

METHOD OF FORMING CARBON-BASED SPACER FOR EUV PHOTORESIST PATTERNS

TECHNICAL FIELD

- 5 [0001] Embodiments of the disclosure relate to methods for depositing a carbon-based film on nanostructures as a liner or spacer. In particular, embodiments of the disclosure are directed to methods of depositing carbon-based layers as a spacer layer on a patterned EUV photoresist.

10 BACKGROUND

- [0002] The semiconductor processing industry continues to strive for larger production yields while increasing the uniformity of layers deposited on substrates having larger surface areas. These same factors in combination with new materials also provide higher integration of circuits per unit area of the substrate. As circuit
15 integration increases, the need for greater uniformity and process control regarding layer thickness rises. As a result, various technologies have been developed to deposit layers on substrates in a cost-effective manner, while maintaining control over the characteristics of the layer.

- [0003] Integrated circuits are made possible by processes which produce intricately
20 patterned material layers on substrate surfaces. Producing patterned material on a substrate requires controlled methods of formation and removal of exposed material. As device sizes continue to shrink, material formation may affect subsequent operations.

- [0004] The semiconductor industry faces many challenges in the pursuit of device
25 miniaturization which involves rapid scaling of nanoscale features. Such issues include the introduction of complex fabrication steps such as multiple lithography steps and integration of high-performance materials. Traditional spacer fabrication processes include conformal film deposition on 3D structures (e.g., fins, mandrel, and the like) followed by directional plasma dry etching to remove the top and bottom layer
30 while keeping the sidewall film as a spacer. However, it has been found that the dry etch process could insidiously damage the sidewall surface and change the film properties; eventually affecting device performance and yield.

[0005] There is an ongoing need in the art, therefore, for methods to deposit carbon-based films as spacers or liners on nanostructures.

SUMMARY

5 [0006] One or more embodiments of the disclosure are directed to a method of depositing a film. The method comprises: flowing a first precursor over a substrate comprising a patterned surface to form a first portion of a carbon-containing film on the patterned surface, the first precursor comprising a first reactive group, and the pattern surface comprises a sidewall and a top surface; removing a first precursor
10 effluent comprising the first precursor from the substrate; flowing a second precursor comprising a second reactive group over the substrate to react with the first reactive group to form the carbon-containing film conformally on the patterned surface, wherein the carbon-containing film acts as an etch protection layer or as a liner; and removing a second precursor effluent comprising the second precursor from the
15 substrate.

[0007] Another embodiment of the disclosure is directed to a method of depositing a spacer film. The method comprises: flowing a first precursor over a substrate comprising a patterned surface, the first precursor having a general formula $R^1-(X)_n$ wherein R^1 comprises one or more of an alkyl group, an alkenyl group, an aryl group, an aromatic group, and a cycloalkyl group, X_n comprises one or more of a hydroxide group, an aldehyde group, a ketone group, an acid group, an amino group, an isocyanate group, a thiocyanate group, and an acyl chloride group, and n is an integer
20 in a range of from 1 to 6, wherein the first precursor reacts with a reactive group on the patterned surface to form a first portion of a carbon-containing film; removing a first precursor effluent comprising the first precursor from the substrate; flowing a second precursor over the substrate, the second precursor having a general formula $R^2-(Y)_n$ wherein R^2 comprises one or more of an alkyl group, an alkenyl group, an aryl group, an aromatic group, and a cycloalkyl group, Y_n comprises one or more of a hydroxide group, an aldehyde group, a ketone group, an acid group, an amino group, an isocyanate group, a thiocyanate group, and an acyl chloride group, and n is an integer
25 in a range of from 1 to 6, wherein the second precursor reacts with the first portion to form a conformal carbon-containing film; removing a second precursor
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effluent comprising the second precursor from the substrate; and etching the substrate to remove a portion of the carbon-containing film from a top surface of the patterned surface to form a spacer layer on a first sidewall and on a second sidewall of the patterned surface.

- 5 [0008] A further embodiment of the disclosure is directed to a non-transitory computer readable medium including instructions, that, when executed by a controller of a processing chamber, causes the processing chamber to perform operations of: flow a first precursor over a substrate comprising a patterned surface to form a first portion of a carbon-containing film on the patterned surface, the first precursor
10 comprising a first reactive group, and the pattern surface comprises a sidewall and a top surface; remove a first precursor effluent comprising the first precursor from the substrate; flow a second precursor comprising a second reactive group over the substrate to react with the first reactive group to conformally form the carbon-containing film on the patterned surface; remove a second precursor effluent
15 comprising the second precursor from the substrate; and etch the substrate to remove a portion of the carbon-containing film from a top surface of the patterned surface to form a spacer layer on a first sidewall and on a second sidewall of the patterned surface.

20 BRIEF DESCRIPTION OF THE DRAWING

- [0009] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the
25 appended drawings illustrate only typical embodiments of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective embodiments. The embodiments as described herein are illustrated by way of example and not limitation in the figures of the accompanying drawings in which like references indicate similar elements.

- 30 [0010] FIG. 1A illustrates a cross-section view of a substrate according to one or more embodiments;

- [0011] FIG. 1B illustrates a cross-section view of a substrate according to one or more embodiments;
- [0012] FIG. 1C illustrates a cross-section view of a substrate according to one or more embodiments;
- 5 [0013] FIG. 1D illustrates a cross-section view of a substrate according to one or more embodiments;
- [0014] FIG. 2 illustrates a process flow diagram of a method of depositing a film on a substrate according to one or more embodiments; and
- [0015] FIG. 3 illustrates a process flow diagram of a method of depositing a film on
- 10 a substrate according to one or more embodiments.

DETAILED DESCRIPTION

[0016] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process

15 steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0017] The term "about" as used herein means approximately or nearly and in the context of a numerical value or range set forth means a variation of $\pm 15\%$, or less, of the numerical value. For example, a value differing by $\pm 14\%$, $\pm 10\%$, $\pm 5\%$, $\pm 2\%$, or

20 $\pm 1\%$, would satisfy the definition of about.

[0018] As used in this specification and the appended claims, the term "substrate" or "wafer" refers to a surface, or portion of a surface, upon which a process acts. It will also be understood by those skilled in the art that reference to a substrate can refer to only a portion of the substrate unless the context clearly indicates otherwise.

25 Additionally, reference to depositing on a substrate can mean both a bare substrate and a substrate with one or more films or features deposited or formed thereon.

[0019] A "substrate" or "substrate surface", as used herein, refers to any portion of a substrate or portion of a material surface formed on a substrate upon which film processing is performed. For example, a substrate surface on which processing can

30 be performed includes materials such as silicon, silicon oxide, silicon nitride, doped silicon, germanium, gallium arsenide, glass, sapphire, and any other materials such as metals, metal nitrides, metal alloys, and other conductive materials, depending on the

application. Substrates include, without limitation, semiconductor wafers. Substrates may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal, UV cure, e-beam cure and/or bake the substrate surface. In addition to film processing directly on the surface of the substrate itself, in the present disclosure, any of the film processing steps disclosed may also be performed on an underlayer formed on the substrate as disclosed in more detail below, and the term "substrate surface" is intended to include such underlayer as the context indicates. Thus, for example, where a film/layer or partial film/layer has been deposited onto a substrate surface, the exposed surface of the newly deposited film/layer becomes the substrate. Substrates may have various dimensions, such as 200 mm or 300 mm diameter wafers, as well as rectangular or square panes. In some embodiments, the substrate comprises a rigid discrete material.

[0020] The term "on" indicates that there is direct contact between elements. The term "directly on" indicates that there is direct contact between elements with no intervening elements.

[0021] As used in this specification and the appended claims, the terms "precursor," "reactant," "reactive gas" and the like are used interchangeably to refer to any gaseous species that can react with the substrate surface.

[0022] As used in this specification and the appended claims, the terms "reactive compound", "reactive gas", "reactive species", "precursor", "process gas" and the like are used interchangeably to mean a substance with a species capable of reacting with the substrate or material on the substrate in a surface reaction (e.g., chemisorption, oxidation, reduction, cycloaddition). The substrate, or portion of the substrate, is exposed sequentially to the two or more reactive compounds which are introduced into a reaction zone of a processing chamber.

[0023] Carbon-containing materials may be used in semiconductor device manufacturing for a number of structures and processes, including as a mask material, an etch resistant material, and a trench fill material, among other applications. More specific examples of applications for carbon-containing materials include the formation of hot implant hard masks, metal gate (MG)-cut hard masks, metal gate fabrication, and reverse tone patterning, self-aligned patterning, among others. One or more embodiments includes the formation of these carbon-containing

materials using molecular layer deposition (MLD) as a spacer or liner on a patterned nanostructure.

[0024] Embodiments of the disclosure provide methods of depositing a film (e.g., carbon-containing) on features with small dimensions. Some embodiments advantageously provide conformal films to completely cover features. Other
5 embodiments advantageously provide conformal films that completely or partially cover features. The carbon-containing film of one or more embodiments has a high conformality. In one or more embodiments, the conformal carbon-containing film is deposited on a logic device comprising alternating layers of silicon and silicon-
10 germanium. In some embodiments, the logic device is a transistor, such as a FinFET or a GAA. In other embodiments, the conformal carbon-containing film is deposited on an EUV photoresist.

[0025] Embodiments of the present technology include molecular layer deposition (MLD) methods and systems to form a carbon-containing material on a patterned
15 nanostructure. Exemplary MLD methods may include providing a first deposition precursor to a surface of a semiconductor substrate, where the precursor forms a first layer (e.g., a first monolayer) on surfaces. During or after the formation of the first layer, unbound deposition effluents, which may include unbound molecules of the first deposition precursor, are removed from a processing region in which the
20 semiconductor substrate is exposed. A second deposition precursor may then be introduced to the semiconductor substrate, where molecules of the second deposition precursor bind to reactive moieties on the first layer to form a second layer (e.g., a second monolayer) on the patterned nanostructure surface. During or after the formation of the second layer, unbound deposition effluent, which may include
25 unbound molecules of the second deposition precursor, are removed from the processing region. The semiconductor substrate now has a carbon containing material layer bound to the patterned nanostructure surface of the semiconductor substrate. Additional compound layers of first and second layers may be built up on the deposited layers until the number of built-up compound layers reaches a desired
30 thickness of carbon-containing material on the patterned surface of the semiconductor substrate. The compound layers may then be annealed, or plasma treated to form the carbon-containing material on the surface of the semiconductor substrate.

[0026] One or more embodiments advantageously provides solutions to problems with conventional methods of forming a carbon-containing material on a semiconductor substrate. For example, the present technology forms a carbon-containing material with significantly fewer voids, fractures, and other physical defects than carbon-containing materials formed using spin-on-carbon (SOC) and flowable chemical-vapor-deposition (FCVD) methods. The present technology may also form carbon-containing materials with higher density and lower porosity than materials formed with SOC and FCVD. The high levels of hydrogen found in many SOC and FCVD precursors result in high levels of shrinkage when the as-deposited materials are treated to form a final material. Shrinkage as high as 50 vol.% is not uncommon for as-deposited SOC and FCVD materials following treatment, which creates gaps, fractures, and voids in treated material, as well as stresses on substrate features in contact with the material. The present technology produces carbon-containing materials with less than 10 vol.% shrinkage of the as-deposited material (e.g., 5-10 vol.% shrinkage, less than about 5 vol.% shrinkage).

[0027] One or more embodiments advantageously provides solutions to problems with conventional plasma deposition methods of forming a carbon-containing material on a semiconductor substrate. Conventional plasma deposition methods such as plasma-enhanced chemical-vapor-deposition (PECVD) and high-density-plasma chemical-vapor-deposition (HDPCVD) often create ion sputtering that causes damage to substrate features on the semiconductor substrate and can also create re-sputtered ions and other species that can cause defects in the deposited carbon-containing material. In addition, they often deposit the material unevenly in and around substrate features, creating voids in and around substrate trenches and steps, and uneven surfaces in planar substrate regions. The present technology may form carbon-containing materials with a high level of conformity in narrow substrate features (e.g., dimension widths less than about 25 nm) and high aspect ratios (e.g., AR of 10: 1 or more) without the need for plasmas that can damage the substrate feature during deposition.

[0028] The embodiments of the disclosure are described by way of the Figures, which illustrate devices (e.g., transistors) and processes for forming semiconductor structures in accordance with one or more embodiments of the disclosure. The

processes shown are merely illustrative possible uses for the disclosed processes, and the skilled artisan will recognize that the disclosed processes are not limited to the illustrated applications.

[0029] FIGS. 1A-1D illustrate cross-sectional views of a semiconductor substrate being processed according to the method of one or more embodiments. FIG. 2 illustrates a process flow diagram of a method 200 of depositing a spacer film according to one or more embodiments. Referring to FIGS. 1A-1D and FIG. 2, in one or more embodiments, at operation 202, a patterned substrate is provided. As used in this specification and the appended claims, the term "provided" means that the substrate is made available for processing (e.g., positioned in a processing chamber).

[0030] Referring to FIG. 1A, in one or more embodiments, a substrate 104 includes a patterned surface 102. In one or more embodiments, the patterned surface 102 comprises one or more of a photoresist, a mandrel, a trench, a via, a hole, and the like. In specific embodiments, the patterned surface 102 comprises a patterned photoresist. A photoresist may be patterned to form the patterned surface 102 using EUV radiation and a developer to expose portions and leave a residue of the photoresist. A "photoresist," as used herein, refers to any light-sensitive material used in such processes as photolithography and photoengraving, to form a patterned coating on a surface.

[0031] In one or more embodiments, the patterned surface 102 includes a top surface 110, a first sidewall 109, and a second sidewall 111. As recognized by one of skill in the art, there may be more than one patterned surface 102 on the substrate 104. In some embodiments, there are at least two patterned surfaces 102 separated by a feature 101.

[0032] In one or more embodiments, the substrate on which the carbon-containing material is formed may include a material in which one or more features 101 may be formed. The substrate features 101 may be characterized by any shape or configuration according to the present technology. In some embodiments, the features 101 may be or include a trench structure, a via structure, or aperture formed within the substrate. Although the substrate features may be characterized by any shapes or sizes, in some embodiments the substrate features 101 may be characterized by higher aspect ratios, or a ratio of a depth of the feature to a width across the feature

101. For example, in some embodiments substrate features may be characterized by aspect ratios greater than or equal to 5:1, and may be characterized by aspect ratios greater than or equal to 10:1, greater than or equal to 15:1, greater than or equal to 20:1, greater than or equal to 25:1, greater than or equal to 30:1, greater than or equal to 40:1, greater than or equal to 50:1, or greater. Additionally, the features 101 may be characterized by narrow widths or diameters across the feature including between two sidewalls, such as a critical dimension in a range of from 5 nm to 500 nm, or in a range of from 10 nm to 200 nm, or in a range of from 20 nm to 100 nm.

[0033] In one or more embodiments, the distance, d_1 , between each of the patterned surfaces 102 is in a range of from 5 nm to 500 nm, or in a range of from 10 nm to 200 nm, or in a range of from 20 nm to 100 nm.

[0034] With reference to FIG. 1B, in one or more embodiments, an optional liner layer 106 may be formed on the patterned surface 102. In some embodiments, the liner layer 106 is not present, and the carbon-containing film 108 is formed directly on the patterned surface 102. In other embodiments, the liner layer 106 is present, and the carbon-containing film 108 is formed on the liner layer 106. The liner layer 106 may comprise a liner. In one or more embodiments, the liner layer 106 may comprise any suitable material. In some embodiments, the liner layer 106 comprises a metal. A "metal," as used herein, refers to metal, metallic, metal alloy, metal oxide, metal nitride, or combination thereof.

[0035] Referring to FIG. 2, in one or more embodiments, at operation 204, the substrate 104 and patterned surface 102 may optionally be exposed to a pretreatment process to polish, coat, dope, etch, reduce, oxidize, hydroxylate, anneal, UV cure, e-beam cure and/or bake the substrate. In addition to the pretreatment directly on the substrate 104 and patterned surface 102 itself, in the present disclosure, any of the treatments or pre-treatments disclosed may also be performed on an underlayer metal surface or liner layer 106.

[0036] In one or more embodiments, a carbon-containing film 108 forms substantially conformally on the substrate 104 and patterned surface 102. As used herein, a layer which is "substantially conformal" refers to a layer where the thickness is about the same throughout (e.g., on the top, middle and bottom of sidewalls and on the bottom of the feature 101). A layer which is substantially conformal varies in

thickness by less than or equal to about 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, or 0.5%.

[0037] With reference to FIG. 2, at operation 206, a first type of precursor is introduced/flowed into the substrate processing region of a processing chamber and over the substrate surface. The first precursor binds strongly to the substrate 104 and patterned surface 102.

[0038] In one or more embodiments, the first precursor may be a carbon-containing precursor that has at least two reactive groups that can form a bond with a group attached to the substrate 104 and patterned surface 102. Molecules of the first precursor react with the surface groups of the substrate 104 and patterned surface 102 to form bonds linking the first precursor molecule to the substrate 104 and patterned surface 102. The reactions between the first precursor molecules and the groups on the substrate 104 and patterned surface 102 continue until most or all the surface groups are bonded to a reactive group on the first precursor molecules. A first portion of a carbon-containing film 108 is formed that blocks further reaction between first precursor molecules in the first precursor effluent and the substrate.

[0039] The first precursor may comprise any suitable precursor known to the skilled artisan. In one or more embodiments, the first precursor may have a general formula $R^1-(X)_n$ wherein n is an integer in a range of from 1 to 6, and R^1 comprises one or more of an alkyl group, an alkenyl group, an aryl, or aromatic group, and a cycloalkyl group. X_n comprises one or more of a hydroxide group, an aldehyde group, a ketone group, an acid group, an amino group, an isocyanate group, a thiocyanate group, and an acyl chloride group.

[0040] Unless otherwise indicated, the term "lower alkyl," "alkyl," or "alk" as used herein alone or as part of another group includes both straight and branched chain hydrocarbons, containing 1 to 20 carbons, or 1 to 10 carbon atoms, in the normal chain, such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, isobutyl, pentyl, hexyl, isohexyl, heptyl, 4,4-dimethylpentyl, octyl, 2,2,4-trimethyl-pentyl, nonyl, decyl, undecyl, dodecyl, the various branched chain isomers thereof, and the like. Such groups may optionally include up to 1 to 4 substituents. The alkyl may be substituted or unsubstituted.

[0041] Such alkyl groups may optionally include up to 1 to 4 substituents such as

halo, for example F, Br, Cl, or I, or CF₃, alkyl, alkoxy, aryl, aryloxy, aryl(aryl) or diaryl, arylalkyl, arylalkyloxy, alkenyl, cycloalkyl, cycloalkylalkyl, cycloalkylalkyloxy, amino, hydroxy, hydroxyalkyl, acyl, heteroaryl, heteroaryloxy, heteroarylalkyl, heteroarylalkoxy, aryloxyalkyl, alkylthio, arylalkylthio, aryloxyaryl, alkylamido, alkanoylamino, arylcarbonylamino, nitro, cyano, thiol, haloalkyl, trihaloalkyl, and/or alkylthio, and the like. In one or more embodiments, R¹ is independently selected from C₁₋₂₀ alkyl. In other embodiments, R¹ is from C₁₋₁₂ alkyl.

[0042] As used herein, the term "alkene" or "alkenyl" or "lower alkenyl" refers to straight or branched chain radicals of 2 to 20 carbons, or 2 to 12 carbons, and 1 to 8 carbons in the normal chain, which include one to six double bonds in the normal chain, such as vinyl, 2-propenyl, 3-butenyl, 2-butenyl, 4-pentenyl, 3-pentenyl, 2-hexenyl, 3-hexenyl, 2-heptenyl, 3-heptenyl, 4-heptenyl, 3-octenyl, 3-nonenyl, 4-decenyl, 3-undecenyl, 4-dodecenyl, 4,8,12-tetradecatrienyl, and the like, and which may be optionally substituted with 1 to 4 substituents, namely, halogen, haloalkyl, alkyl, alkoxy, alkenyl, alkynyl, aryl, arylalkyl, cycloalkyl, amino, hydroxy, heteroaryl, cycloheteroalkyl, alkanoylamino, alkylamido, arylcarbonyl-amino, nitro, cyano, thiol, alkylthio, and/or any of the alkyl substituents set out herein.

[0043] As used herein, the term "alkynyl" or "lower alkynyl" refers to straight or branched chain radicals of 2 to 20 carbons, or 2 to 12 carbons, or 2 to 8 carbons in the normal chain, which include one triple bond in the normal chain, such as 2-propynyl, 3-butylnyl, 2-butylnyl, 4-pentylnyl, 3-pentylnyl, 2-hexynyl, 3-hexynyl, 2-heptynyl, 3-heptynyl, 4-heptynyl, 3-octynyl, 3-nonylnyl, 4-decynyl, 3-undecynyl, 4-dodecynyl, and the like, and which may be optionally substituted with 1 to 4 substituents, namely, halogen, haloalkyl, alkyl, alkoxy, alkenyl, alkynyl, aryl, arylalkyl, cycloalkyl, amino, heteroaryl, cycloheteroalkyl, hydroxy, alkanoylamino, alkylamido, arylcarbonylamino, nitro, cyano, thiol, and/or alkylthio, and/or any of the alkyl substituents set out herein.

[0044] The term "halogen" or "halo" as used herein alone or as part of another group refers to chlorine, bromine, fluorine, and iodine as well as CF₃.

[0045] As used herein, the term "aryl" refers to monocyclic and bicyclic aromatic groups containing 6 to 10 carbons in the ring portion (such as phenyl, biphenyl or naphthyl, including 1-naphthyl and 2-naphthyl) and may optionally include 1 to 3

additional rings fused to a carbocyclic ring or a heterocyclic ring (such as aryl, cycloalkyl, heteroaryl, or cycloheteroalkyl rings). The aryl group may be optionally substituted through available carbon atoms with 1, 2, or 3 substituents, for example, hydrogen, halo, haloalkyl, alkyl, haloalkyl, alkoxy, haloalkoxy, alkenyl, trifluoromethyl, trifluoromethoxy, alkynyl, and the like.

[0046] Specific examples of first precursor include, but are not limited to, one or more of terephthalaldehyde, phenylenediamine, ethylenediamine, hexamethylenediamine, terephthaloyl chloride, 1,3,5-benzenetricarbonyl trichloride, pyromellitic dianhydride, benzene-1,3,5-tricarboxaldehyde, 1,4-phenylene diisocyanate, 4,4'-oxydianiline, tris(2-aminoethyl) amine, and the like.

[0047] In one or more embodiments, the formation rate of the first portion of the carbon-containing film may depend on the temperature of the substrate as well as the temperature of the deposition precursors that flow into the substrate processing region. Exemplary substrate temperatures during the formation operations may be greater than or equal to 50 °C, greater than or equal to 60 °C, greater than or equal to 70 °C, greater than or equal to 80 °C, greater than or equal to 90 °C, greater than or equal to 100 °C, greater than or equal to 110 °C, greater than or equal to 120 °C, greater than or equal to 130 °C, greater than or equal to 140 °C, greater than or equal to 150 °C, or higher. By maintaining the substrate temperature elevated, such as above or about 100 °C in some embodiments, an increased number of nucleation sites may be available along the substrate 104 and patterned surface 102, which may improve formation and reduce void formation by improving coverage at each location.

[0048] The first precursor effluent may remain in the substrate processing region for a period of time to nearly, or completely, form the first portion of the carbon-containing film 108. The precursors may be delivered in alternating pulses to grow the material. In some embodiments, the pulse times of either or both of the first precursor and the second precursor may be greater than or equal to 0.1 seconds, greater than or equal to 1 second, greater than or equal to 2 seconds, greater than or equal to 3 seconds, greater than or equal to 4 seconds, greater than or equal to 5 seconds, greater than or equal to 10 seconds, greater than or equal to 20 seconds, greater than or equal to 40 seconds, greater than or equal to 60 seconds, greater than or equal to 80 seconds, greater than or equal to 100 seconds, or more.

- [0049] With reference to FIG. 2, at operation 208, the first precursor is purged or removed from the substrate processing region following formation of the first portion 110 of the carbon-containing film 108. The effluents of the first precursor may be removed by pumping them out of the substrate deposition region for a period of time ranging from about 10 seconds to about 100 seconds. Additional exemplary time ranges may include about 20 seconds to about 50 seconds, and 25 seconds to about 45 seconds, among other exemplary time ranges. In some embodiments, however, increased purge time may begin to remove reactive sites, which may reduce uniform formation. Accordingly, in some embodiments the purge may be performed for less than or equal to 60 seconds and may be performed for less than or equal to 50 seconds, less than or equal to 40 seconds, less than or equal to 30 seconds, or less. In some embodiments, a purge gas may be introduced to the substrate processing region to assist in the removal of the effluents. Exemplary purge gases include argon (Ar), helium (He), and nitrogen (N₂), among other purge gases.
- 15 [0050] Referring to FIG. 1C and FIG. 2, at operation 210, a second type of precursor, reacts with the first precursor to form a second portion of carbon-containing film 108. The second precursor may advantageously have functional groups on one end that increase the thickness of the carbon-containing film 108.
- 20 [0051] In one or more embodiments, the second precursor may be a carbon-containing precursor that has at least two reactive groups that can form bonds with unreacted reactive groups of the first precursor that formed the first portion of the carbon-containing film 108. Molecules of the second precursor react with the unreacted reactive groups of the first precursor to form bonds linking the second precursor molecules to the first precursor molecules. The reactions between the second and first precursor molecules continue until most or all the unreacted reactive groups on the first precursor molecules have reacted with second precursor molecules. A second portion of a carbon-containing film 108 of the deposition precursors is formed that blocks further reaction between second precursor molecules in the second precursor effluent and the first portion of the carbon-containing film 108.
- 25 [0052] The second precursor may comprise any suitable precursor known to the skilled artisan. In one or more embodiments, the second precursor may have a general formula $R^2-(Y)_n$ wherein n is an integer in a range of from 1 to 6, and R^2
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comprises one or more of an alkyl group, an alkenyl group, an aryl, or aromatic group, and a cycloalkyl group. In one or more embodiments, R^2 is independently selected from C_{1-20} alkyl. In other embodiments, R^2 is from C_{1-12} alkyl. Y_n comprises one or more of a hydroxide group, an aldehyde group, a ketone group, an acid group, an amino group, an isocyanate group, a thiocyanate group, and an acyl chloride group.

[0053] Without intending to be bound by theory, it is thought that the second precursor includes a reactive group that can form a covalent bond with a reactive group of the first precursor.

[0054] Specific examples of second precursor include, but are not limited to, one or more of terephthalaldehyde, phenylenediamine, ethylenediamine, hexamethylenediamine, terephthaloyl chloride, 1,3,5-benzenetricarbonyl trichloride, pyromellitic dianhydride, benzene-1,3,5-tricarboxaldehyde, 1,4-phenylene diisocyanate, 4,4'-Oxydianiline, tris(2-aminoethyl) amine, and the like.

[0055] Referring to FIG. 2, in one or more embodiments, the method 200 also includes an operation 212 to purge or remove the second precursor effluents from the substrate processing region following the formation of the second portion of the carbon-containing film 108. The effluents may be removed by pumping them out of the substrate deposition region for a period of time ranging from about 10 seconds to about 100 seconds. Additional exemplary time ranges may include about 20 seconds to about 50 seconds, and 25 seconds to about 45 seconds, among other exemplary time ranges. In some embodiments, a purge gas may be introduced to the substrate processing region to assist in the removal of the effluents. Exemplary purge gases include argon, helium, and nitrogen, among other purge gases.

[0056] In one or more embodiments, the formation rate of the second portion of the carbon-containing film 108 may also depend on the pressure of the second precursor effluent in the substrate processing region. Exemplary effluent pressures in the substrate processing region may range from about 1 mTorr to about 20 Torr. Additional exemplary ranges include 5 Torr to 15 Torr, and 9 Torr to 12 Torr, among other exemplary ranges.

[0057] With reference to FIG. 2, in one or more embodiments of the method 200 there is a determination/decision point 214 of whether a target thickness of the as-deposited carbon-containing film 108 on substrate 104 and patterned surface 102 has

been achieved following one or more cycles of forming a carbon-containing film 108 (e.g., following the formation of the first and second portions of a compound layer). If a target thickness of as-deposited carbon-containing film 108 has not been achieved, another cycle of forming first and second portions of a carbon-containing film 108 is performed. If a target thickness of as-deposited carbon-containing film 108 has been achieved, another cycle to form another carbon-containing film 108 is not started. Exemplary numbers of cycles for the formation of carbon-containing films may include 1 cycle to 2000 cycles. Additional exemplary ranges for the number of cycles may include 50 cycles to 1000 cycles, and 100 cycles to 750 cycles, among other exemplary ranges.

[0058] Accordingly, in one or more embodiments, the method 200 further includes depositing at least one additional carbon-containing film on the initial carbon-containing film, where the initial carbon-containing film and the at least one additional carbon-containing film form the carbon-containing film 108 on the metal surface of the substrate.

[0059] In one or more embodiments, the carbon-containing film 108 may have any suitable thickness. In one or more embodiments, the thickness of the carbon-containing film 108 is in a range of from 0.1 nm to 200 nm, or in a range of from 1 nm to 20 nm, or in a range of from 1 nm to 10 nm.

[0060] In the embodiment shown in method 200 of FIG. 2, the as-deposited carbon-containing film 108 on the substrate 104 and patterned surface 102 may be optionally post-processed at operation 216. The optional post-processing operation 216 can be, for example, a process to modify film properties (e.g., annealing or plasma treatment) or a further film deposition process (e.g., additional ALD or CVD processes) to grow additional films. In some embodiments, the optional post-processing operation 216 can be a process that modifies a property of the deposited film. In some embodiments, the optional post-processing operation 216 comprises annealing the carbon-containing film 108. In some embodiments, annealing is done at temperatures in the range of about 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, 900 °C or 1000 °C. The annealing environment of some embodiments comprises one or more of an inert gas (e.g., molecular nitrogen (N₂), argon (Ar)) or a reducing gas (e.g., molecular hydrogen (H₂) or ammonia (NH₃)) or an oxidant, such as, but not

limited to, oxygen (O₂), ozone (O₃), or peroxides. Annealing can be performed for any suitable length of time. In some embodiments, the carbon-containing film is annealed for a predetermined time in the range of about 15 seconds to about 90 minutes, or in the range of about 1 minute to about 60 minutes. In some embodiments, annealing
5 the as-deposited carbon-containing film increases the density, decreases the resistivity, and/or increases the purity of the film.

[0061] With reference to FIG. 1D, in one or more embodiments, the carbon-containing film 108 is subjected to an etching process to remove a portion of the carbon-containing film 108 and expose a top surface 110 of the patterned surface 102
10 and to expose a portion of the substrate 104 between the patterned surface 102. The etching processing may be any suitable etching process known to the skilled artisan. In one or more embodiments, the etching process is a dry etching process.

[0062] In one or more embodiments, removing the portion of the carbon-containing film from the top surface 110 of the patterned surface forms a spacer on the patterned
15 structure. The critical dimension, d2, between the adjacent spacers on the patterned surface 102 is less than the critical dimension, d1, prior to formation of the carbon-containing film 108. In one or more embodiments, the critical dimension, d2, after removing the carbon-containing film from the top surface 110 of the patterned surface 102 is in a range of from 5 nm to 500 nm, or in a range of from 10 nm to 200 nm, or in
20 a range of from 20 nm to 100 nm.

[0063] FIG. 3 illustrates a process flow diagram of a method 300 of depositing a spacer film according to one or more embodiments. In one or more embodiments, the spacer film formed according to method 300 is a metal-doped carbon-containing film. In one or more embodiments, the carbon-containing film 108 may be doped with a
25 metal selected from one or more of aluminum (Al), tin (Sn), zinc (Zn), titanium (Ti), and the like. Referring to FIGS. 1A-1D and FIG. 3, in one or more embodiments, at operation 302, a patterned substrate is provided.

[0064] Referring to FIG. 3, in one or more embodiments, at operation 304, the substrate 104 and patterned surface 102 may optionally be exposed to a pretreatment
30 process to polish, coat, dope, etch, reduce, oxidize, hydroxylate, anneal, UV cure, e-beam cure and/or bake the substrate, as discussed above with respect to FIG. 2.

[0065] At operation 306, a first type of precursor is introduced/flowed into the substrate processing region of a processing chamber and over the substrate surface. The first precursor binds strongly to the substrate 104 and patterned surface 102.

[0066] In one or more embodiments, the first precursor may be a carbon-containing precursor that has at least two reactive groups that can form a bond with a group attached to the substrate 104 and patterned surface 102, as discussed above with respect to FIG. 2. Molecules of the first precursor react with the surface groups of the substrate 104 and patterned surface 102 to form bonds linking the first precursor molecule to the substrate 104 and patterned surface 102. The reactions between the first precursor molecules and the groups on the substrate 104 and patterned surface 102 continue until most or all the surface groups are bonded to a reactive group on the first precursor molecules. A first portion of a carbon-containing film 108 is formed that blocks further reaction between first precursor molecules in the first precursor effluent and the substrate.

[0067] The first precursor may comprise any suitable precursor known to the skilled artisan, such as those discussed above. In other embodiments, the first precursor may comprise one or more of trimethyl aluminum (TMA), titanium tetrachloride (TiCl_4), tin tetrachloride (SnCl_4), diethyl zinc ($(\text{C}_2\text{H}_5)_2\text{Zn}$), and mixtures thereof.

[0068] With reference to FIG. 3, at operation 308, the first precursor is purged or removed from the substrate processing region following formation of the first portion 110 of the carbon-containing film 108. The effluents of the first precursor may be removed by pumping them out of the substrate deposition region for a period of time ranging from about 10 seconds to about 100 seconds. Exemplary purge gases include argon (Ar), helium (He), and nitrogen (N_2), among other purge gases.

[0069] At operation 310, a second type of precursor, reacts with the first precursor to form a second portion of carbon-containing film 108. The second precursor may advantageously have functional groups on one end that increase the thickness of the carbon-containing film 108.

[0070] In one or more embodiments, the second precursor may be a carbon-containing precursor that has at least two reactive groups that can form bonds with unreacted reactive groups of the first precursor that formed the first portion of the carbon-containing film 108, as discussed above with respect to FIG. 2. Molecules of

the second precursor react with the unreacted reactive groups of the first precursor to form bonds linking the second precursor molecules to the first precursor molecules. The reactions between the second and first precursor molecules continue until most or all the unreacted reactive groups on the first precursor molecules have reacted with
5 second precursor molecules. A second portion of a carbon-containing film 108 of the deposition precursors is formed that blocks further reaction between second precursor molecules in the second precursor effluent and the first portion of the carbon-containing film 108.

[0071] The second precursor may comprise any suitable precursor known to the
10 skilled artisan, such as those discussed above. In other embodiments, the second precursor may comprise one or more of trimethyl aluminum (TMA), titanium tetrachloride (TiCl₄), tin tetrachloride (SnCl₄), diethyl zinc ((C₂H₅)₂Zn), and mixtures thereof.

[0072] Without intending to be bound by theory, it is thought that the second
15 precursor includes a reactive group that can form a covalent bond with a reactive group of the first precursor.

[0073] Referring to FIG. 3, in one or more embodiments, the method 300 also includes an operation 312 to purge or remove the second precursor effluents from the substrate processing region following the formation of the second portion of the
20 carbon-containing film 108. The effluents may be removed by pumping them out of the substrate deposition region for a period of time ranging from about 10 seconds to about 100 seconds. Exemplary purge gases include argon, helium, and nitrogen, among other purge gases.

[0074] At operation 314, a third type of precursor, reacts with the second precursor
25 to form a third portion of carbon-containing film 108. The third precursor may advantageously have functional groups on one end that increase the thickness of the carbon-containing film 108.

[0075] In one or more embodiments, the third precursor may be a carbon-containing precursor that has at least two reactive groups that can form bonds with
30 unreacted reactive groups of the second precursor that formed the second portion of the carbon-containing film 108. Molecules of the third precursor react with the unreacted reactive groups of the second precursor to form bonds linking the third

precursor molecules to the second precursor molecules. The reactions between the third and second precursor molecules continue until most or all the unreacted reactive groups on the second precursor molecules have reacted with third precursor molecules. A third portion of a carbon-containing film 108 of the deposition precursors is formed that blocks further reaction between third precursor molecules in the third precursor effluent and the first portion of the carbon-containing film 108.

[0076] The third precursor may comprise any suitable precursor known to the skilled artisan, including, but not limited to any of the precursors described with respect to FIG. 2. In one or more embodiments, the third precursor may comprise one or more of TMA, titanium chloride (TiCl_4), tin chloride (SnCl_4), diethylzinc (Et_2Zn), and the like.

[0077] Without intending to be bound by theory, it is thought that the third precursor includes a reactive group that can form a covalent bond with a reactive group of the second precursor.

[0078] Specific examples of second precursor include, but are not limited to, one or more of terephthalaldehyde, phenylenediamine, ethylenediamine, hexamethylenediamine, terephthaloyl chloride, 1,3,5-benzenetricarbonyl trichloride, pyromellitic dianhydride, benzene-1,3,5-tricarboxaldehyde, 1,4-phenylene diisocyanate, 4,4'-Oxydianiline, tris(2-aminoethyl) amine, trimethyl aluminum (TMA), titanium tetrachloride (TiCl_4), tin tetrachloride (SnCl_4), diethyl zinc ($(\text{C}_2\text{H}_5)_2\text{Zn}$), and the like, and mixtures thereof.

[0079] Referring to FIG. 3, in one or more embodiments, the method 300 also includes an operation 316 to purge or remove the third precursor effluents from the substrate processing region following the formation of the third portion of the carbon-containing film 108. The effluents may be removed by pumping them out of the substrate deposition region for a period of time ranging from about 10 seconds to about 100 seconds. Additional exemplary time ranges may include about 20 seconds to about 50 seconds, and 25 seconds to about 45 seconds, among other exemplary time ranges. In some embodiments, a purge gas may be introduced to the substrate processing region to assist in the removal of the effluents. Exemplary purge gases include argon, helium, and nitrogen, among other purge gases.

- [0080] With reference to FIG. 3, in one or more embodiments of the method 300 there is a determination/decision point 318 of whether a target thickness of the as-deposited carbon-containing film 108, which may now be a metal-doped carbon-containing film, on substrate 104 and patterned surface 102 has been achieved following one or more cycles of forming a carbon-containing film 108 (e.g., following the formation of the first and second portions of a compound layer). If a target thickness of as-deposited carbon-containing film 108 has not been achieved, another cycle of forming first and second portions of a carbon-containing film 108 is performed. If a target thickness of as-deposited carbon-containing film 108 has been achieved, another cycle to form another carbon-containing film 108 is not started. Exemplary numbers of cycles for the formation of carbon-containing films may include 1 cycle to 2000 cycles. Additional exemplary ranges for the number of cycles may include 50 cycles to 1000 cycles, and 100 cycles to 750 cycles, among other exemplary ranges.
- [0081] Accordingly, in one or more embodiments, the method 300 further includes depositing at least one additional carbon-containing film on the initial carbon-containing film, where the initial carbon-containing film and the at least one additional carbon-containing film form the carbon-containing film 108 on the metal surface of the substrate.
- [0082] In one or more embodiments, the carbon-containing film 108 may have any suitable thickness. In one or more embodiments, the thickness of the carbon-containing film 108 is in a range of from 0.1 nm to 200 nm, or in a range of from 1 nm to 20 nm, or in a range of from 1 nm to 10 nm.
- [0083] In the embodiment shown in method 300 of FIG. 3, the as-deposited carbon-containing film 108 on the substrate 104 and patterned surface 102 may be optionally post-processed at operation 320. The optional post-processing operation 320 can be any of the optional post-processing operations described above with respect to FIG. 2.
- [0084] With reference to FIG. 1D, in one or more embodiments, the carbon-containing film 108 is subjected to an etching process to remove a portion of the carbon-containing film 108 and expose a top surface 110 of the patterned surface 102 and to expose the substrate 104 between the patterns. The etching processing may

be any suitable etching process known to the skilled artisan. In one or more embodiments, the etching process is a dry etching process.

[0085] Some embodiments of the disclosure are directed to electronic devices comprising nanostructures having the carbon-containing film 108 as a spacer layer
5 remaining after the etch process removes the carbon-containing film 108 and optional liner layer 106 from the bottom part of the trench between the structures. The carbon-containing film 108 may act as an etch protection layer or an etch resistance layer for the sidewall of the nanostructures. In some embodiments, the carbon-containing film 108 acts as a liner material when no etch is performed. In some embodiments, the
10 carbon-containing film 108 acts as a spacer when formed on the sidewall of the EUV photoresist pattern to reduce the critical dimension (CD) or for CD shrinkage.

[0086] In some embodiments, the processing region is in a modular system comprising multiple chambers which perform various functions including substrate center-finding and orientation, degassing, annealing, deposition and/or etching.
15 According to one or more embodiments, the modular system includes at least a first processing chamber and a central transfer chamber. The central transfer chamber may house a robot that can shuttle substrates between and among processing chambers and load lock chambers. The transfer chamber is typically maintained at a vacuum condition and provides an intermediate stage for shuttling substrates from
20 one chamber to another and/or to a load lock chamber positioned at a front end of the cluster tool. However, the exact arrangement and combination of chambers may be altered for purposes of performing specific steps of a process as described herein. Other processing chambers which may be used include, but are not limited to, cyclical layer deposition (CLD), atomic layer deposition (ALD), chemical vapor deposition
25 (CVD), physical vapor deposition (PVD), etch, pre-clean, chemical clean, thermal treatment such as RTP, plasma nitridation, degas, orientation, hydroxylation, and other substrate processes. By carrying out processes in the processing chamber of modular system, surface contamination of the substrate with atmospheric impurities can be avoided without oxidation prior to depositing a subsequent film.

30 [0087] According to one or more embodiments, the substrate is continuously under vacuum or "load lock" conditions and is not exposed to ambient air when being moved from one chamber to the next. The transfer chambers are thus under vacuum and are

"pumped down" under vacuum pressure. Inert gases may be present in the processing chambers or the transfer chambers. In some embodiments, the inert gas is used to purge or remove some or all of the reactants (e.g., reactant). According to one or more embodiments, the inert gas is injected at the exit of the processing chamber to prevent reactants (e.g., reactant) from moving from the processing chamber to the transfer chamber and/or additional processing chamber. Thus, the flow of inert gas forms a curtain at the exit of the chamber.

[0088] The substrate can be processed in single substrate deposition chambers, where a single substrate is loaded, processed, and unloaded before another substrate is processed. The substrate can also be processed in a continuous manner, similar to a conveyer system, in which multiple substrates are individually loaded into a first part of the chamber, move through the chamber, and are unloaded from a second part of the chamber. The shape of the chamber and associated conveyer system can form a straight path or curved path. Additionally, the processing chamber may be a carousel in which multiple substrates are moved about a central axis and are exposed to deposition, etch, annealing, cleaning, etc. processes throughout the carousel path.

[0089] During processing, the substrate can be heated or cooled. Such heating or cooling can be accomplished by any suitable means including, but not limited to, changing the temperature of the substrate support, and flowing heated or cooled gases to the substrate surface. In some embodiments, the substrate support includes a heater/cooler which can be controlled to change the substrate temperature conductively. In one or more embodiments, the gases (either reactive gases or inert gases) being employed are heated or cooled to locally change the substrate temperature. In some embodiments, a heater/cooler is positioned within the chamber adjacent the substrate surface to convectively change the substrate temperature.

[0090] The substrate can also be stationary or rotated during processing. A rotating substrate can be rotated (about the substrate axis) continuously or in discrete steps. For example, a substrate may be rotated throughout the entire process, or the substrate can be rotated by a small amount between exposures to different reactive or purge gases. Rotating the substrate during processing (either continuously or in steps) may help produce a more uniform deposition or etch by minimizing the effect of, for example, local variability in gas flow geometries.

[0091] In a spatial ALD process, the reactive gases are flowed into different processing regions within a processing chamber. The different processing regions are separated from adjacent processing regions so that the reactive gases do not mix. The substrate can be moved between the processing regions to separately expose
5 the substrate to the reactive gases. During substrate movement, different portions of the substrate surface, or material on the substrate surface, are exposed to the two or more reactive gases so that any given point on the substrate is substantially not exposed to more than one reactive gas simultaneously. As will be understood by those skilled in the art, there is a possibility that a small portion of the substrate may
10 be exposed to multiple reactive gases simultaneously due to diffusion of the gases within the processing chamber, and that the simultaneous exposure is unintended, unless otherwise specified.

[0092] In another aspect of the spatial ALD process, the reactive gases are delivered simultaneously to the reaction zone but are separated by an inert gas
15 curtain and/or a vacuum curtain. The gas curtain can be combination of inert gas flows into the processing chamber and vacuum stream flows out of the processing chamber. The substrate is moved relative to the gas delivery apparatus so that any given point on the substrate is exposed to only one reactive gas.

[0093] A "pulse" or "dose" as used herein refers to a quantity of a source gas that is
20 intermittently or non-continuously introduced into the process chamber. The quantity of a particular compound within each pulse may vary over time, depending on the duration of the pulse. A particular process gas may include a single compound or a mixture/combination of two or more compounds.

[0094] In a time-domain ALD process in some embodiments, exposure to each
25 reactive gas, which includes but not limited to the metal and dielectric material to be used for the ALD film, is separated by a time delay to allow each compound to adhere and/or react on the substrate surface and then be purged from the processing chamber. The reactive gases are prevented from mixing by the purging of the processing chamber between subsequent exposures.

[0095] In another aspect of a time-domain ALD process of some embodiments, a
30 time delay exists between pulses of reactive gases. During each time delay, a purge gas, such as argon, is introduced into the processing chamber to purge the reaction

zone or otherwise remove any residual reactive gas or reaction products or by-products from the reaction zone. Alternatively, the purge gas may flow continuously throughout the deposition process so that only the purge gas flows during the time delay between pulses of reactive gases. The reactive gases are alternatively pulsed with a pulse of purge gas there between multiple times. The purge may also be achieved with a vacuum pump with or without an inert gas.

[0096] The durations for each pulse/dose are variable and may be adjusted to accommodate, for example, the volume capacity of the processing chamber as well as the capabilities of a vacuum system coupled thereto. Additionally, the dose time of a reactive gas may vary according to the flow rate of the reactive gas, the temperature of the process gas, the type of control valve, the type of process chamber employed, as well as the ability of the components of the process gas to adsorb onto the substrate. Dose times may also vary based upon the type of layer being formed and the geometry of the device being formed. A dose time should be long enough to provide a volume of compound sufficient to adsorb/chemisorb onto substantially the entire surface of the substrate and form a layer of a process gas component thereon.

[0097] Once the carbon-containing film is deposited, the method may optionally include further processing (e.g., bulk deposition of a dielectric film). In some embodiments, the further processing may be an ALD process.

[0098] The disclosure provides that the processes may generally be stored in the memory as a software routine that, when executed by the processor, causes the process chamber to perform processes of the present disclosure. The software routine may also be stored and/or executed by a second processor (not shown) that is remotely located from the hardware being controlled by the processor. Some or all of the method of the present disclosure may also be performed in hardware. As such, the process may be implemented in software and executed using a computer system, in hardware as, e.g., an application specific integrated circuit or other type of hardware implementation, or as a combination of software and hardware. The software routine, when executed by the processor or controller, transforms the general-purpose computer into a specific purpose computer (controller) that controls the chamber operation such that the processes are performed. The process can be stored on non-transitory computer readable medium including instructions, that, when executed by a

controller of a substrate processing chamber, causes the substrate processing chamber to perform the operations of: flow a first precursor over a substrate comprising a patterned surface to form a first portion of a carbon-containing film on the patterned surface, the first precursor comprising a first reactive group, and the pattern surface comprises a sidewall and a top surface; remove a first precursor effluent comprising the first precursor from the substrate; flow a second precursor comprising a second reactive group over the substrate to react with the first reactive group to form the carbon-containing film on the patterned surface; remove a second precursor effluent comprising the second precursor from the substrate; and etch the substrate to remove a portion of the carbon-containing film from a top surface of the patterned surface to form a spacer layer on a first sidewall and on a second sidewall of the patterned surface.

[0099] Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments" or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the disclosure. Thus, the appearances of the phrases such as "in one or more embodiments," "in certain embodiments," "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily referring to the same embodiment of the disclosure. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

[00100] Although the disclosure herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present disclosure. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present disclosure without departing from the spirit and scope of the disclosure. Thus, it is intended that the present disclosure include modifications and variations that are within the scope of the appended claims and their equivalents.

What is claimed is:

1. A method of depositing a spacer film, the method comprising:
flowing a first precursor over a substrate comprising a patterned surface to form
5 a first portion of a carbon-containing film on the patterned surface, the first precursor
comprising a first reactive group, and the pattern surface comprises a sidewall and a
top surface;
removing a first precursor effluent comprising the first precursor from the
substrate;
10 flowing a second precursor comprising a second reactive group over the
substrate to react with the first reactive group to form the carbon-containing film
conformally on the patterned surface, wherein the carbon-containing film acts as an
etch protection layer or as a liner; and
removing a second precursor effluent comprising the second precursor from
15 the substrate.
2. The method of claim 1, wherein the first precursor has a general formula $R^1-(X)_n$
wherein R^1 comprises one or more of an alkyl group, an alkenyl group, an
20 aryl group, an aromatic group, and a cycloalkyl group, X_n comprises one or more of a
hydroxide group, an aldehyde group, a ketone group, an acid group, an amino group,
an isocyanate group, a thiocyanate group, and an acyl chloride group, and n is an
integer in a range of from 1 to 6.
- 25 3. The method of claim 1, wherein the second precursor has a general formula $R^2-(Y)_n$
wherein R^2 comprises one or more of an alkyl group, an alkenyl group, an
aryl group, an aromatic group, and a cycloalkyl group, Y_n comprises one or more of a
hydroxide group, an aldehyde group, a ketone group, an acid group, an amino group,
30 an isocyanate group, a thiocyanate group, and an acyl chloride group, and n is an
integer in a range of from 1 to 6.

4. The method of claim 1, wherein the first precursor and the second precursor are independently selected from one or more of terephthalaldehyde, phenylenediamine, ethylenediamine, hexamethylenediamine, terephthaloyl chloride, 1,3,5-benzenetricarbonyl trichloride, pyromellitic dianhydride, benzene-1,3,5-
5 tricarboxaldehyde, 1,4-phenylene diisocyanate, 4,4'-oxydianiline, and tris(2-aminoethyl) amine.
5. The method of claim 4, wherein the first precursor comprises terephthalaldehyde and the second precursor comprises phenylenediamine.
- 10 6. The method of claim 1, further comprising etching the patterned surface to remove a portion of the carbon-containing film from the top surface of the patterned surface and from the substrate to form a spacer layer on the sidewall of the patterned surface, wherein the carbon-containing film acts as an etch protection layer.
- 15 7. The method of claim 1, further comprising repeating the method to form the carbon-containing film having a thickness in a range of from 1 nm to 20 nm.
8. The method of claim 1, wherein removing the first precursor comprises:
20 flowing a purge gas over the substrate; and
 removing a mixture of the first precursor effluent and the purge gas from the substrate.
9. The method of claim 1, wherein the patterned surface is an EUV photoresist
25 pattern, and the carbon-containing film is formed on the sidewall and acts as a spacer to reduce the critical dimension (CD).
10. The method of claim 1, further comprising flowing a third precursor over the
30 substrate to form a third portion of the carbon-containing film on the patterned surface, wherein one or more of the first precursor, the second precursor, or the third precursor comprises trimethyl aluminum (TMA), titanium tetrachloride

(TiCl₄), tin tetrachloride (SnCl₄), diethyl zinc ((C₂H₅)₂Zn), and the carbon-containing film is doped with a metal.

11. The method of claim 10, further comprising removing a third precursor effluent
5 comprising the third precursor from the substrate.

12. A method of depositing a spacer film, the method comprising:
flowing a first precursor over a substrate comprising a patterned surface, the
first precursor having a general formula R¹-(X)_n
10 wherein R¹ comprises one or more of an alkyl group, an alkenyl
group, an aryl group, an aromatic group, and a cycloalkyl group, X_n
comprises one or more of a hydroxide group, an aldehyde group, a
ketone group, an acid group, an amino group, an isocyanate group, a
thiocyanate group, and an acyl chloride group, and n is an integer in a
15 range of from 1 to 6,

wherein the first precursor reacts with a reactive group on the
patterned surface to form a first portion of a carbon-containing film;
removing a first precursor effluent comprising the first precursor from the
substrate;

20 flowing a second precursor over the substrate, the second precursor having a
general formula R²-(Y)_n

wherein R² comprises one or more of an alkyl group, an alkenyl
group, an aryl group, an aromatic group, and a cycloalkyl group, Y_n
comprises one or more of a hydroxide group, an aldehyde group, a
25 ketone group, an acid group, an amino group, an isocyanate group, a
thiocyanate group, and an acyl chloride group, and n is an integer in a
range of from 1 to 6,

wherein the second precursor reacts with the first portion to form
a conformational carbon-containing film;

30 removing a second precursor effluent comprising the second precursor from
the substrate; and

etching the substrate to remove a portion of the carbon-containing film from a top surface of the patterned surface to form a spacer layer on a first sidewall and on a second sidewall of the patterned surface.

5 13. The method of claim 12, wherein the first precursor and the second precursor are independently selected from one or more of terephthalaldehyde, phenylenediamine, ethylenediamine, hexamethylenediamine, terephthaloyl chloride, 1,3,5-benzenetricarbonyl trichloride, pyromellitic dianhydride, benzene-1,3,5-tricarboxaldehyde, 1,4-phenylene diisocyanate, 4,4'-oxydianiline, and tris(2-
10 aminoethyl) amine.

14. The method of claim 13, wherein the first precursor comprises terephthalaldehyde and the second precursor comprises phenylenediamine.

15 15. The method of claim 12, further comprising depositing a liner on the patterned surface prior to flowing the first precursor over the substrate.

16. The method of claim 12, wherein removing the first precursor comprises:
flowing a purge gas over the substrate; and
20 removing a mixture of the first precursor effluent and the purge gas from the substrate.

17. The method of claim 12, wherein the patterned surface is an EUV photoresist pattern, and the carbon-containing film is formed on the sidewall and acts as a spacer
25 to reduce the critical dimension (CD).

18. The method of claim 12, further comprising flowing a third precursor over a substrate comprising a patterned surface to form a third portion of the carbon-containing film on the patterned surface, wherein the third precursor is selected
30 from the group consisting of trimethyl aluminum (TMA), titanium tetrachloride (TiCl₄), tin tetrachloride (SnCl₄), diethyl zinc ((C₂H₅)₂Zn), and mixtures thereof, and wherein the carbon-containing film is doped with a metal.

19. The method of claim 18, further comprising removing a third precursor effluent comprising the third precursor from the substrate.
20. A non-transitory computer readable medium including instructions, that, when
5 executed by a controller of a processing chamber, causes the processing chamber to perform operations of:
- flow a first precursor over a substrate comprising a patterned surface to form a first portion of a carbon-containing film on the patterned surface, the first precursor comprising a first reactive group, and the pattern surface comprises a
10 sidewall and a top surface;
- remove a first precursor effluent comprising the first precursor from the substrate;
- flow a second precursor comprising a second reactive group over the substrate to react with the first reactive group to conformally form the carbon-
15 containing film on the patterned surface;
- remove a second precursor effluent comprising the second precursor from the substrate; and
- etch the substrate to remove a portion of the carbon-containing film from a top surface of the patterned surface to form a spacer layer on a first sidewall
20 and on a second sidewall of the patterned surface.