris(dimethylamino)silane (3DMAS).

[00107] In some examples, the silicon-containing film precursor is a halogen-containing silane. In some examples, a halogen-containing silane can comprise at least one hydrogen atom. Such a silane can have a general formula of SiX_aH_y where $y \geq 1$. Example halosilanes include dichlorosilane (H_2SiCl_2), hexachlorodisilane (Si_2Cl_6), and diiodosilane (H_2SiI_2).

[00108] More specific examples of silicon-containing film precursors include polysilanes (($\text{Si}_n\text{H}_{2n+2}$, where $n \geq 1$, such as silane, disilane, trisilane, and tetrasilane), trisilylamine, tetraethyl orthosilicate (TEOS), methylsilane, trimethylsilane (3MS), ethylsilane, butasilanes, pentasilanes, octasilanes, heptasilane, hexasilane, cyclobutasilane, cycloheptasilane, cyclohexasilane, cyclooctasilane, cyclopentasilane, 1,4-dioxa-2,3,5,6-tetrasilacyclohexane, triethoxysiloxane (TRIES), and tetraoxymethylcyclotetrasiloxane (TOMCTS).

[00109] FIGS. 3A-3G schematically show example structures formed during PEALD processing using method 200. First, FIG. 3A shows a substrate 300 comprising a gap 302. FIG. 3B shows substrate 300 following dosing step 204. Here, substrate 300 is exposed to a film precursor 304. The film precursor 304 adsorbs to surfaces on substrate 300, including surfaces 308 within gap 302.

[00110] PEALD cycle 202 further comprises a purge step 206 that is performed after dosing step 204. FIG. 3C shows the result of purge step 206 where residual film precursor is removed from the processing chamber.

[00111] Next, PEALD cycle 202 comprises a conversion step 208. Conversion step comprises forming a plasma using a gas mixture comprising a reactant and an inhibitor. This allows the inhibitor to adsorb to surfaces on the substrate. Further, the plasma facilitates a reaction between the reactant and the adsorbed film precursor. As such, conversion step 208 comprises exposing the substrate to the inhibitor at 210. Conversion step 208 also comprises converting film precursor into film at 212.

[00112] Any suitable reactant can be used. In some examples, the reactant can comprise a nitrogen-containing precursor for formation of a silicon nitride film. Examples include nitrogen (N_2). In some examples, an oxygen-containing oxidant is used to react with the film precursor. Examples include molecular oxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2), ozone (O_3), carbon dioxide (CO_2), and nitrogen oxides such as nitrous oxide (N_2O). An example precursor for providing nitrogen and oxygen for formation of a silicon oxynitride film is N_2O .

[00113] Any suitable inhibitor can be used at conversion step 208. Examples include hydrogen, nitrogen-containing inhibitors, fluorine-containing inhibitors, and carbon-containing inhibitors. Examples of nitrogen-containing inhibitors include nitrogen, ammonia, amines, diamines, and aminoalcohols. Examples of fluorine-containing inhibitors include fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, and fluorocarbons such as tetrafluoromethane or

hexafluoroethane. Examples of carbon-containing inhibitors include alkanes, alkenes, alkynes, cyclic hydrocarbons, aromatics, alcohols, aldehydes, esters, ethers, ketones, aldehydes, alkyl halides, alkyl amines, and alkyl diamines.

[00114] As a more particular example, a silicon-containing precursor, such as an aminosilane, can be used with an oxygen-containing reactant to form a silicon oxide film. In such examples, a fluorine-containing inhibitor, such as nitrogen trifluoride, can be used to inhibit growth on upper surfaces within the gap and promote bottom-up growth of the silicon oxide film.

[00115] FIG. 3D shows the result of conversion step 208. Here, substrate 300 is exposed to a reactant 310 and an inhibitor 312. A plasma is formed, as indicated at 316. The plasma 316 facilitates conversion of the film precursor 304 to form a film 318 on substrate 300 and within gap 302.

[00116] Returning to FIG. 2, the conversion step 208 can be performed using any suitable processing conditions. Example pressures include pressures of 1 to 30 Torr. Example temperatures include substrate heater temperatures of 50 °C to 800 °C. The conversion step 208 also can comprise any suitable plasma conditions. For example, radiofrequency power at a selected frequency and power can be supplied to an electrode of an electrode pair in the processing chamber to form a capacitively coupled plasma. Example plasma conditions include radiofrequency powers of 50 to 6000 W. Example frequencies for the radiofrequency plasma include frequencies of 400 kHz, 13.56 MHz, 27MHz, 60MHz, and 90MHz. In some examples, the plasma can comprise a higher frequency radiofrequency energy component (“HF component”) and a lower frequency radiofrequency energy component (“LF component”). The HF component can comprise frequencies of 3 MHz to 300 MHz. The LF component can comprise frequencies of 3 MHz and below. In some examples, the gas mixture used to form the plasma can further comprise one or more inert gases in addition to the reactant and inhibitor. Examples of inert gases include helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe).

[00117] The conversion step 208 can be performed under conditions configured to deposit the inhibitor into a gap on the substrate such that a concentration of inhibitor deposited at a first depth within the gap is greater than a concentration of the inhibitor deposited at a second depth within the gap. The second depth is deeper than the first depth. For example, as shown in FIG. 3D, a relatively greater concentration of inhibitor

312 adsorbs on upper surfaces 320 than lower surfaces 322 within gap 302. Lower surfaces 322 are deeper in gap 302 than upper surfaces 320.

[00118] The concentration gradient of the inhibitor on sidewalls within the gap can be controlled by controlling various processing conditions. Example processing conditions include total processing chamber pressure, partial pressure of the inhibitor, partial pressure of other gases (for example, a diluent gas), substrate temperature, gas flow rates, inhibitor gas flow duration, and plasma characteristics. For example, the use of a capacitively coupled plasma can cause directional effects that drive the inhibitor into a gap. As described above, the capacitively coupled plasma can comprise a HF component and a LF component. Examples of frequencies for the HF component can comprise frequencies of 3 MHz to 300 MHz. In some examples, the HF component can comprise a power of 50 to 6000 W. Increasing the power of the higher frequency component can drive the inhibitor deeper within the gap. Further, in some examples, the LF component also can comprise a power of 0 to 5000 W. Examples of frequencies for the LF component can include frequencies of 3 MHz and below. The use of the LF component also can help drive the inhibitor deeper within the gap. Increasing the power of the LF component also can drive the inhibitor deeper within the gap. In some examples, increasing the flow rate of the inhibitor can help achieve a deeper effective depth for inhibition. For example, in one experiment of a high-aspect ratio gapfill, increasing a flow rate of NF_3 inhibitor from 12 standard cubic-centimeters per second (sccm) to 20 sccm while maintaining other processing conditions helped drive the inhibition-effective depth from 0.46 μm to 2.2 μm . Thus, radiofrequency powers, frequencies, and gas flow rates can be adjusted to help deposit inhibitor on deeper locations within the gap.

[00119] Continuing with method 200, the PEALD cycle 202 further comprises performing an in-situ passivation step 214. In-situ passivation step 214 comprises forming a plasma using a passivation agent to remove at least some of the inhibitor from surfaces within the gap. Any suitable passivation agent can be used. Examples include hydrogen-based passivation, carbon-based passivation, and nitrogen-based passivation. In some examples, the passivation agent comprises one or more of NH_3 and H_2 .

[00120] In some examples, at 216, the PEALD cycle comprises switching gas flow while keeping the plasma on continuously. In such examples, one or more valves of flow control hardware can be operated to switch gas flowing into the processing

chamber from the conversion step gas mixture to the passivation agent. This can be performed without pre-charging the gas lines. Further, switching the gas flow is performed while supplying radiofrequency power continuously. By keeping the plasma on and switching gas flow, the PEALD cycle 202 can help reduce processing time and increase throughput.

[00121] The in-situ passivation step 214 can be performed for any suitable duration. In some examples, each passivation step is 0.05 to 0.5 seconds. In some examples, each passivation step is approximately 0.1 seconds. In some examples, each passivation step is approximately 0.3 seconds. In some examples, the cumulative passivation time for the plurality of PEALD cycles 202 is 20 to 150 seconds. In some examples, the cumulative passivation time is 30 to 60 seconds. In some examples, the cumulative passivation time is 100 to 140 seconds. Use of relatively shorter duration passivation steps and/or lesser cumulative passivation time can help improve throughput. This can help speed up gapfill processes in applications where a relatively higher inhibitor concentration is acceptable, such as 3D NAND (three-dimensional NOT AND memory) device applications. Alternatively, use of relatively longer duration passivation steps and/or greater cumulative passivation time can help remove more inhibitor than shorter passivation steps. This can help reduce inhibitor concentration in gapfill applications where a high film quality is desired, such as DRAM STI applications. In other examples, each passivation step and/or a cumulative passivation time can be outside of these ranges.

[00122] FIG. 3E shows the result of an in-situ passivation step 214 performed on substrate 300. Plasma 316 remains on while a passivation agent 330 is flowed into the processing chamber. As shown in FIG. 3E, the passivation agent 330 can react with adsorbed inhibitor to form volatile species 332. This helps remove inhibitor from film 318 and helps avoid buildup of inhibitor in film 318 during PEALD processing.

[00123] In some examples, the PEALD cycle 202 further comprises performing an optional purge step 218. In other examples, the optional purge step at 218 can be omitted. For example, by introducing the passivation agent at 214, residual reactant and inhibitor can be purged from the processing chamber. In this manner, the in-situ passivation step can serve as the purge step in PEALD cycle to separate oxidizer and incoming film precursor of the subsequent PEALD cycle.

[00124] Continuing, at 220, method 200 determines whether to perform additional PEALD cycles 202. If additional PEALD cycles 202 are to be performed,

method 200 returns to 204 and performs a dosing step of a next PEALD cycle. If no additional PEALD cycles are to be performed, method 200 can proceed to 224 and terminate. Any suitable number of PEALD cycles 202 can be performed during PEALD processing.

[00125] FIG. 3F shows the result of an arbitrary number of PEALD cycles 202 to deposit additional layers of film 318 onto substrate 300. Due to in-situ passivation, film 318 comprises relatively less inhibitor than oxide film 104 in FIG. 1D. As such, less inhibitor will be trapped by additional layers of film 318.

[00126] FIG. 3G shows substrate 300 after further PEALD processing to fill gap 302 with film 318. By performing sequential PEALD cycles 202 with in-situ passivation steps 214, film 318 comprises relatively less inhibitor than oxide film 104 in FIG. 1F. This helps form film 318 that is higher quality than films formed without in-situ passivation.

[00127] As mentioned above, the duration of passivation step 214 can be varied in accordance with a desired performance characteristic. A relatively longer passivation step duration can help reduce inhibitor concentration. A relatively shorter passivation step duration can help reduce processing time and improve throughput. FIG. 4 shows a graph 400 of fluorine concentration as a function of depth for various silicon oxide films. Line 402 (dotted line) shows fluorine concentration for a film deposited using a PEALD process that omits inhibitor and passivation. Line 404 (dashed line) shows fluorine concentration for a film deposited with an inhibited PEALD process that omits passivation. The fluorine concentration for this film is approximately $1\text{--}1.5 \times 10^{21}$ F atoms/cm³.

[00128] Line 406 (short-dashed line) shows fluorine concentration for a film deposited with an inhibited PEALD process and a conventional post-deposition passivation. The passivation was performed for approximately 120 seconds. As a result of passivation, the fluorine concentration is less than that of line 404, which omits passivation.

[00129] Line 408 (dash-dot) shows fluorine concentration for a film deposited using PEALD and in-situ passivation steps of 0.1 second duration in each PEALD cycle. Over approximately 400 PEALD cycles, the total passivation time budget is approximately 40 seconds. Thus, a similar fluorine concentration can be achieved with less passivation time budget. This can help throughput in some examples. Line 410 (solid line) shows fluorine concentration for a film deposited using PEALD and in-situ

passivation steps of 0.3 second duration in each PEALD cycle. Over approximately 400 PEALD cycles, the total passivation time budget is approximately 120 seconds. The fluorine concentration is less than that of line 406. Thus, in comparison to post-deposition passivation, a lesser concentration of fluorine can be achieved with a similar passivation time budget. In some examples, a film deposited using PEALD cycles and in-situ passivation can comprise a fluorine concentration that is less than 4×10^{20} F atoms/cm³.

[00130] FIG. 5 shows a flow diagram of an example method 500 for processing a substrate. Method 500 comprises, at 502, performing a plurality of PEALD cycles to deposit a film into a gap on the substrate. At 504, PEALD cycle 502 comprises, in a first step, introducing a film precursor into the processing chamber to adsorb the film precursor to surfaces within the gap. Any suitable film precursor can be used. Examples include silicon-containing precursors, such as those described above. Method 500 further comprises, at 506, purging the processing chamber after the first step.

[00131] Continuing, at 508, PEALD cycle 502 comprises a second step. In the second step at 508, method 500 comprises forming a plasma using a gas mixture comprising a reactant and an inhibitor. This exposes the substrate to the inhibitor and converts the film precursor into a film within the gap. In some examples, at 510, the film comprises one or more of silicon oxide, silicon oxynitride, silicon oxycarbide, or silicon oxycarbonitride.

[00132] In some examples, at 512, the amount of inhibitor deposited at a first depth is greater than a concentration of inhibitor deposited at a second depth, the second depth being deeper in the gap than the first depth. In this manner, the inhibitor provides a greater inhibition effect on upper surfaces within the gap than lower surfaces within the gap. As mentioned above, processing conditions can be adjusted to help control the concentration gradient of the inhibitor on sidewalls within the gap. For example, increasing the radiofrequency power used to form the plasma can drive the inhibitor deeper within the gap. The use of the LF component in addition to a HF component also can help drive the inhibitor deeper within the gap. In some examples, increasing the flow rate of the inhibitor can help achieve a deeper effective depth for inhibition. Further, the use of a relatively lower pressure can help achieve a deeper effective depth for inhibition than the use of a relatively higher pressure in the processing chamber. In some examples, at 514, the inhibitor comprises one or more of molecular fluorine,

nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane.

[00133] Continuing to FIG. 5B, at 520, each PEALD cycle 502 comprises a third step performed after the second step at 508. In the third step at 520, method 500 comprises exposing the substrate to a plasma comprising a passivation agent to remove at least some of the inhibitor from surfaces within the gap. In some examples, at 522, the passivation agent comprises one or more of NH_3 and H_2 . In other examples, any other suitable passivation agent can be used. In some examples, at 524, method 500 comprises switching gas flow from the gas mixture to the passivation agent while maintaining the plasma. As such, at 524, radiofrequency power is supplied continuously such that the plasma remains on between the second step and the third step. This can help reduce processing times and increase throughput.

[00134] In some examples, at 526, each third step is 0.05 to 0.5 seconds. In some examples, at 528, each third step is 0.3 seconds or less. In some examples, at 530, the cumulative passivation time for the plurality of PEALD cycles is 20 to 150 seconds. Use of relatively shorter duration passivation steps and/or lesser cumulative passivation time can help improve throughput. Alternatively, use of relatively longer duration passivation steps and/or greater cumulative passivation time can help remove more inhibitor than shorter passivation steps.

[00135] In some examples, at 532, the PEALD cycle 502 comprises purging the processing chamber after performing the third step. In some such examples, the purge step at 532 can comprise forming a radiofrequency plasma in an “RF purge” step. However, in other examples, the optional purge step at 532 can be omitted. For example, by performing passivation at 520 after the second step at 508, the reactant can be separated from the film precursor of the subsequent PEALD cycle by the passivation agent. By omitting a purge step between PEALD cycles, the examples can help reduce processing times and improve throughput.

[00136] As mentioned above, performing in-situ passivation can help reduce inhibitor residual levels compared to examples that omit in-situ passivation. In some examples that use a fluorine-containing inhibitor, after performing the plurality of PEALD cycles at 502, the film can comprise a fluorine concentration that is less than 4×10^{20} F atoms/cm³.

[00137] Continuing, at 534, method 500 optionally comprises performing a modified PEALD cycle that omits exposing the substrate to the passivation agent. Additionally, in some examples, at 536, method 500 optionally comprises performing a modified PEALD cycle that omits exposing the substrate to the inhibitor in the second step. As such, a PEALD process can include one or more modified PEALD cycles without inhibition and/or passivation. Such modified PEALD cycles can be performed prior to, or after, the PEALD cycles performed at 502.

[00138] FIG. 6 schematically shows an example ALD tool that can implement the examples described above with reference to FIGS. 2-5. ALD tool 600 comprises a processing chamber 602 and a substrate support 604 within the processing chamber. The substrate support 604 is configured to support a substrate 606 disposed within the processing chamber 602. The substrate support 604 comprises a substrate heater 608. In other examples, a heater can be omitted, or can be located elsewhere within processing chamber 602. In some examples, the substrate heater is configured to heat to a temperature of 50 °C to 800 °C. In other examples, a temperature outside this range can be used.

[00139] The ALD tool 600 further comprises a showerhead 610. In other examples, a processing tool can comprise a nozzle or other apparatus for introducing gas into processing chamber 602, as opposed to or in addition to a showerhead. The ALD tool 600 further comprises flow control hardware 612. The flow control hardware 612 connects processing gas source(s) to the processing chamber. In the depicted example, the flow control hardware 612 connects a film precursor source 616, a reactant source 618, an inhibitor source 620, a passivation agent source 622, and optionally an inert gas source 624 to the processing chamber. The flow control hardware 612 can include any suitable components. Examples include mass flow controllers, valves, and conduits. For example, the flow control hardware 612 can comprise one or more valves controllable to place a selected gas source or selected gas sources in fluid connection with showerhead 610. The flow control hardware 612 also can comprise one or more mass flow controllers or other controllers for controlling a mass flow rate of gas. Any suitable flow rates can be used.

[00140] The silicon-containing film precursor source 616 comprises any suitable precursor chemical(s) for forming a silicon-containing film. Examples silicon-containing films include films comprising silicon oxide, silicon nitride, silicon oxynitride, silicon carbide, silicon oxycarbide, silicon carbonitride, and silicon

oxycarbonitride. Examples of silicon-containing film precursors include those listed above. In some examples, a film precursor source can comprise a mixture of chemicals. In other examples, two or more separate film precursor sources can be used to provide a respective two or more film precursors. An example precursor for providing nitrogen for formation of a silicon nitride film or silicon oxynitride film is N_2O .

[00141] Optionally, a carbon-containing precursor source (not shown) can be used to provide a carbon-containing precursor for forming a silicon carbide film. Example carbon-containing precursors include those listed above.

[00142] Reactant source 618 can comprise any suitable compound for converting film precursor to a film on substrate 606. In some examples, reactant source 618 comprises an oxidant. Examples include molecular oxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2), ozone (O_3), carbon dioxide (CO_2), and nitrogen oxides such as nitrous oxide (N_2O).

[00143] The inhibitor source 620 can comprise any suitable inhibitor. Examples include hydrogen, nitrogen-containing inhibitors such as nitrogen or ammonia, fluorine-containing inhibitors such as nitrogen trifluoride, carbon-containing inhibitors, and mixtures thereof. Examples of suitable fluorine-containing inhibitors can include fluorine (F_2), nitrogen trifluoride (NF_3), sulfur hexafluoride (SF_6), hydrogen fluoride (HF), xenon difluoride (XeF_2), and fluorocarbons such as tetrafluoromethane (CF_4) or hexafluoroethane (C_2F_6). Examples of suitable nitrogen-containing inhibitors can include nitrogen (N_2), ammonia (NH_3), amines, diamines, and aminoalcohols. Examples of suitable carbon-containing inhibitors can include alkanes, alkenes, alkynes, cyclic hydrocarbons, aromatics, alcohols, aldehydes, esters, ethers, ketones, aldehydes, alkyl halides, alkyl amines, and alkyl diamines.

[00144] Passivation agent source 622 can comprise any suitable passivation agent. In some examples, passivation agent source 622 comprises one or more of ammonia and hydrogen. This can provide a reducing environment in processing chamber 602 during a passivation step to help remove inhibitor from surfaces of substrate 606.

[00145] The optional inert gas source 624 can comprise any suitable inert gas. Examples include argon, helium, neon, krypton, and xenon. An inert gas can be flowed into processing chamber 602 during a purge step, for example.

[00146] The ALD tool 600 further comprises an exhaust system 632. The exhaust system 632 is configured to exhaust gases from the processing chamber 602.

The exhaust system 632 can comprise any suitable hardware, including one or more low vacuum pumps and one or more high vacuum pumps. Together, flow control hardware 612 and exhaust system 632 can be operated to achieve a selected pressure in processing chamber 602 during substrate processing. Further, exhaust system 632 can be operated to purge processing chamber 602.

[00147] The ALD tool 600 further comprises a radiofrequency power source 634 that is electrically connected to showerhead 610. Radiofrequency power source 634 is configured to form a plasma using a gas mixture.

[00148] For example, during a conversion step, radiofrequency power source 634 can be operated to form a plasma using a gas mixture comprising a reactant and an inhibitor. Additionally, during a passivation step, radiofrequency power source 634 can be operated to form a plasma using a passivation agent. As described above, in some examples, radiofrequency power source 634 is operated continuously between a conversion step and a passivation step. The substrate support 604 is configured as a grounded opposing electrode in this example. In other examples, the radiofrequency power source 634 can supply radiofrequency power to substrate support 604, or to another suitable electrode structure. Thus, the radiofrequency power source 634 forms a capacitively coupled plasma (CCP) when operated. Further, the radiofrequency power source 634 can be operated to pulse the plasma, for example, using any suitable duty cycle. Alternatively, the radiofrequency power source 634 can be operated to form a continuous-wave plasma.

[00149] The ALD tool 600 further includes a matching network 636 for impedance matching of the radiofrequency power source 634. The radiofrequency power source 634 can be configured to provide radiofrequency energy of any suitable frequency and power. Examples frequencies include 400 kHz, 13.56 MHz, 27 MHz, 60 MHz, and 90 MHz. In some examples, the radiofrequency power source 634 is configured to operate at a plurality of different frequencies and/or powers. For example, as described above, a plasma can comprise a LF radiofrequency energy component and a HF radiofrequency energy component. Examples of frequencies for the LF radiofrequency energy component can include frequencies of 3 MHz and below. The LF radiofrequency energy component can comprise a power of 0 to 5000 W, in some examples. Further, the HF radiofrequency energy component can comprise frequencies of 3 MHz to 300 MHz. The HF radiofrequency energy component can comprise a power of 50 to 6000 W, in some examples.

[00150] The ALD tool 600 further comprises a controller 650 configured to control operation of the processing tool. The controller 650 is operatively coupled to the substrate heater 608, the flow control hardware 612, the exhaust system 632, and the radiofrequency power source 634. The controller 650 is configured to control various functions of ALD tool 600 to perform PEALD cycles including dosing steps, purge steps, conversion steps, and passivation steps. For example, the controller 650 is configured to operate the flow control hardware 612 to flow a selected gas or mixture of gases at a selected rate into the processing chamber 602. The controller 650 is further configured to operate the exhaust system 632 to remove gases from processing chamber 602. The controller 650 can, for example, control the exhaust system 632 and/or the flow control hardware 612 to purge the processing chamber 602. The controller 650 is configured to operate the radiofrequency power source 634 to form a plasma, as well as to control any other suitable functions of ALD tool 600. In some examples, the controller can operate the radiofrequency power source 634 to form a plasma and, while keeping the plasma on, operate the flow control hardware to switch gas flow from the reactant and inhibitor to the passivation agent. The controller 650 can comprise any suitable computing system. Example computing systems are described below with reference to FIG. 7.

[00151] FIG. 7 schematically shows a non-limiting example of a computing system 700 that can enact one or more of the methods and processes described above. Computing system 700 is shown in simplified form. Computing system 700 can take the form of one or more personal computers, workstations, computers integrated with substrate processing tools, and/or network accessible server computers.

[00152] Computing system 700 includes a logic subsystem 702 and a storage subsystem 704. Computing system 700 can optionally include a display subsystem 706, input subsystem 708, communication subsystem 710, and/or other components not shown in FIG. 7. Controller 650 is an example of computing system 700.

[00153] Logic subsystem 702 includes one or more physical devices configured to execute instructions. For example, the logic subsystem can be configured to execute instructions that are part of one or more applications, services, programs, routines, libraries, objects, components, data structures, or other logical constructs. Such instructions can be implemented to perform a task, implement a data type, transform the state of one or more components, achieve a technical effect, or otherwise arrive at a desired result.

[00154] The logic subsystem can include one or more processors configured to execute software instructions. Additionally or alternatively, the logic subsystem can include one or more hardware or firmware logic subsystems configured to execute hardware or firmware instructions. Processors of the logic subsystem can be single-core or multi-core, and the instructions executed thereon can be configured for sequential, parallel, and/or distributed processing. Individual components of the logic subsystem optionally can be distributed among two or more separate devices, which can be remotely located and/or configured for coordinated processing. Aspects of the logic subsystem can be virtualized and executed by remotely accessible, networked computing devices configured in a cloud-computing configuration.

[00155] Storage subsystem 704 includes one or more physical devices configured to hold instructions 712 executable by the logic subsystem to implement the methods and processes described herein. When such methods and processes are implemented, the state of storage subsystem 704 can be transformed—e.g., to hold different data.

[00156] Storage subsystem 704 can include removable and/or built-in devices. Storage subsystem 704 can include optical memory (e.g., CD, DVD, HD-DVD, Blu-Ray Disc, etc.), semiconductor memory (e.g., RAM, EPROM, EEPROM, etc.), and/or magnetic memory (e.g., hard-disk drive, floppy-disk drive, tape drive, MRAM, etc.), among others. Storage subsystem 704 can include volatile, nonvolatile, dynamic, static, read/write, read-only, random-access, sequential-access, location-addressable, file-addressable, and/or content-addressable devices.

[00157] It will be appreciated that storage subsystem 704 includes one or more physical devices. However, aspects of the instructions described herein alternatively can be propagated by a communication medium (e.g., an electromagnetic signal, an optical signal, etc.) that is not held by a physical device for a finite duration.

[00158] Aspects of logic subsystem 702 and storage subsystem 704 can be integrated together into one or more hardware-logic components. Such hardware-logic components can include field-programmable gate arrays (FPGAs), program- and application-specific integrated circuits (PASIC / ASICs), program- and application-specific standard products (PSSP / ASSPs), system-on-a-chip (SOC), and complex programmable logic devices (CPLDs), for example.

[00159] When included, display subsystem 706 can be used to present a visual representation of data held by storage subsystem 704. This visual representation can

take the form of a graphical user interface (GUI). As the herein described methods and processes change the data held by the storage subsystem, and thus transform the state of the storage subsystem, the state of display subsystem 706 can likewise be transformed to visually represent changes in the underlying data. Display subsystem 706 can include one or more display devices utilizing virtually any type of technology. Such display devices can be combined with logic subsystem 702 and/or storage subsystem 704 in a shared enclosure, or such display devices can be peripheral display devices.

[00160] When included, input subsystem 708 can comprise or interface with one or more user-input devices such as a keyboard, mouse, or touch screen. In some examples, the input subsystem can comprise or interface with selected natural user input (NUI) componentry. Such componentry can be integrated or peripheral, and the transduction and/or processing of input actions can be handled on- or off-board. Example NUI componentry can include a microphone for speech and/or voice recognition, and an infrared, color, stereoscopic, and/or depth camera for machine vision and/or gesture recognition.

[00161] When included, communication subsystem 710 can be configured to communicatively couple computing system 700 with one or more other computing devices. Communication subsystem 710 can include wired and/or wireless communication devices compatible with one or more different communication protocols. As non-limiting examples, the communication subsystem can be configured for communication via a wireless telephone network, or a wired or wireless local- or wide-area network. In some examples, the communication subsystem can allow computing system 700 to send and/or receive messages to and/or from other devices via a network such as the Internet.

[00162] As mentioned above, it can be challenging to fill a relatively deep and/or high aspect ratio gaps using a conformal deposition process such as ALD without forming voids. Even where void formation is avoided, low density seams can form where the growth fronts of the gapfill film converge, thereby preventing ion flux from the plasma from densifying the film.

[00163] To avoid void and/or low density seam formation, etching can be utilized to form a tapered profile within gaps on a substrate. The tapered profile allows for ion bombardment in a deposition process to densify the seam while filling the gap. In this manner, the seam can have a similar density to other portions of the gapfill film.

[00164] A tapered profile can be formed using a plasma etching process. However, a plasma etching process used to form the tapered profile can also cause damage to some substrate structures. As one illustrative example, etching to form a tapered profile in a silicon oxide-based (e.g., SiO, SiON, SiOC, etc.) gapfill film also can damage a silicon nitride hardmask (e.g., that was used as a patterning mask to form the gap itself). More particularly, fluorine-based etching chemistries (e.g., nitrogen trifluoride, hydrogen fluoride, tungsten fluoride, molybdenum fluoride, etc.), used to etch silicon oxide-based gapfill films also can etch such a silicon nitride hardmask. Damaging the silicon nitride hardmask can impact downstream processing steps, and thereby decrease process yields and/or throughput.

[00165] One possible method of protecting a hardmask, such as a silicon nitride hardmask, during such an etching process is to use a passivator. A passivator is a chemical agent that decreases an etching rate at surfaces to which the passivator adsorbs. The passivator can reduce a reactivity of the surface to the etching chemistry, and/or react preferentially with the etching agent. However, even with the use of a passivator, some hardmask damage can result. As an illustrative example, when etching a silicon oxide-based film, hydrogen (H₂) can be used as a passivator. However, while hydrogen does passivate silicon oxide-based surfaces, hydrogen does not have the same effect on silicon nitride surfaces. As such, if the etching process removes the silicon oxide from over the silicon nitride hardmask, the hydrogen does not passivate the silicon nitride surface effectively. As such, the silicon nitride hardmask can be damaged by etching.

[00166] FIG. 8A schematically shows a method 800 of forming a tapered profile in a film deposited in a gap on a substrate in which a silicon nitride hardmask is damaged. Method 800 uses hydrogen as a passivator. FIGS. 8B-8C illustrates an example substrate on which method 800 is performed. First referring to FIG. 8A at 802, initially a substrate has a partial gapfill film formed in a gap. FIG. 8B shows an example partial gapfill film 810 formed in gaps between pillars (e.g., pillars 812A, 812B) and over a hardmask 813 of a substrate 814. The partial gapfill film 810 has been conformally deposited on substrate 814 using, for example, plasma-enhanced atomic layer deposition (PEALD). As can be seen, a relatively narrow opening 816 remains to be filled. As the growth fronts of the partial gapfill film 810 converge within opening 816, ions from the plasma can have a harder time reaching the growth front compared to when the opening is wider earlier in the gapfill process. As such, continuing the

gapfill deposition process can result in the formation of a lower density seam compared to the density of other regions of the gapfill film. The lower density seam can cause downstream processing issues, such as seam blowout during a subsequent etching process.

[00167] As such, and returning to FIG. 8A, method 800 comprises an etching process utilizing a plurality of etch cycles 804 to form a tapered profile in the partial gapfill film. After forming the tapered profile, the gapfill deposition process can continue with less risk of forming a low-density seam.

[00168] Each etch cycle comprises, at 806, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched, the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆). The etch cycle further comprises, at 808, passivating the substrate surface with an Ar/H₂ plasma. The etch cycle can be repeated until the tapered profile is formed.

[00169] The etching at 806 can be diffusion limited, such that the depth of the etching in the gap is a function of etching time. Shorter etching times can thus result in less etching deeper within the gap, leading to the tapered profile. Further, the etching at 806 can remove passivator at a faster rate closer to an opening of the gap than deeper within the gap. As such, the etch rate is higher closer to the opening of the gap rather than deeper within the gap. This can contribute to the production of a tapered profile.

[00170] However, the gapfill film covering the hardmask (e.g., hardmask 813 of substrate 814) also can be etched at a relatively higher rate than the gapfill film within the gap. The passivator thus may provide inadequate protection during the etching. This can cause the partial gapfill film to be etched away from over the hardmask, resulting in damage to the hardmask.

[00171] FIG. 8C shows the substrate 814 of FIG. 8B after performing the etching process of FIG. 8A. As can be seen, a tapered profile formed has been formed in partial gapfill film 810. However, hardmask 813 also has been fully etched away. In other examples, a hardmask may be partially etched, but still damaged.

[00172] Accordingly, examples are disclosed that relate to protecting a hardmask from damage when etching a tapered profile into a partial gapfill film. Some disclosed examples utilize one or more ALD cycles at intermediate points during an etching

process to deposit a protective layer over the hardmask. The protective layer can be formed from a same material as the partial gapfill film in some examples. Performing one or more of such ALD cycles provides added protection to the hardmask, while still enabling the tapered profile to be formed.

[00173] Examples also are disclosed that relate to topographically selective passivation methods. The disclosed topographically selective passivation methods can be performed alternatively or additionally to depositing a protective layer using one or more ALD cycles. The disclosed example topographically selective passivation methods utilize a hydrogen-containing passivator and an oxygen-containing passivator to passivate a partial gapfill film deposited over a hardmask. The hydrogen-containing passivator and the oxygen-containing passivator can be deposited using conditions, such as plasma characteristics and/or exposure times, that deposit more passivator on surfaces at and closer to a substrate surface than deeper within the gap. The oxygen-containing passivator can provide for stronger passivation compared to the use of hydrogen-containing passivators alone. This results in greater passivation of the partial gapfill film in regions over the hardmask than deeper within the gap. In various examples, the substrate can be exposed to the hydrogen-containing passivator and the oxygen-containing passivator simultaneously or sequentially.

[00174] Referring now to FIG. 9A, an example method 900 for forming a tapered profile in a film deposited in a gap on a substrate using a deposition-etch cycle is shown. FIGS. 9B-9C illustrates an example substrate on which method 900 is performed. In some examples, method 900 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized. First referring to FIG. 9A at 902, initially a substrate has a partial gapfill film formed in a gap. FIG. 9B shows an example partial gapfill film 910 formed in gaps between pillars (e.g., pillars 912A, 912B) and over a hardmask 913 of a substrate 914. The partial gapfill film 910 has been conformally deposited on substrate 914 using, for example, plasma-enhanced atomic layer deposition (PEALD). As can be seen, a relatively narrow opening 916 remains to be filled. In some examples, the partial gapfill film 910 comprises a silicon oxide-based film. Example silicon oxide-based films can include silicon oxide, silicon oxynitride, and silicon oxycarbide, among others. The hardmask 913 can be a silicon nitride hardmask, a silicon hardmask, or other suitable hardmask.

[00175] Returning to FIG. 9A, method 900 comprises performing a deposition-etching process utilizing a plurality of deposition-etch cycles 904 to form a tapered

profile in the partial gapfill film while protecting a hardmask on a substrate. Each deposition-etch cycle comprises, at 906, depositing a protective layer. In some examples the protective layer can be the same material as the partial gapfill film 910. In other examples, the protective layer can comprise a different, but related, material composition that etches using a same chemistry as the chemistry used to etch the partial gapfill film 910. As examples, where the gapfill film is a silicon oxide film, the protective layer can be silicon oxide, or a doped silicon oxide (e.g., SiON, SiOC, etc.).

[00176] In some examples, depositing the protective layer comprises performing one or cycles of PEALD to conformally deposit a protective film over structures of FIG. 9B. Performing a cycle of PEALD deposition comprises first adsorbing a silicon-containing precursor onto the substrate 914. Example silicon-containing precursors include those listed above with reference to FIG. 2.

[00177] After adsorbing the silicon-containing precursor, the adsorbed silicon-containing precursor is chemically converted to a silicon oxide-based film by introducing an oxygen-containing reactant to react with the adsorbed silicon-containing precursor. Example oxygen-containing precursors include molecular oxygen (O₂), water (H₂O), hydrogen peroxide (H₂O₂), ozone (O₃), carbon dioxide (CO₂), and nitrogen oxides such as nitrous oxide (N₂O). An example precursor for providing nitrogen and oxygen for formation of a silicon oxynitride film is N₂O.

[00178] Returning to FIG. 9A, method 900 comprises performing an etching process utilizing a plurality of etch cycles 908 to form a tapered profile in the partial gapfill film. Each etch cycle comprises, at 918, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched, the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆).

[00179] Etching step 918 can be performed under any suitable conditions. In some examples, etching step 918 can be carried out at a temperature within a range of 300 °C and 650 °C. Similarly, in some examples, the etching step 918 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. In some examples, the etching step 918 can be carried out at an HF RF power within a range of 0.5 kW to 6 kW. In some examples an LF power component also can be used. In other examples, a single frequency HF plasma is used. Example HF and RF frequencies include those listed

above. In further examples, temperatures, pressures, and/or RF powers outside of these ranges can be utilized when performing etching step 918.

[00180] The etch cycle 908 further comprises, at 920, passivating the substrate surface with a plasma. In some examples the plasma can comprise a hydrogen-containing plasma. In some such examples, the plasma can comprise an Ar/H₂ plasma. In other examples, the plasma can comprise an ammonia plasma (e.g., an Ar/NH₃ plasma) or a methane plasma (e.g., an Ar/CH₄ plasma). In even further examples, the plasma can comprise a plasma with another hydrogen-containing molecule that can be used as a passivator.

[00181] Passivation step 920 can be performed under any suitable conditions. In some examples, the passivation step 920 can be carried out at a temperature within a range of 300 °C and 650°C. Further, in some examples, the passivation step 920 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. Additionally, the passivation step 920 can be carried out using HF RF plasma power within a range of 0.5 kW to 6 kW. In other examples, any suitable temperature, pressure, and plasma conditions outside of these ranges can be utilized when performing passivation step 920.

[00182] The deposition-etch cycle 904 can be performed a plurality of times until the tapered profile has been formed. In some examples, the deposition-etch cycle comprises performing one to ten cycles of ALD deposition followed by five to thirty etch cycles 908. In such examples, the deposition-etch cycle 904 can be repeated twenty to one hundred times. In other examples, the deposition-etch cycle 904 comprises performing any other suitable number of ALD deposition, etch cycles 908, and/or deposition-etch cycles.

[00183] FIG. 9C shows the substrate 914 of FIG. 9B after performing the deposition-etching process of FIG. 9A. As can be seen, a tapered profile formed has been formed in partial gapfill film 910. Further, hardmask 913 remains unetched and undamaged.

[00184] As mentioned above, topographically selective passivation methods alternatively or additionally can be used to help protect a hardmask when etching a partial gapfill film to form a tapered profile. In such examples, a hydrogen-containing passivator and an oxygen-containing passivator are used. The hydrogen-containing passivator and the oxygen-containing passivator can be introduced together (co-flowed) or sequentially.

[00185] FIG. 10 shows an example method 1000 for forming a tapered profile in a film deposited in a gap on a substrate using a co-flow passivation-etch cycle 1004. At 1002, initially a substrate has a partial gapfill film formed in a gap. The partial gapfill film can be conformally deposited on substrate using, for example, plasma-enhanced atomic layer deposition (PEALD). In some examples the partial gapfill film comprises an oxide film. Example oxide films include silicon oxide, silicon oxynitride, and silicon oxycarbide.

[00186] Method 1000 further comprises performing a co-flow passivation-etch process utilizing a plurality of co-flow passivation-etch cycles 1004 to form a tapered profile in the partial gapfill film while protecting a hardmask on a substrate. In some examples, method 1000 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized.

[00187] The co-flow passivation-etch cycle 1004 comprises, at 1006, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched, the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆).

[00188] Etching step 1006 can be performed under any suitable conditions. In some examples, etching step 1006 can be carried out at a temperature within a range of 300 °C and 650 °C. Similarly, in some examples, the etching step 1006 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. In some examples, the etching step 1006 can be carried out at using HF RF power within a range of 0.5 kW to 6 kW. In some examples, an LF RF power component also can be used. In other examples, the LF RF power component can be omitted.

[00189] The co-flow passivation-etch cycle 1004 further comprises, at 1008, passivating the substrate surface with a plasma comprising a hydrogen-containing passivator and an oxygen-containing passivator. In this example, the hydrogen-containing passivator is hydrogen, and the oxygen-containing passivator is nitrous oxide (N₂O). In other examples, a different hydrogen-containing passivator and/or a different oxygen-containing passivator can be used. Examples of other hydrogen-containing passivators include ammonia, hydrazine, and amines. Examples of other oxygen-containing passivators include O₂.

[00190] The passivation step performed at 1008 utilizes a plasma to form reactive species from the hydrogen-containing passivator and the oxygen-containing passivator. The plasma conditions and/or plasma exposure time(s) are configured to perform a topologically selective application of the passivator onto the substrate. This can cause a greater concentration of the hydrogen-containing passivator and the oxygen-containing passivator to be adsorbed to substrate surfaces over the hardmask than on sidewall surfaces. This helps protect the hardmask while still permitting formation of the tapered profile by etching.

[00191] Passivation step 1008 can be performed under any suitable conditions. In some examples, the passivation step 1008 can be carried out at a temperature within a range of 300 °C and 650°C. In some examples, the passivation step 1008 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. In some examples, the passivation step 1008 can be carried out at an HF power within a range of 0.5 kW to 6 kW. In other examples, suitable temperatures, pressures, and/or plasma conditions outside of these ranges can be utilized when performing passivation step 1008.

[00192] Performing passivation step 1008 using conditions in the above ranges can selectively deposit greater concentrations of the hydrogen-containing passivator and the oxygen-containing passivator onto substrate surfaces over the hardmask than on sidewall surfaces. Pressures within the above range can result in a higher ion flux from the plasma onto the substrate in a direction normal to the substrate surface than compared to higher pressures. This can provide for greater topographical selectivity for the passivator exposure compared to the use of higher pressures. Similarly, using HF RF powers within the above range can provide relatively higher plasma densities compared to lower powers. Higher plasma densities can increase the ion bombardment and enable shorter passivation times to be utilized, compared to passivation performed at lower powers. On the other hand, higher plasma powers can cause higher rates of sputtering of the substrate surface compared to lower plasma powers, which can remove adsorbed passivator from the surface. As such, the RF power for the passivation step 1008 can be selected to balance these factors. In some examples, an LF RF power component can be used along with an HF RF power component to perform passivation step 1008. In other examples, the LF RF power component can be omitted.

[00193] Further, passivation step 1008 can be performed for any suitable length of time. Longer passivation times of the hydrogen-containing passivator and the oxygen-containing passivator can result in greater passivation within gaps on a

substrate than the hydrogen-containing passivator alone. As such, longer exposure times to the hydrogen-containing passivator and the oxygen containing passivator can result in enhanced passivation in the gap. In contrast, shorter exposures to the hydrogen-containing passivator and the oxygen-containing passivator primarily affects the field, where the hardmask is located on the substrate, and thereby reduces passivation within the gap compared to longer exposures. Thus, varying the time of exposure to the hydrogen-containing passivator and the oxygen-containing passivator can allow for tunability of the desired etch profile. Passivation step 1008 can be performed for any suitable length of time. In some examples, the passivation time can include times between 0.1 seconds and 5 seconds. In other examples, times outside of this range can be used.

[00194] The co-flow passivation-etch cycle 1004 can be performed a plurality of times until the tapered profile has been formed. In some examples, the co-flow passivation-etch cycle 1004 can be performed twenty to one hundred times. In other examples, the co-flow passivation-etch cycle 1004 can be performed a number of times outside this range.

[00195] As described above, topographically selective passivation methods can utilize a hydrogen-containing passivator and an oxygen-containing passivator introduced together (co-flowed), or sequentially. FIG. 11 shows an example method 1100 for forming a tapered profile in a film deposited in a gap on a substrate using a first sequential passivation-etch cycle 1104. First, at 1102, initially a substrate has a partial gapfill film formed in a gap. The partial gapfill film can be conformally deposited on substrate using, for example, plasma-enhanced atomic layer deposition (PEALD). In some examples the partial gapfill film comprises an oxide film. Example oxide films include silicon oxide, silicon oxynitride, and silicon oxycarbide.

[00196] Method 1100 further comprises performing a sequential passivation-etch process utilizing a plurality of sequential passivation-etch cycles 1104 to form a tapered profile in the partial gapfill film while protecting a hardmask on a substrate. In some examples, method 1100 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized.

[00197] The sequential passivation-etch cycle 1104 comprises, at 1106, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen

trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆).

[00198] Etching step 1106 can be performed under any suitable conditions. In some examples, etching step 1106 can be carried out at a temperature within a range of 300 °C and 650 °C. Similarly, in some examples, the etching step 1106 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. In some examples, the etching step 1106 can be carried out at an HF RF power within a range of 0.5 kW to 6 kW. In some examples, an LF RF power component with a frequency below 1 MHz can be used along with the HF RF power component. In other examples, the LF RF power component can be omitted.

[00199] The sequential passivation-etch cycle 1104 further comprises, at 1108, performing a hydrogen passivation step in which the substrate surface is exposed to a plasma comprising a hydrogen-containing passivator. In this example, the hydrogen containing passivator is hydrogen. In other examples, a different hydrogen-containing passivator can be used. Examples of other hydrogen-containing passivators include ammonia, hydrazine, and amines.

[00200] The hydrogen passivation step 1108 utilizes a plasma to form reactive species from the hydrogen-containing passivator. The plasma conditions are configured to perform a topologically selective application of the passivator onto the substrate. As described above, this can cause a greater concentration of the hydrogen-containing passivator to be adsorbed to substrate surfaces over the hardmask than on sidewall surfaces. This helps protect the hardmask while still permitting formation of the tapered profile by etching.

[00201] The hydrogen passivation step 1108 can be performed under any suitable conditions. In some examples, the hydrogen passivation step 1108 can be carried out at a temperature within a range of 300 °C and 650°C. In some examples, the hydrogen passivation step 1108 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. In some examples, the hydrogen passivation step 1108 can be carried out at an HF RF power within a range of 0.5 kW to 6 kW. In other examples, any suitable temperature, pressure, and power outside of these ranges can be utilized when performing the hydrogen passivation step 1108.

[00202] Further, the hydrogen passivation step 1108 can be performed for any suitable length of time. In some examples, the passivation time can include times

between 0.1 seconds and 5 seconds. In other examples, times outside of this range can be used.

[00203] The sequential passivation-etch cycle 1104 further comprises an oxygen passivation step 1110 in which the substrate surface is exposed to a plasma comprising an oxygen-containing passivator. In this example, the oxygen-containing passivator is nitrous oxide (N_2O). In other examples, a different oxygen-containing passivator can be used. Examples of other oxygen-containing passivators include O_2 .

[00204] The oxygen passivation step 1110 utilizes a plasma to form reactive species from the oxygen-containing passivator. The plasma conditions again are configured to perform a topologically selective application of the passivator onto the substrate. This can cause a greater concentration of the oxygen-containing passivator to be adsorbed to substrate surfaces over the hardmask than on sidewall surfaces. This helps protect the hardmask while still permitting formation of the tapered profile by etching.

[00205] The oxygen passivation step 1110 can be performed under any suitable conditions. In some examples, the oxygen passivation step 1110 can be carried out at a temperature within a range of 300 °C and 650°C. In some examples, the oxygen passivation step 1110 can be carried out at a pressure within a range of 0.5 Torr to 30 Torr. In some examples, the oxygen passivation step 1110 can be carried out at a high frequency (HF) power within a range of 0.5 kW to 6 kW. In other examples, passivation step 1110 can be performed outside of these ranges.

[00206] Further, the oxygen passivation step 1110 can be performed for any suitable length of time. In some examples, the passivation time can include times between 0.1 seconds and 5 seconds. In other examples, times outside of this range can be used.

[00207] The sequential passivation-etch cycle 1104 can be performed a plurality of times until the tapered profile has been formed. In some examples, the sequential passivation-etch cycle 1104 can be performed twenty to one hundred times. In other examples, the sequential passivation-etch cycle 1104 can be performed a number of times outside this range.

[00208] FIG. 12 shows an example method 1200 for forming a tapered profile in a film deposited in a gap on a substrate using a second sequential passivation-etch cycle 1204. In method 1200, oxygen passivation is performed before hydrogen passivation. First, at 1202, initially a substrate has a partial gapfill film formed in a gap, as described

above with regard to FIGS. 9-11. Method 1200 further comprises performing a sequential passivation-etch process utilizing a plurality of sequential passivation-etch cycles 1204 to form a tapered profile in the partial gapfill film while protecting a hardmask on a substrate. In some examples, method 1200 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized.

[00209] The sequential passivation-etch cycle 1204 comprises, at 1206, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched, the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆). Suitable conditions for the etching step 1206 include those listed above for FIGS. 9-11.

[00210] The sequential passivation-etch cycle 1204 further comprises an oxygen passivation step 1208 in which the substrate surface is exposed to a plasma comprising an oxygen-containing passivator. In this example, the oxygen-containing passivator is nitrous oxide (N₂O). In other examples, a different oxygen-containing passivator can be used. Examples of other oxygen-containing passivators include O₂. The plasma conditions are configured to perform a topologically selective application of the passivator onto the substrate, again to cause a greater concentration of the oxygen-containing passivator to be adsorbed to substrate surfaces over the hardmask than on sidewall surfaces. Suitable plasma conditions and exposure times for performing the oxygen passivation step at 1208 include those listed above for the oxygen passivation step performed at 1110 of FIG. 11.

[00211] The sequential passivation-etch cycle 1204 further comprises a hydrogen passivation step 1210 in which the substrate surface is exposed to a plasma comprising a hydrogen-containing passivator. In this example, the hydrogen-containing passivator is hydrogen. In other examples, a different hydrogen-containing passivator can be used. Examples of other hydrogen-containing passivators include ammonia, hydrazine, and amines. Suitable plasma conditions and exposure times for performing the hydrogen passivation step 1210 include those listed above for hydrogen passivation step performed at 1108 of FIG. 11.

[00212] The sequential passivation-etch cycle 1204 can be performed a plurality of times until the tapered profile has been formed. In some examples, the sequential

passivation-etch cycle 1204 can be performed twenty to one hundred times. In other examples, the sequential passivation-etch cycle 1204 can be performed a number of times outside this range.

[00213] As mentioned above, the topographically selective passivation methods of FIG. 10, FIG. 11, and FIG. 12 can be performed in addition to the above-described deposition-etch cycle of FIG. 9. FIG. 13 shows an example method 1300 for forming a tapered profile in a film deposited in a gap on a substrate using a co-flow passivation deposition-etch cycle 1304. At 1302, initially a substrate has a partial gapfill film formed in a gap, as described above with regard to FIGS. 9-11. Method 1300 further comprises performing a co-flow passivation deposition-etch process utilizing a plurality of co-flow passivation deposition-etch cycles 1304 to form a tapered profile in the partial gapfill film while protecting a hardmask on a substrate. In some examples, method 1300 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized.

[00214] The co-flow passivation deposition-etch cycle 1304 comprises, at 1306, depositing a protective layer. In some examples the protective layer can be the same material as the partial gapfill film formed at 1302. In other examples, the protective layer can comprise a different, but related, material composition that etches using a same chemistry as the chemistry used to etch the partial gapfill film formed at 1302. As examples, where the gapfill film is a silicon oxide film, the protective layer can be silicon oxide, or a doped silicon oxide (e.g., SiON, SiOC, etc.). In some examples, depositing the protective layer comprises performing one or cycles of PEALD to conformally deposit a protective film over the substrate with the partial gapfill film formed in a gap, as described above with regard to FIG. 9.

[00215] Method 1300 further comprises performing a co-flow passivation-etch process utilizing a plurality of co-flow passivation-etch cycles 1308. The co-flow passivation-etch cycle 1308 comprises, at 1310, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched, the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆). Suitable conditions for etching step 1310 include those listed above for FIGS. 9-11.

[00216] The co-flow passivation-etch cycle 1308 further comprises a co-flow passivation step 1312 in which the substrate surface is exposed to a plasma comprising a hydrogen-containing passivator and an oxygen-containing passivator. In this example, the hydrogen containing passivator is hydrogen, and the oxygen-containing passivator is nitrous oxide (N_2O). In other examples, a different hydrogen-containing passivator and/or a different oxygen-containing passivator can be used. Examples of other hydrogen-containing passivators include ammonia, hydrazine, amines. . . . Examples of other oxygen-containing passivators include O_2 .

[00217] The co-flow passivation step performed at 1312 utilizes a plasma to form reactive species from the hydrogen-containing passivator and the oxygen-containing passivator. The plasma conditions are configured to perform a topologically selective application of the passivator onto the substrate, again to cause a greater concentration of the hydrogen-containing passivator and the oxygen-containing passivator to be adsorbed to substrate surfaces over the hardmask than on sidewall surfaces. Suitable plasma conditions and exposure times for performing the passivation step at 1312 include those listed above for the passivation step performed at 1008 of FIG. 10.

[00218] The co-flow passivation deposition-etch cycle 1304 can be performed a plurality of times until the tapered profile has been formed. In some examples, the co-flow passivation deposition-etch cycle 1304 comprises performing one to ten cycles of ALD deposition followed by five to thirty co-flow passivation-etch cycles 1308. In such examples, the co-flow passivation deposition-etch cycle 1304 can be performed twenty to one hundred times. In other examples, the co-flow passivation deposition-etch cycle 1304 comprises performing any suitable number of ALD deposition cycles followed by any other suitable number of co-flow passivation-etch cycles 1308. In such examples, any other suitable number of co-flow passivation deposition-etch cycles 1304 can be performed.

[00219] FIG. 14 shows an example method 1400 for forming a tapered profile in a film deposited in a gap on a substrate using a first sequential passivation deposition-etch cycle 1404. At 1402, initially a substrate has a partial gapfill film formed in a gap, as described above with regard to FIGS. 9-11. Method 1400 further comprises performing a sequential passivation deposition-etch process utilizing a plurality of sequential passivation deposition-etch cycles 1404 to form a tapered profile in the partial gapfill film while protecting a hardmask on a substrate. In some examples,

method 1400 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized.

[00220] The sequential passivation deposition-etch cycle 1404 comprises, at 1406, depositing a protective layer. In some examples the protective layer can be the same material as the partial gapfill film formed at 1402. In other examples, the protective layer can comprise a different, but related, material composition that etches using a same chemistry as the chemistry used to etch the partial gapfill film formed at 1402. As examples, where the gapfill film is a silicon oxide film, the protective layer can be silicon oxide, or a doped silicon oxide (e.g., SiON, SiOC, etc.). In some examples, depositing the protective layer comprises performing one or cycles of PEALD to conformally deposit a protective film over the substrate with the partial gapfill film formed in a gap, as described above with regard to FIG. 9.

[00221] Method 1400 further comprises performing a sequential passivation-etch process utilizing a plurality of sequential passivation-etch cycles 1408. The sequential passivation-etch cycle 1408 comprises, at 1410, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆). Suitable conditions for etching step 1410 include those listed above for FIGS. 9-11.

[00222] The sequential passivation-etch cycle 1408 further comprises performing a hydrogen passivation step 1412 comprising exposing the substrate surface to a plasma comprising a hydrogen-containing passivator. In this example, the hydrogen containing passivator is hydrogen. In other examples, a different hydrogen-containing passivator can be used. Examples of other hydrogen-containing passivators include ammonia, hydrazine, and amines. Suitable plasma conditions and exposure times for performing the hydrogen passivation step at 1412 include those listed above for hydrogen passivation step performed at 1108 of FIG. 11.

[00223] The sequential passivation-etch cycle 1408 further comprises an oxygen passivation step 1414 comprising exposing the substrate surface to a plasma comprising an oxygen-containing passivator. In this example, the oxygen-containing passivator is nitrous oxide (N₂O). In other examples, a different oxygen-containing passivator can

be used. Examples of other oxygen-containing passivators include O₂. Suitable plasma conditions and exposure times for performing the oxygen passivation step at 1414 include those listed above for the oxygen passivation step performed at 1110 of FIG. 11.

[00224] The sequential passivation deposition-etch cycle 1404 can be performed a plurality of times until the tapered profile has been formed. In some examples, the sequential passivation deposition-etch cycle 1404 comprises performing one to ten cycles of ALD deposition followed by five to thirty sequential passivation-etch cycles 1408. In such examples, the sequential passivation deposition-etch cycle 1404 can be performed twenty to one hundred times. In other examples, the sequential passivation deposition-etch cycle 1404 comprises performing any suitable number of ALD deposition cycles followed by any other suitable number of sequential passivation-etch cycles 1408. In such examples, any other suitable number of sequential passivation deposition-etch cycles 1404 can be performed.

[00225] FIG. 15 shows an example method 1500 for forming a tapered profile in a film deposited in a gap on a substrate using a second sequential passivation deposition-etch cycle 1504. First, at 1502, initially a substrate has a partial gapfill film formed in a gap, as described above with regard to FIGS. 9-11. Method 1500 further comprises performing a sequential passivation deposition-etch process utilizing a plurality of sequential passivation deposition-etch cycles 1504 to form a tapered profile in the partial gapfill film while protecting a hardmask on a substrate. In some examples, method 1500 can be performed in the ALD deposition tool of FIG. 6. In other examples, other suitable tools can be utilized.

[00226] The sequential passivation deposition-etch cycle 1504 comprises, at 1506, depositing a protective layer. In some examples the protective layer can be the same material as the partial gapfill film formed at 1502. In other examples, the protective layer can comprise a different, but related, material composition that etches using a same chemistry as the chemistry used to etch the partial gapfill film formed at 1502. As examples, where the gapfill film is a silicon oxide-based film, the protective layer also can be silicon oxide-based film. In some examples, depositing the protective layer comprises performing one or cycles of PEALD to conformally deposit a protective film over the substrate with the partial gapfill film formed in a gap, as described above with regard to FIG. 9.

[00227] Method 1500 further comprises performing a sequential passivation-etch process utilizing a plurality of sequential passivation-etch cycles 1508. The sequential passivation-etch cycle 1508 comprises, at 1510, etching the film with a plasma comprising an etchant. In some examples, such as where a silicon oxide-based film is being etched the etchant can comprise a fluorine-containing etchant. Example fluorine-containing etchants include hydrogen fluoride (HF), nitrogen trifluoride (NF₃), carbon tetrafluoride (CF₄), sulfur hexafluoride (SF₆), chlorine trifluoride (ClF₃), difluoride (F₂), silicon tetrafluoride (SiF₄), and various fluorocarbons (C_xF_y, for example, C₂F₆). Suitable conditions for etching step 1510 include those listed above for FIGS. 9-11.

[00228] The sequential passivation-etch cycle 1508 further comprises an oxygen passivation step 1512 comprising exposing the substrate surface to a plasma comprising an oxygen-containing passivator. In this example, the oxygen-containing passivator is nitrous oxide (N₂O). In other examples, a different oxygen-containing passivator can be used. Examples of other oxygen-containing passivators include O₂. Suitable plasma conditions and exposure times for performing the oxygen passivation step at 1512 include those listed above for the oxygen passivation step performed at 1110 of FIG. 11. The oxygen passivation step 1512 is topographically selective, as described above.

[00229] The sequential passivation-etch cycle 1508 further comprises a hydrogen passivation step 1514 comprising exposing the substrate surface to a plasma comprising a hydrogen-containing passivator. In this example, the hydrogen containing passivator is hydrogen. In other examples, a different hydrogen-containing passivator can be used. Examples of other hydrogen-containing passivators include ammonia, hydrazine, and amines. Suitable plasma conditions and exposure times for performing the hydrogen passivation step at 1514 include those listed above for hydrogen passivation step performed at 1108 of FIG. 11. The hydrogen passivation step 1514 also is topographically selected, as described above.

[00230] The sequential passivation deposition-etch cycle 1504 can be performed a plurality of times until the tapered profile has been formed. In some examples, the sequential passivation deposition-etch cycle 1504 comprises performing one to ten cycles of ALD deposition followed by five to thirty sequential passivation-etch cycles 1508. In such examples, the sequential passivation deposition-etch cycle 1504 can be performed twenty to one hundred times. In other examples, the sequential passivation deposition-etch cycle 1504 comprises performing any suitable number of ALD

deposition cycles followed by any other suitable number of sequential passivation-etch cycles 1508. In such examples, any other suitable number of sequential passivation deposition-etch cycles 1504 can be performed.

[00231] It will be understood that the configurations and/or approaches described herein are exemplary in nature, and that these specific examples or examples are not to be considered in a limiting sense, because numerous variations are possible. The specific routines or methods described herein can represent one or more of any number of processing strategies. As such, various acts illustrated and/or described can be performed in the sequence illustrated and/or described, in other sequences, in parallel, or omitted. Likewise, the order of the above-described processes can be changed.

[00232] The subject matter of the present disclosure includes all novel and non-obvious combinations and sub-combinations of the various processes, systems and configurations, and other features, functions, acts, and/or properties disclosed herein, as well as any and all equivalents thereof.

CLAIMS

1. A method of processing a substrate comprising a gap, the method comprising:
performing a plurality of plasma-enhanced atomic layer deposition (PEALD) cycles to deposit a film into the gap, each PEALD cycle of the plurality of PEALD cycles comprising
in a first step, introducing a film precursor into a processing chamber to adsorb the film precursor to surfaces within the gap,
purging the processing chamber after the first step,
in a second step, forming a plasma using a gas mixture comprising a reactant and an inhibitor to
expose the substrate to the inhibitor, and
convert the film precursor into a film within the gap; and
after the second step, in a third step, exposing the substrate to a plasma comprising a passivation agent to remove at least some of the inhibitor from the surfaces in the gap.
2. The method of claim 1, further comprising performing one or more modified PEALD cycles that omits exposing the substrate to the plasma comprising the passivation agent.
3. The method of claim 1, further comprising performing one or more modified PEALD cycles that omits exposing the substrate to the inhibitor in the second step.
4. The method of claim 1, wherein exposing the substrate to the plasma comprising the passivation agent comprises switching gas flow from the gas mixture to the passivation agent while maintaining the plasma.
5. The method of claim 1, wherein the PEALD cycle further comprises purging the processing chamber after performing the third step.
6. The method of claim 1, wherein the second step is performed under conditions configured to deposit the inhibitor into the gap such that a concentration of the inhibitor deposited at a first depth within the gap is greater than a concentration of the inhibitor

deposited at a second depth within the gap, the second depth being deeper in the gap than the first depth.

7. The method of claim 1, wherein the film comprises one or more of silicon oxide, silicon oxynitride, silicon oxycarbide, and silicon oxycarbonitride.

8. The method of claim 1, wherein the inhibitor comprises one or more of molecular fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane.

9. The method of claim 8, wherein, after performing the plurality of PEALD cycles, the film comprises a F concentration that is less than 4×10^{20} F atoms/cm³.

10. The method of claim 1, wherein the passivation agent comprises one or more of NH₃ and H₂.

11. The method of claim 1, wherein the third step is performed for 0.05 to 0.5 seconds in each PEALD cycle.

12. The method of claim 11, wherein the third step is performed for 0.3 seconds or less in each PEALD cycle.

13. The method of claim 1, wherein the substrate comprises dynamic random access memory shallow trench isolation structures.

14. An atomic layer deposition (ALD) tool, comprising:
a processing chamber;
a substrate support disposed in the processing chamber;
flow control hardware configured to control flow of a film precursor, an oxidant, an inhibitor, and a passivation agent into the processing chamber;
an exhaust system;
a radiofrequency power source configured to form a plasma in the processing chamber; and

a controller configured to control the ALD tool to perform a plurality of plasma-enhanced ALD (PEALD) cycles sequentially to process a substrate disposed on the substrate support, the controller configured to,

in a first step of a PEALD cycle, operate the flow control hardware to flow the film precursor into the processing chamber to adsorb the film precursor within a gap on the substrate,

in a second step of the PEALD cycle after the first step, operate the exhaust system to purge the processing chamber,

in a third step of the PEALD cycle after the second step,

operate the flow control hardware to flow the oxidant and the inhibitor into the processing chamber, and

operate the radiofrequency power source to form a plasma using the oxidant and the inhibitor to expose the substrate to the inhibitor and convert the precursor into a film within the gap, and

in a fourth step of the PEALD cycle after the third step, operate the flow control hardware to flow the passivation agent into the processing chamber and operate the radiofrequency power source to form a plasma using the passivation agent to remove at least some of the inhibitor from the surfaces in the gap.

15. The ALD tool of claim 14, wherein the controller is configured to operate the radiofrequency power source continuously between the third step and the fourth step.

16. The ALD tool of claim 14, wherein the inhibitor comprises one or more of molecular fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane and the passivation agent comprises one or more of NH_3 and H_2 .

17. The ALD tool of claim 14, wherein the fourth step is performed for 0.3 seconds or less in each PEALD cycle.

18. A method of processing a substrate comprising a gap, the method comprising:
performing a plurality of plasma-enhanced atomic layer deposition (PEALD) cycles sequentially to deposit a film into the gap, each PEALD cycle of the plurality of PEALD cycles comprising

in a first step, introducing a film precursor into a processing chamber to adsorb the film precursor to surfaces within the gap,
purging the processing chamber after the first step,
in a second step, supplying radiofrequency power to form a plasma in the processing chamber using a gas mixture comprising a reactant and an inhibitor to
expose the substrate to the inhibitor, and
convert the precursor into a film within the gap, and
after the second step, in a third step, switching gas flow to a passivation agent while supplying the radiofrequency power, thereby forming a plasma comprising the passivation agent to remove at least some of the inhibitor from the surfaces in the gap; and
wherein the method omits a purge step between PEALD cycles.

19. The method of claim 18, further comprising performing a modified PEALD cycle that omits exposing the substrate to the plasma comprising the passivation agent.

20. The method of claim 18, wherein the inhibitor comprises one or more of molecular fluorine, nitrogen trifluoride, sulfur hexafluoride, hydrogen fluoride, xenon difluoride, tetrafluoromethane, or hexafluoroethane and the passivation agent comprises one or more of NH_3 and H_2 .

21. A method of forming a tapered profile in a film deposited in a gap on a substrate, the substrate comprising a hardmask located on a field region adjacent to the gap, the method comprising:

performing a plurality of etching cycles, each etching cycle comprising:
exposing the substrate to a plasma comprising an etchant, and
exposing the substrate to a plasma comprising a passivator; and
performing at least one atomic layer deposition process between a first etching cycle and a second etching cycle at an intermediate point in the plurality of etching cycles to deposit a protective layer that protects the hardmask during the plurality of etching cycles.

22. The method of claim 21, wherein the protective layer and the film deposited in the gap are a same material.

23. The method of claim 21, wherein the etchant comprises a fluorine-containing etchant and the passivator comprises a hydrogen-containing passivator.

24. The method of claim 21, wherein the film deposited in the gap is a silicon oxide-containing film and wherein the hardmask is a silicon nitride-containing hardmask.

25. The method of claim 21, wherein performing the at least one atomic layer deposition process comprises performing the at least one atomic layer deposition process every two to fifty etching cycles.

26. The method of claim 25, wherein the performing the at least one atomic layer deposition process every two to fifty etching cycles comprises a deposition-etch cycle, and wherein an etching process comprises performing from twenty to one hundred deposition-etch cycles.

27. The method of claim 21, wherein exposing the substrate to the plasma comprising the passivator comprises exposing the substrate to a hydrogen-containing passivator and an oxygen-containing passivator.

28. The method of claim 27, wherein exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate simultaneously to the hydrogen-containing passivator and the oxygen-containing passivator.

29. The method of claim 27, wherein exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate sequentially to the hydrogen-containing passivator and the oxygen-containing passivator.

30. A method of forming a tapered profile in a film deposited in a gap on a substrate, the substrate comprising a hardmask located on a field region adjacent to the gap, the method comprising:

performing a plurality of etching cycles, each etching cycle comprising:

exposing the substrate to a plasma comprising an etchant, and
exposing the substrate to a hydrogen-containing passivator and an
oxygen-containing passivator using one or more plasmas.

31. The method of claim 30, wherein exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate simultaneously to the hydrogen-containing passivator and the oxygen-containing passivator.

32. The method of claim 30, wherein exposing the substrate to the hydrogen-containing passivator and the oxygen-containing passivator comprises exposing the substrate sequentially to the hydrogen-containing passivator and the oxygen-containing passivator.

33. The method of claim 30, wherein the etchant comprises a fluorine-containing etchant.

34. The method of claim 30, wherein the film deposited in the gap is a silicon oxide-containing film and wherein the hardmask is a silicon nitride-containing hardmask.

35. The method of claim 30, further comprising performing at least one atomic layer deposition process between a first etching cycle and a second etching cycle at an intermediate point in the plurality of etching cycles to deposit a protective layer that protects the hardmask during the plurality of etching cycles.

36. The method of claim 35, wherein the protective layer and the film deposited in the gap are a same material.

37. The method of claim 35, wherein performing the at least one atomic layer deposition process comprises performing the at least one atomic layer deposition process every two to fifty etching cycles.

38. The method of claim 37, wherein performing the at least one atomic layer deposition process every two to fifty etching cycles comprises a deposition-etch cycle,

and wherein an etching process comprises performing from twenty to one hundred deposition-etch cycles.

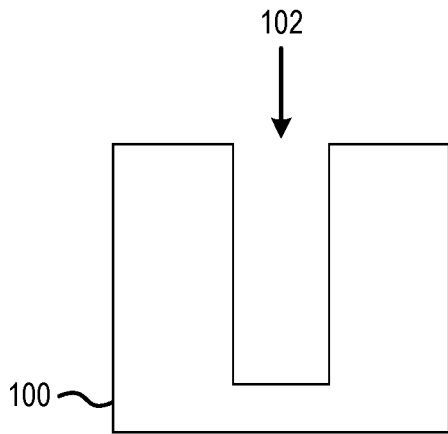


FIG. 1A

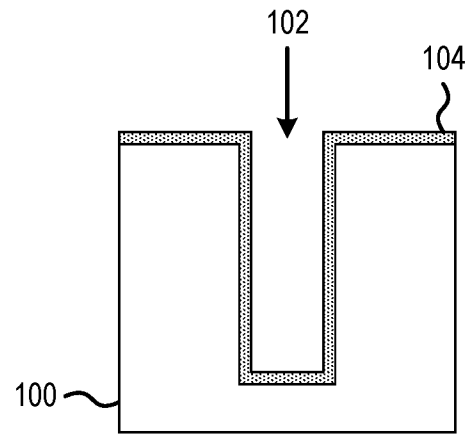


FIG. 1B

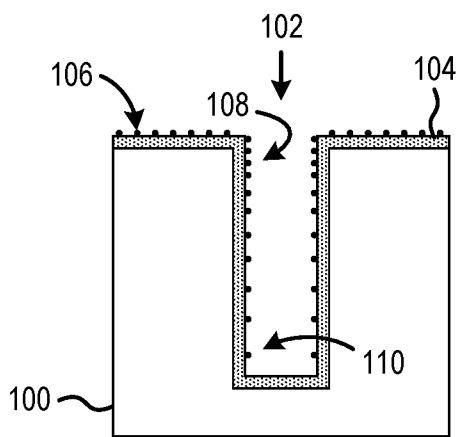


FIG. 1C

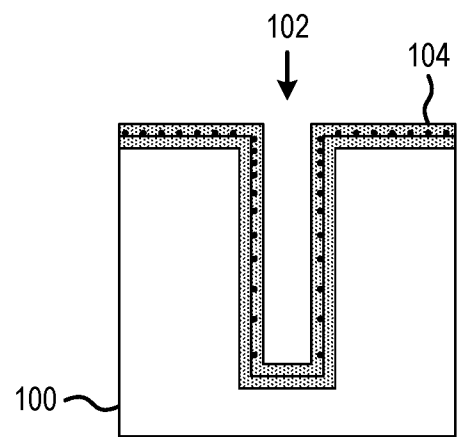


FIG. 1D

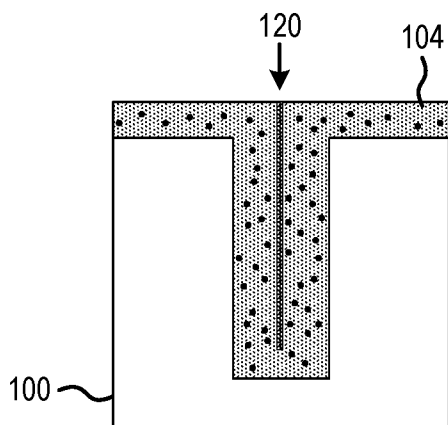


FIG. 1E

Passivate

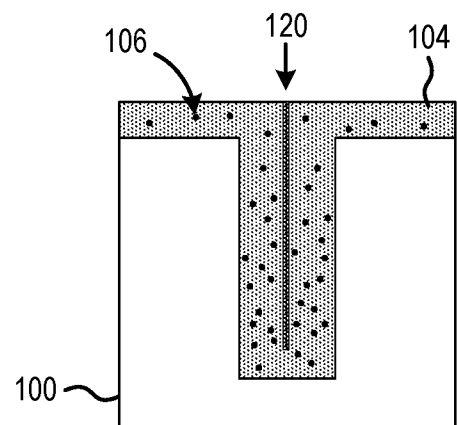


FIG. 1F

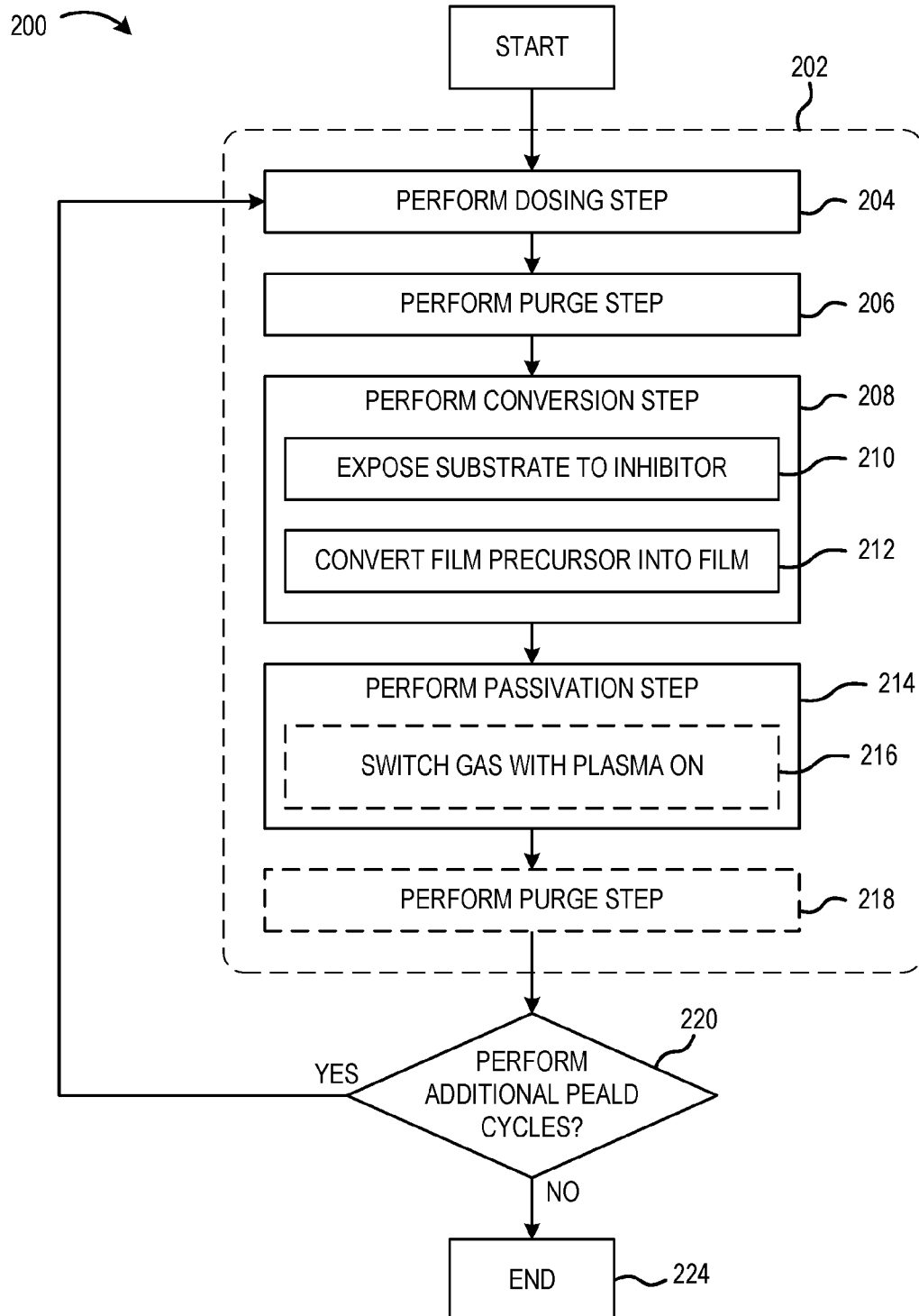


FIG. 2

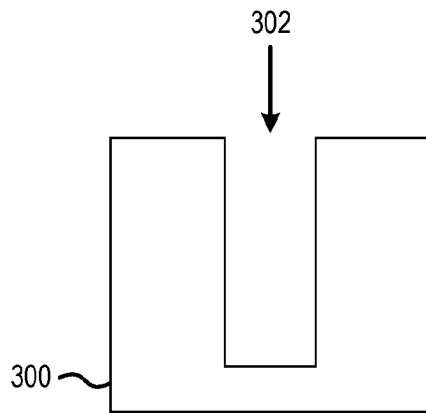


FIG. 3A

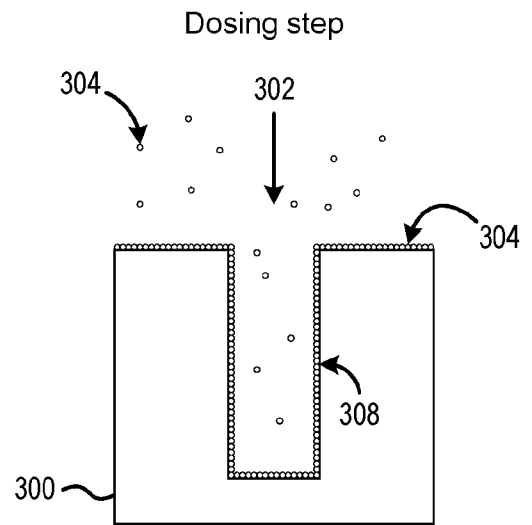


FIG. 3B

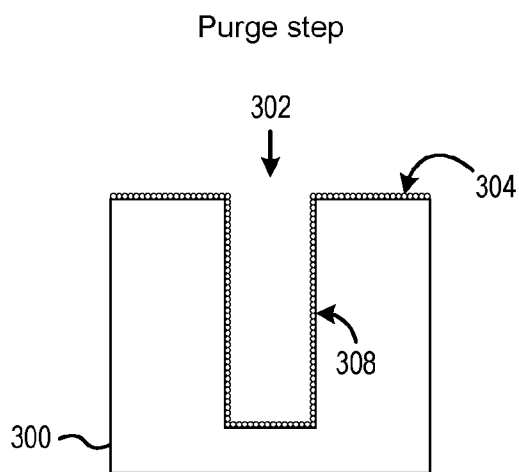


FIG. 3C

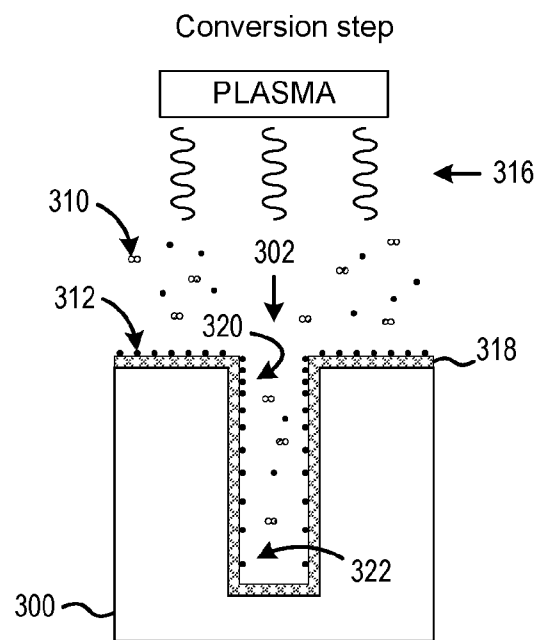


FIG. 3D

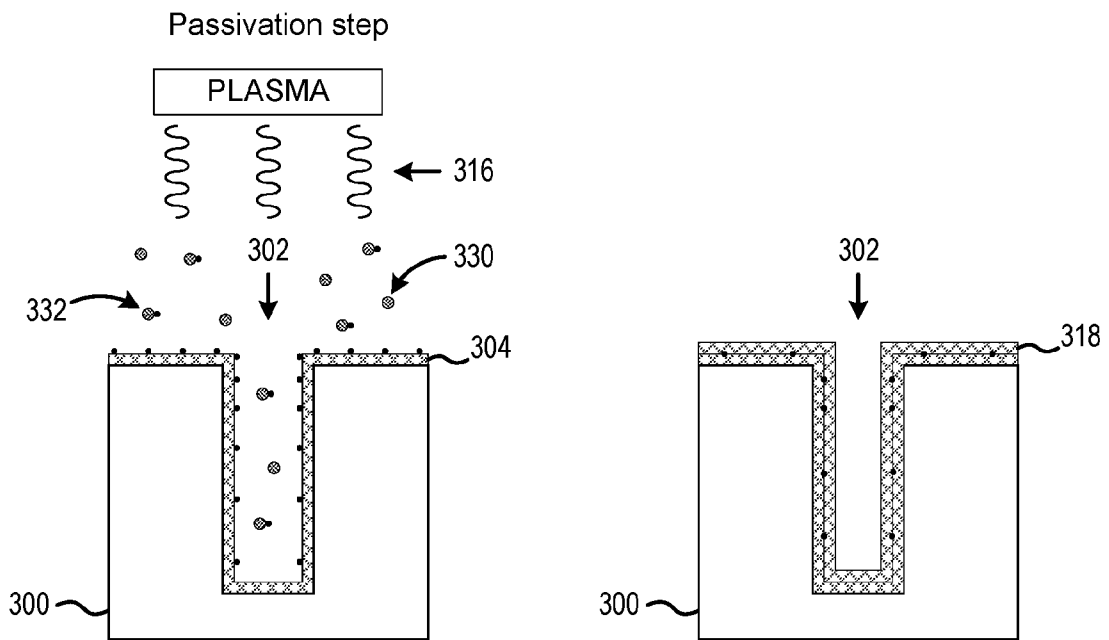


FIG. 3E

FIG. 3F

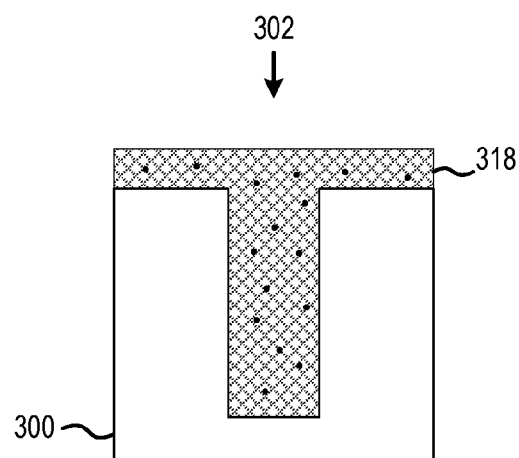


FIG. 3G

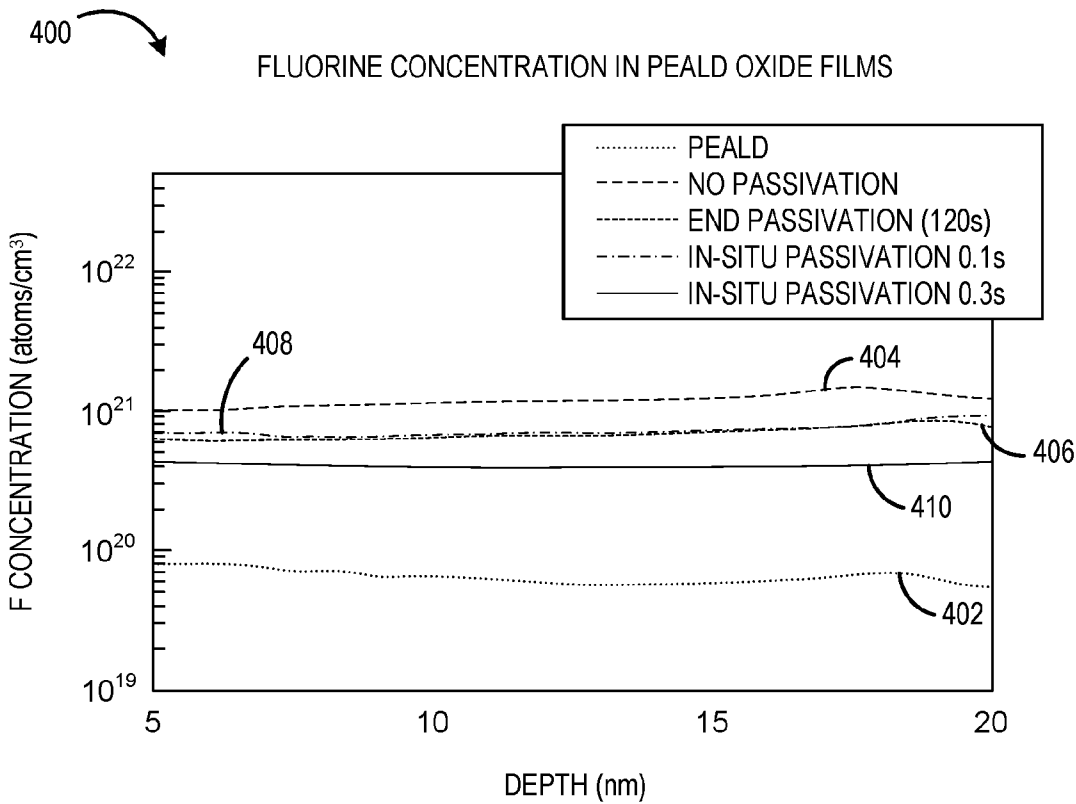


FIG. 4

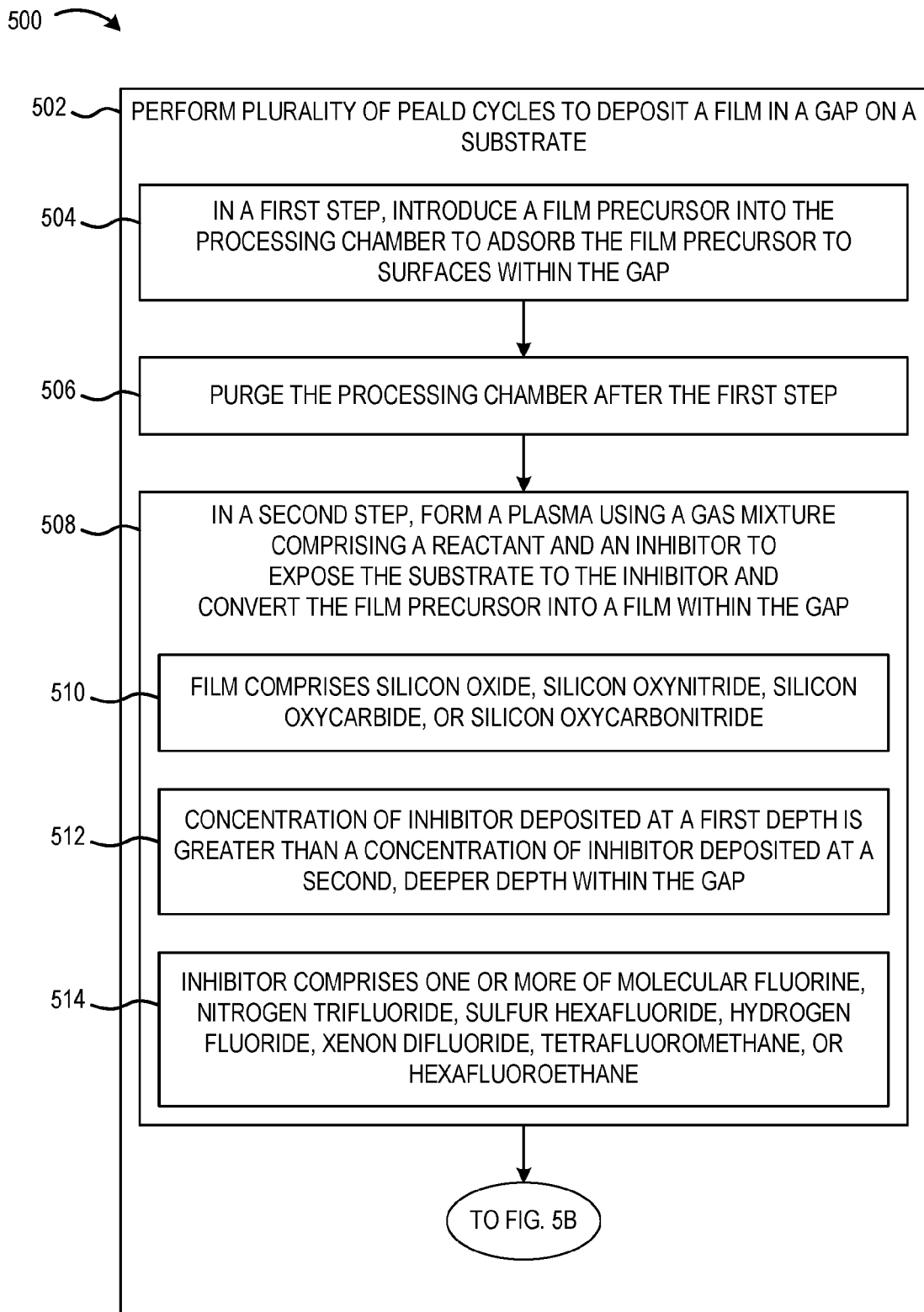


FIG. 5A

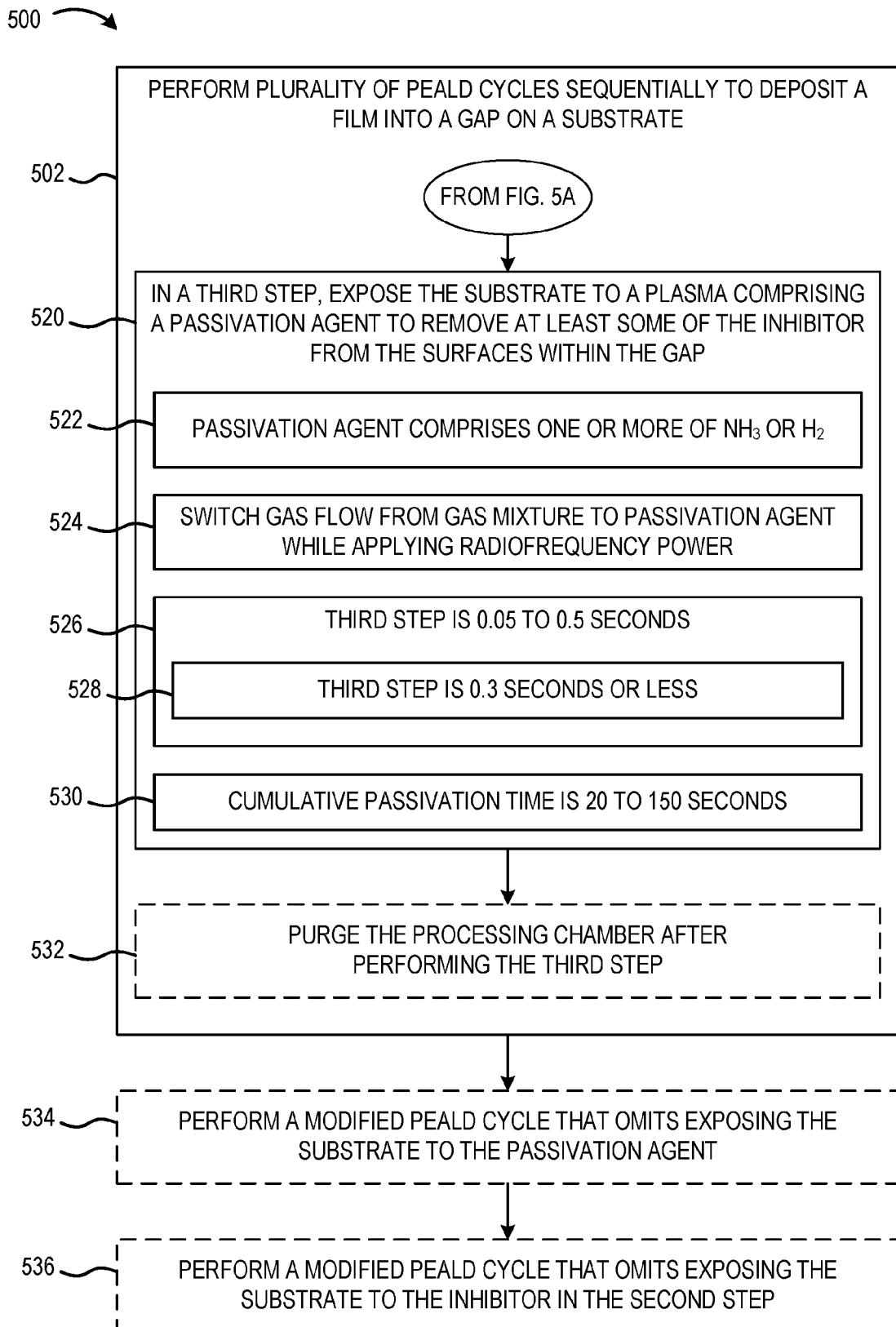


FIG. 5B

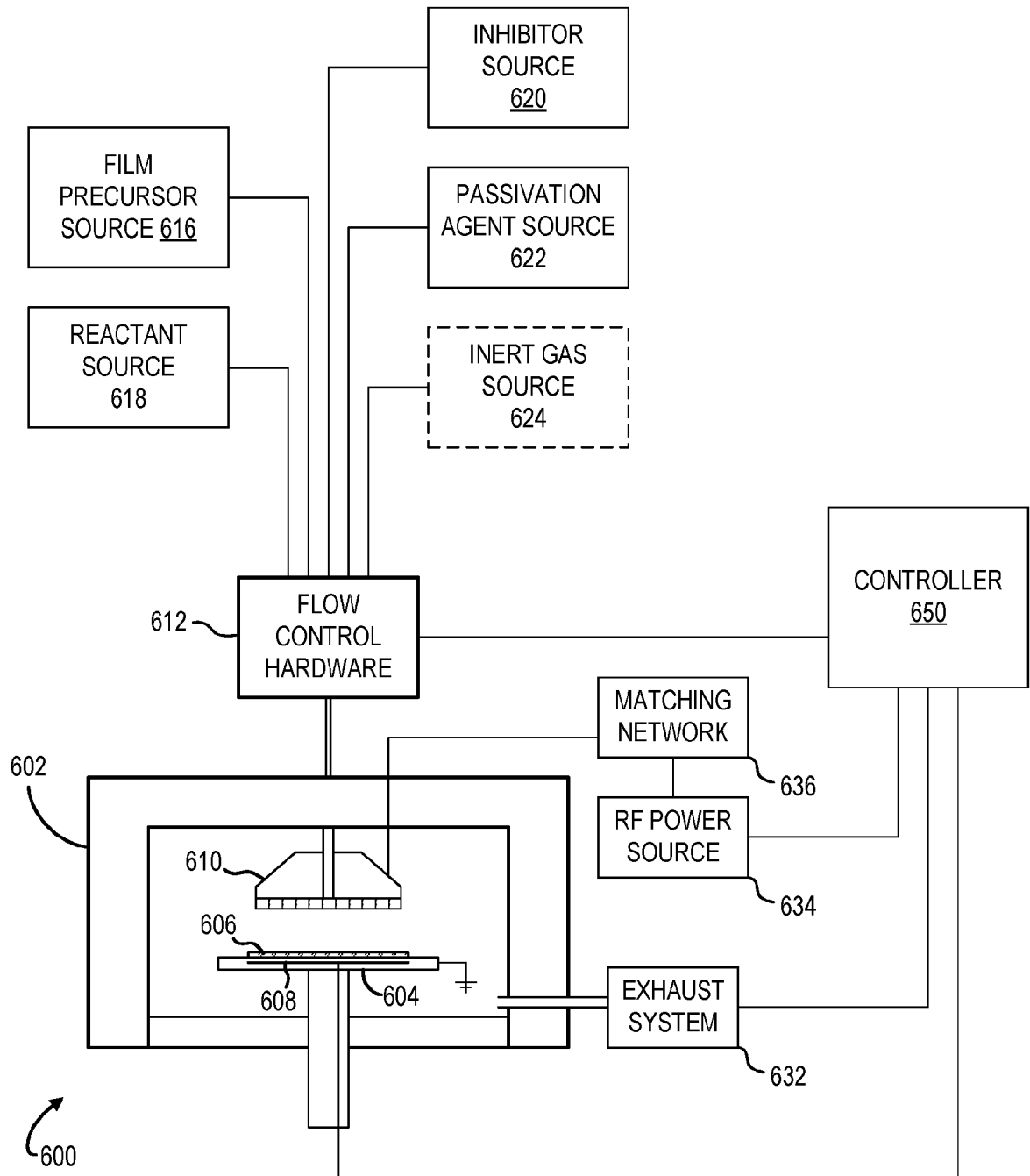


FIG. 6

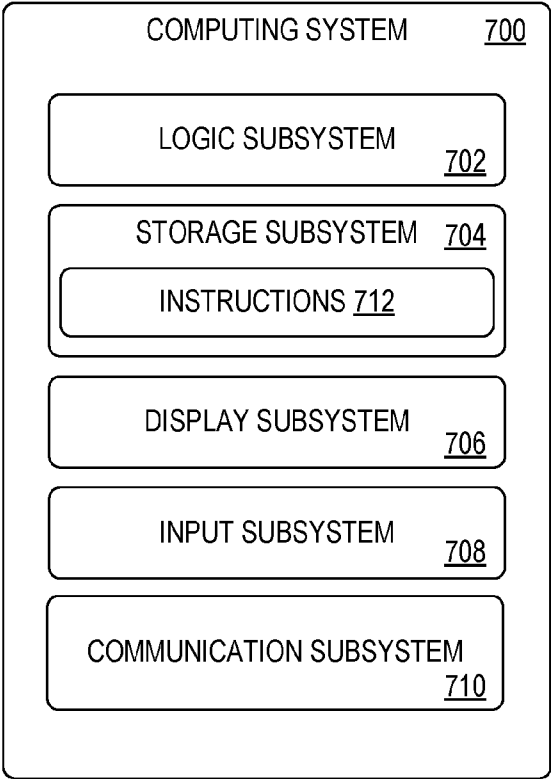


FIG. 7

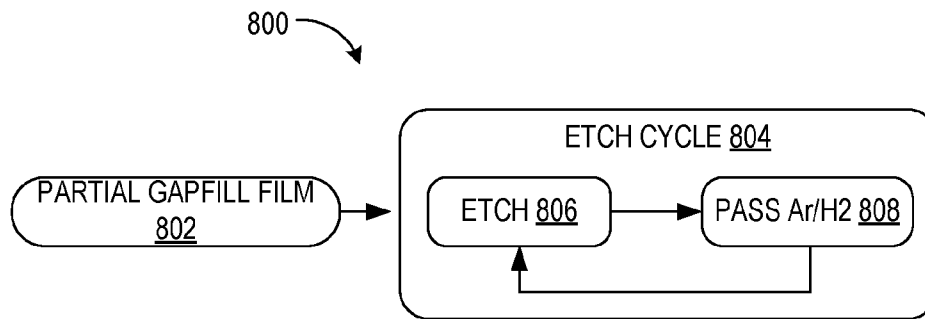


FIG. 8A

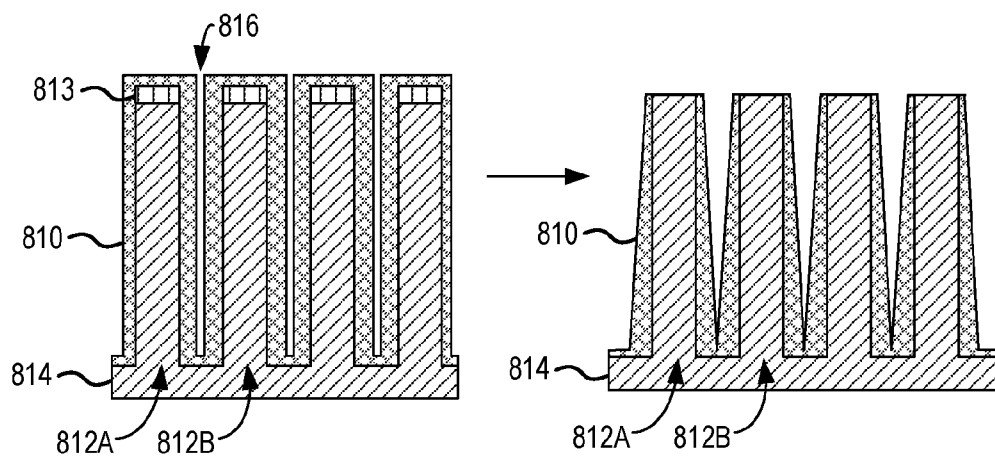


FIG. 8B

FIG. 8C

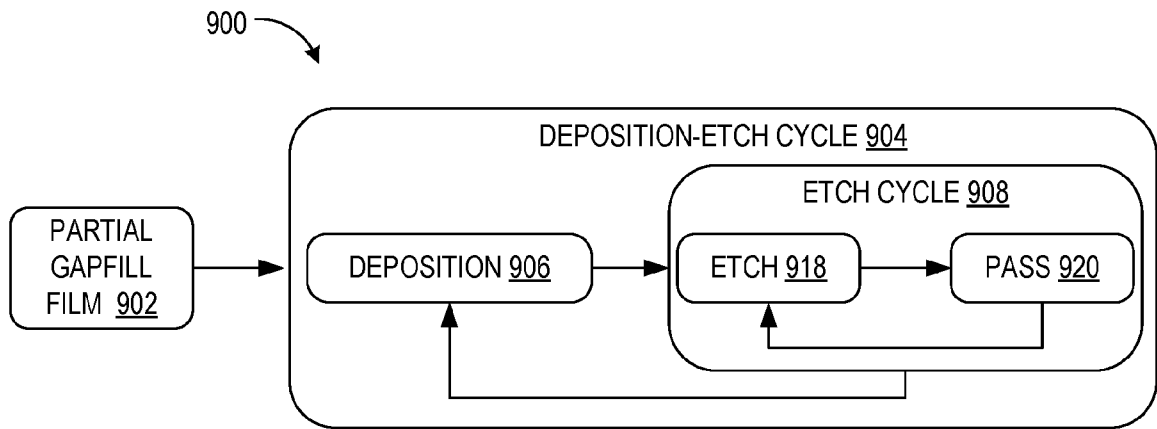


FIG. 9A

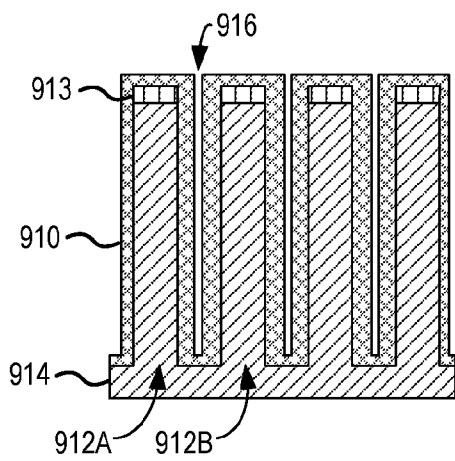


FIG. 9B

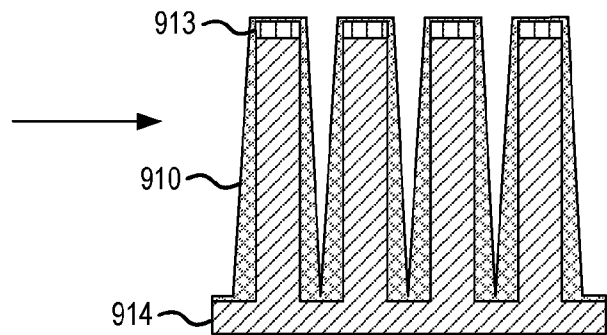


FIG. 9C

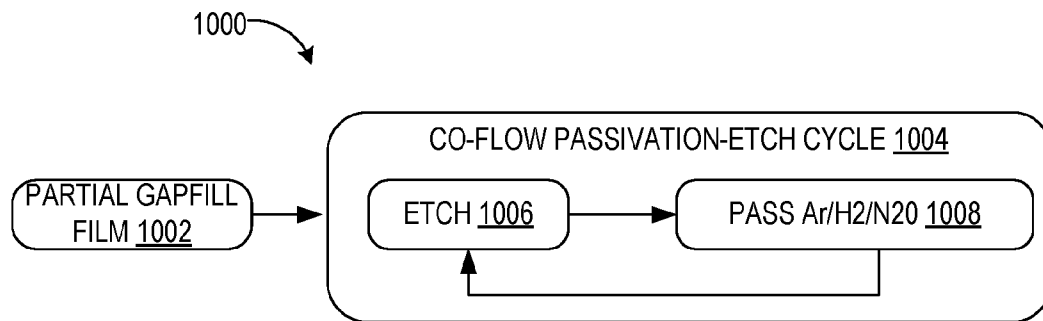


FIG. 10

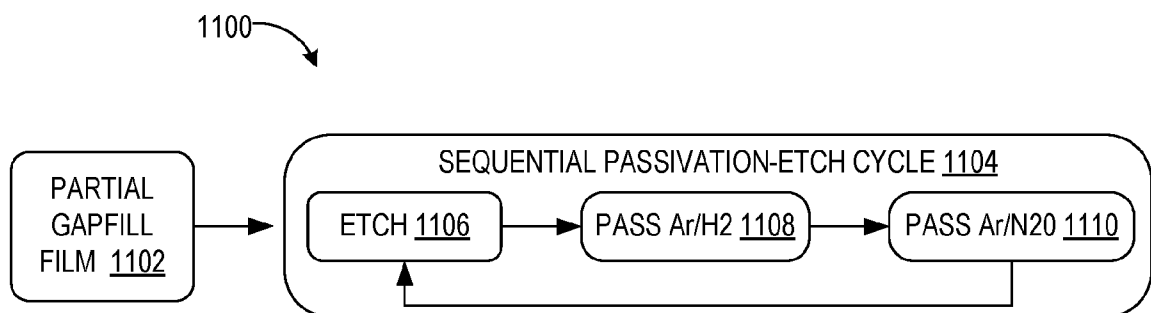


FIG. 11

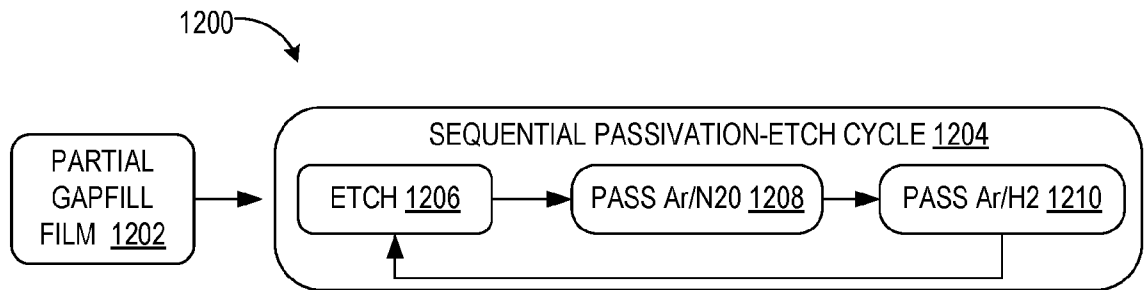


FIG. 12

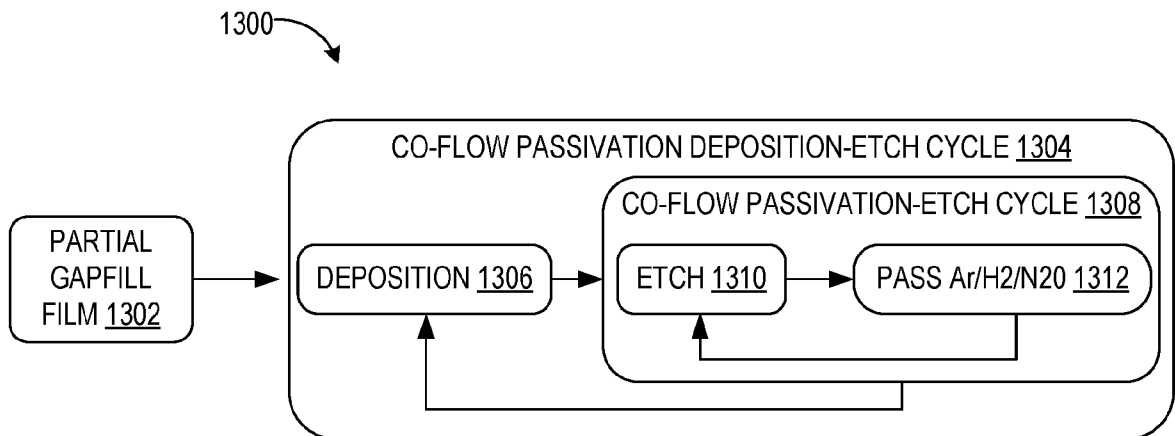


FIG. 13

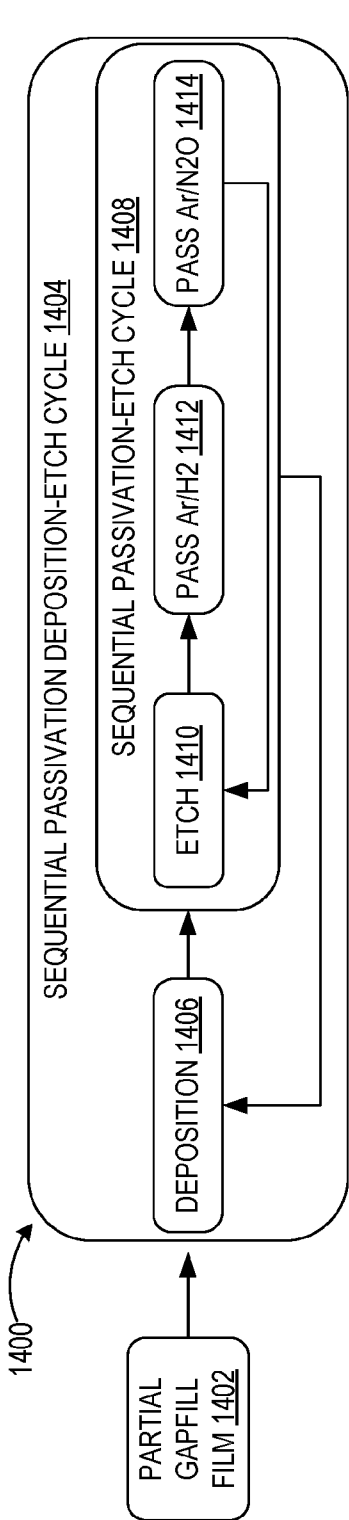


FIG. 14

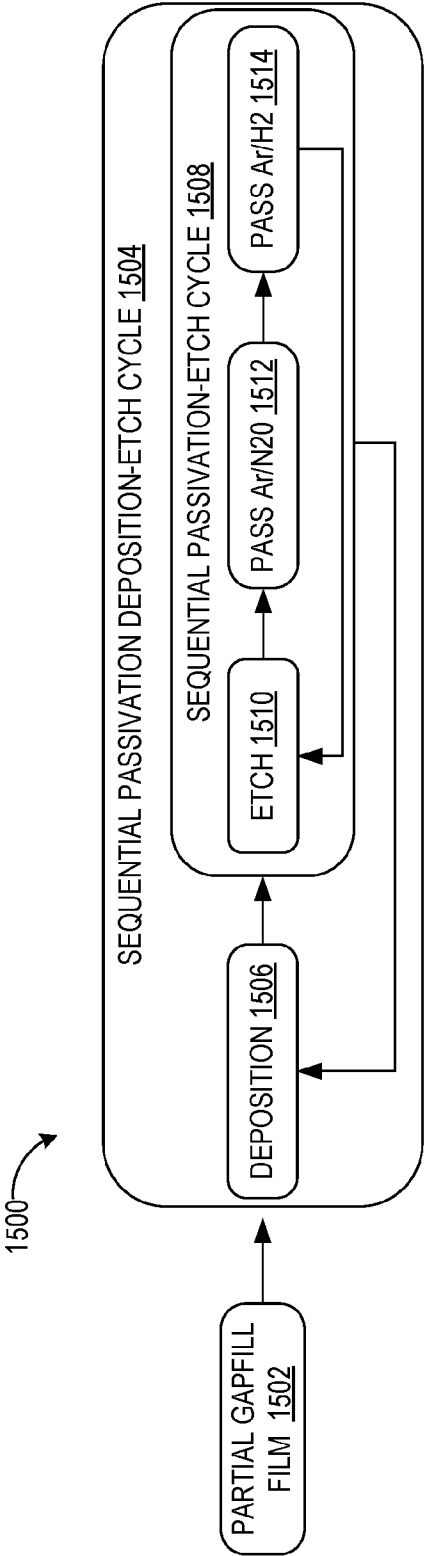


FIG. 15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/055002

A. CLASSIFICATION OF SUBJECT MATTER H01L 21/02(2006.01)i; C23C 16/455(2006.01)i; C23C 16/56(2006.01)i; H01L 21/762(2006.01)i; H01L 21/311(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 21/02(2006.01); C23C 16/458(2006.01); H01J 37/32(2006.01); H01L 21/3065(2006.01); H01L 21/308(2006.01); H01L 21/339(2006.01); H01L 21/762(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: plasma-enhanced atomic layer deposition (PEALD), etch, hardmask, inhibitor, passivator, hydrogen, oxygen		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2016-0329238 A1 (LAM RESEARCH CORPORATION) 10 November 2016 (2016-11-10) See paragraph [0042], claims 1, 3 and figure 6.	1-38
A	US 2021-0398780 A1 (LAM RESEARCH CORPORATION) 23 December 2021 (2021-12-23) See paragraph [0016], claims 1-2, 14 and figure 1.	1-38
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A	JP 3371611 B2 (SONY CORP.) 27 January 2003 (2003-01-27) See paragraphs [0009]-[0010] and claim 1.	1-38
☐ 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 February 2025		Date of mailing of the international search report 26 February 2025
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 LEE, Kang Ha Telephone No. +82-42-481-5687

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