

MOLYBDENUM(0) PRECURSORS FOR DEPOSITION OF MOLYBDENUM FILMS

TECHNICAL FIELD

[0001] Embodiments of the disclosure relate to molybdenum precursors and methods
5 for depositing molybdenum-containing films. More particularly, embodiments of the
disclosure are directed to bis(arene)molybdenum(0) precursors and methods of use
thereof.

BACKGROUND

10 [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 integration
increases, the need for greater uniformity and process control regarding layer thickness
15 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] Chemical vapor deposition (CVD) is one of the most common deposition
processes employed for depositing layers on a substrate. CVD is a flux-dependent
20 deposition technique that requires precise control of the substrate temperature and the
precursors introduced into the processing chamber in order to produce a desired layer
of uniform thickness. These requirements become more critical as substrate size
increases, creating a need for more complexity in chamber design and gas flow
technique to maintain adequate uniformity.

25 [0004] A variant of CVD that demonstrates excellent step coverage is cyclical
deposition or atomic layer deposition (ALD). ALD employs chemisorption techniques to
deliver precursor molecules on a substrate surface in sequential cycles. A cycle, for
example, includes exposing the substrate surface to a first precursor, a purge gas, a
second precursor and the purge gas. The first and second precursors react to form a
30 product compound as a film on the substrate surface. The cycle is repeated to form the
layer to a desired thickness.

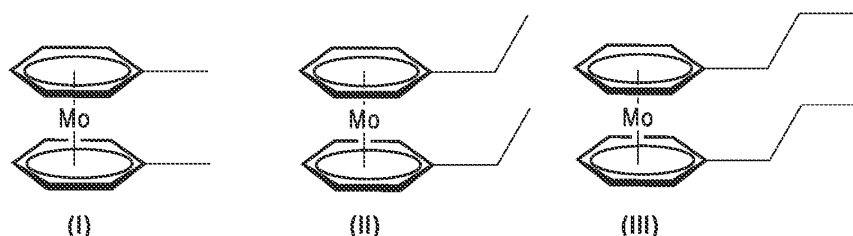
[0005] The advancing complexity of advanced microelectronic devices is placing stringent demands on currently used deposition techniques. Unfortunately, there is a limited number of viable chemical precursors available that have the requisite properties of robust thermal stability, high reactivity, and vapor pressure suitable for film growth to occur. In addition, precursors that often meet these requirements still suffer from poor long-term stability and lead to thin films that contain elevated concentrations of contaminants such as oxygen, nitrogen, and/or halides that are often deleterious to the target film application.

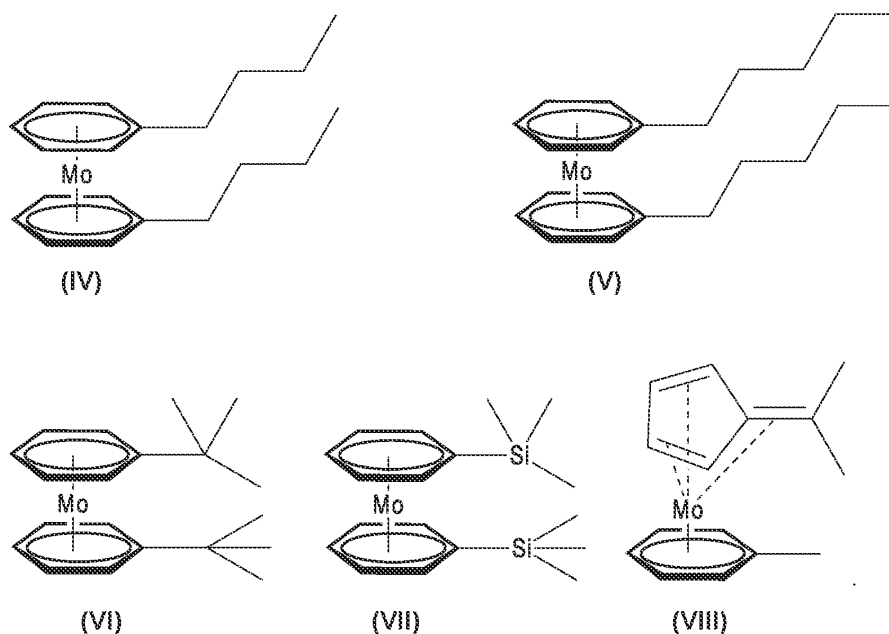
[0006] Molybdenum and molybdenum-based films have attractive material and conductive properties. These films have been proposed and tested for applications from front end to back end parts of semiconductor and microelectronic devices. Processing a molybdenum precursor often involves use of halogen and carbonyl-based substituents. It is thought that the presence of halogens in the structure of molybdenum (Mo) precursors can pose challenges, as halogen contamination may affect device performance and hence require additional removal procedures. Additionally, the presence of halogens in the structure of molybdenum (Mo) precursors may undesirably etch other metal films. Carbonyl-based substituents, for example, are less thermally stable, and usually require lower temperature.

[0007] There is, therefore, a need in the art for molybdenum precursors that are free of halogen groups that react to form molybdenum metal and molybdenum-based films.

SUMMARY

[0008] One or more embodiments of the disclosure are directed to a molybdenum(0) precursor comprising of Formula (I), Formula (II), Formula (III), Formula (IV), Formula (V), Formula (VI), Formula (VII), or Formula (VIII):





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In some embodiments, the molybdenum(0) precursor has a purity of greater than or equal to 90% molybdenum (Mo) on a molar basis.

[0009] Additional embodiments of the disclosure are directed to a method of forming a molybdenum-containing film. In one or more embodiments, the method comprises: exposing a substrate surface to a molybdenum(0) precursor; and exposing the substrate surface to a reactant to form the molybdenum-containing film on the substrate surface.

[0010] Further embodiments of the disclosure are directed to methods of forming a molybdenum-containing film. In one or more embodiments, the method comprises: performing a process cycle comprising sequential exposure of a substrate surface to a molybdenum(0) precursor, purge gas, reactant, and purge gas.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] So that the manner in which the above recited features of the 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 appended

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drawings illustrate only typical embodiments of the disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective embodiments.

[0012] FIG. 1 illustrates a process flow diagram of a method in accordance with one
5 or more embodiments of the disclosure.

DETAILED DESCRIPTION

[0013] 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 steps
10 set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0014] A "substrate" as used herein, refers to any substrate or material surface formed on a substrate upon which film processing is performed during a fabrication process. For example, a substrate surface on which processing can be performed
15 include materials such as silicon, silicon oxide, strained silicon, silicon on insulator (SOI), carbon doped silicon oxides, amorphous silicon, doped silicon, germanium, gallium arsenide, glass, sapphire, and any other materials such as metals, metal oxides, metal nitrides, metal alloys, and other conductive materials, depending on the application. Substrates include, without limitation, semiconductor wafers. Substrates
20 may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal and/or bake the substrate surface. In addition to film processing directly on the surface of the substrate itself, in the present invention, 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
25 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 surface.

[0015] According to one or more embodiments, the method uses an atomic layer deposition (ALD) process. In such embodiments, the substrate surface is exposed to
30 the precursors (or reactive gases) sequentially or substantially sequentially. As used herein throughout the specification, "substantially sequentially" means that a majority of

the duration of a precursor exposure does not overlap with the exposure to a co-reagent, although there may be some overlap.

[0016] 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.

[0017] "Atomic layer deposition" or "cyclical deposition" as used herein refers to the sequential exposure of two or more reactive compounds to deposit a layer of material on a substrate surface. 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 surface or material on the substrate surface in a surface reaction (e.g., chemisorption, oxidation, reduction). 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. In a time-domain ALD process, exposure to each reactive compound is separated by a time delay to allow each compound to adhere and/or react on the substrate surface. In a spatial ALD process, different portions of the substrate surface, or material on the substrate surface, are exposed simultaneously to the two or more reactive compounds so that any given point on the substrate is substantially not exposed to more than one reactive compound simultaneously. As used in this specification and the appended claims, the term "substantially" used in this respect means, as will be understood by those skilled in the art, that there is the possibility that a small portion of the substrate may be exposed to multiple reactive gases simultaneously due to diffusion, and that the simultaneous exposure is unintended.

[0018] In one aspect of a time-domain ALD process, a first reactive gas (i.e., a first precursor or compound A) is pulsed into the reaction zone followed by a first time delay. Next, a second precursor or compound B is pulsed into the reaction zone followed by a second delay. 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 compound 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 compounds. The reactive

compounds are alternatively pulsed until a desired film or film thickness is formed on the substrate surface. In either scenario, the ALD process of pulsing compound A, purge gas, compound B and purge gas is a cycle. A cycle can start with either compound A or compound B and continue the respective order of the cycle until achieving a film with the desired thickness. In some embodiments, there may be two reactants, A and B, that are alternately pulsed and purged. In other embodiments, there may be three or more reactants, A, B, and C, that are alternately pulsed and purged.

[0019] In an aspect of a spatial ALD process, a first reactive gas and second reactive gas (e.g., hydrogen radicals) are delivered simultaneously to the reaction zone but are separated by an inert gas curtain and/or a vacuum curtain. The substrate is moved relative to the gas delivery apparatus so that any given point on the substrate is exposed to the first reactive gas and the second reactive gas.

[0020] Current molybdenum precursors for ALD of metallic films use halogen and carbonyl-based substituents, which provide sufficient stability at the expense of reduced reactivity, increasing process temperature. Halogen substituents, such as chloride, for example, provide good thermal stability and reactivity. Halogen substituents do not pose restrictions in terms of temperature, and being stable at higher process temperatures may, in some cases, be beneficial (e.g., for metal films). However, without intending to be bound by theory, it is thought that the presence of halogens in the structure of molybdenum (Mo) precursors can pose challenges, as halogen contamination may affect device performance and hence require additional removal procedures. Additionally, the presence of halogens in the structure of molybdenum (Mo) precursors may undesirably etch other metal films. Carbonyl-based substituents, for example, are less thermally stable, and usually require lower temperature. Other molybdenum precursors include anionic nitrogen ligands, which may lead to the formation of nitride impurities.

[0021] Embodiments of the present disclosure advantageously provide molybdenum(0) precursors that can be used in the formation of molybdenum-containing films on semiconductor substrates. In one or more embodiments, the molybdenum(0) precursors are heteroatom-free liquid precursors.

[0022] The molybdenum precursors described herein have been proposed for the vapor deposition of molybdenum-containing films because of their low molecular weight,

higher vapor pressure and higher thermal stability, which have either a number of gaseous ligands or volatile liquid ligands. All the precursors exist in zero oxidation state and would not require external reducing agents during precursor preparation. The molybdenum(0) precursors can advantageously be prepared as a single compound in a single step via ligand exchange reaction starting from a commercially available molybdenum(0) precursor. In one or more embodiments, a commercially available molybdenum(0) precursor may be formed from any known molybdenum-containing compound, such as molybdenum chloride (MoCl_5), and the commercially available molybdenum(0) precursor can be used to prepare the molybdenum(0) precursors described herein as a single compound in a single step via ligand exchange reaction.

[0023] The molybdenum(0) precursors of one or more embodiments advantageously avoid additional processes for metal reduction, are free of halogen atoms, are free of oxygen atoms, are free of molybdenum-oxygen (Mo-O) bonds, are thermally stable for delivery, have high vapor pressure, are deliverable by vapor methods, are reactive for ALD processes at low temperatures ($<400^\circ\text{C}$), and achieve successful synthesis of precursors comprising a single compound in one step starting from a commercially available molybdenum(0) precursor with high yield and purity. The zero oxidation state molybdenum complexes advantageously provide molybdenum(0) precursors having improved thermal stability, while retaining high volatility.

[0024] The molybdenum(0) precursors of one or more embodiments advantageously have a purity of greater than or equal to 90% molybdenum (Mo), greater than or equal to 95% molybdenum (Mo), greater than or equal to 99% molybdenum (Mo), or greater than or equal to 99.9% molybdenum (Mo), on a molar basis. Stated differently, a purity of greater than or equal to 90% molybdenum (Mo), greater than or equal to 95% molybdenum (Mo), greater than or equal to 99% molybdenum (Mo), or greater than or equal to 99.9% molybdenum (Mo), for example, means that greater than or equal to 90%, greater than or equal to 95%, greater than or equal to 99%, or greater than or equal to 99.9% of the molecules in the stated molybdenum(0) precursor include a molybdenum (Mo) species. Advantageously, the molybdenum(0) precursors can be prepared as a single compound in a single step starting from a commercially available molybdenum(0) precursor and have a purity of greater than or equal to 90%

molybdenum (Mo), on a molar basis. It is believed that the purity of the molybdenum(0) precursor, on a molar basis, increases after subsequent reaction cycles.

[0025] Without intending to be bound by theory, it is thought that precursors comprising multiple compounds or a mixture of compounds, such as commercially available bis(ethylbenzene)molybdenum, for example, may be prone to processing issues and/or film quality issues.

[0026] In some embodiments, the molybdenum(0) precursor is free of halogen. In some embodiments, the molybdenum(0) precursor is free of oxygen and molybdenum-oxygen (Mo-O) bonds. In one or more embodiments, the molybdenum(0) precursor is free of halogen, oxygen, and molybdenum-oxygen (Mo-O) bonds. In one or more embodiments, the molybdenum(0) precursor is substantially free of halogen, oxygen, and molybdenum-oxygen (Mo-O) bonds.

[0027] As used herein, the term "substantially free" means that there is less than less than about 5%, including less than about 4%, less than about 3%, less than about 2%, less than about 1%, and less than about 0.5% of halogen, on an atomic basis, in the molybdenum-containing film. In some embodiments, the molybdenum-containing film is substantially free of oxygen, and there is less than about 10%, less than about 9%, less than about 8%, less than about 7%, less than about 6%, less than about 5%, including less than about 4%, less than about 3%, less than about 2%, less than about 1%, and less than about 0.5% of oxygen, on an atomic basis, in the molybdenum-containing film. In some embodiments, the molybdenum-containing film is substantially free of molybdenum-oxygen (Mo-O) bonds, and there is less than about 10%, less than about 9%, less than about 8%, less than about 7%, less than about 6%, less than about 5%, including less than about 4%, less than about 3%, less than about 2%, less than about 1%, and less than about 0.5% of molybdenum-oxygen (Mo-O) bonds, on an atomic basis, in the molybdenum-containing film.

[0028] The process of various embodiments uses vapor deposition techniques, such as an atomic layer deposition (ALD) or chemical vapor deposition (CVD) to provide molybdenum-containing films. The molybdenum(0) precursors of one or more embodiments are volatile and thermally stable, and, thus, suitable for vapor deposition.

[0029] Molybdenum (Mo) can be grown by atomic layer deposition (ALD) or chemical vapor deposition (CVD) for many applications. One or more embodiments of the

disclosure advantageously provide processes for atomic layer deposition (ALD) or chemical vapor deposition (CVD) to form molybdenum-containing films.

[0030] As described herein, the term "molybdenum-containing film" refers to a film that comprises molybdenum atoms and has greater than or equal to about 1 atomic % molybdenum, greater than or equal to about 2 atomic % molybdenum, greater than or equal to about 3 atomic % molybdenum, greater than or equal to about 4 atomic % molybdenum, greater than or equal to about 5 atomic % molybdenum, greater than or equal to about 10 atomic % molybdenum, greater than or equal to about 15 atomic % molybdenum, greater than or equal to about 20 atomic % molybdenum, greater than or equal to about 25 atomic % molybdenum, greater than or equal to about 30 atomic % molybdenum, greater than or equal to about 35 atomic % molybdenum, greater than or equal to about 40 atomic % molybdenum, greater than or equal to about 45 atomic % molybdenum, greater than or equal to about 50 atomic % molybdenum, greater than or equal to about 60 atomic % molybdenum, greater than or equal to about 70 atomic % molybdenum, greater than or equal to about 80 atomic % molybdenum, greater than or equal to about 90 atomic % molybdenum, or greater than or equal to about 95 atomic % molybdenum.

[0031] In one or more embodiments, the molybdenum-containing film comprises greater than or equal to 90% molybdenum (Mo), greater than or equal to 95% molybdenum (Mo), greater than or equal to 99% molybdenum (Mo), or greater than or equal to 99.9% molybdenum (Mo), on a molar basis. Stated differently, a molybdenum-containing film comprising greater than or equal to 90% molybdenum (Mo), greater than or equal to 95% molybdenum (Mo), greater than or equal to 99% molybdenum (Mo), or greater than or equal to 99.9% molybdenum (Mo), for example, means that greater than or equal to 90%, greater than or equal to 95%, greater than or equal to 99%, or greater than or equal to 99.9% of the molecules in the stated molybdenum-containing film include a molybdenum (Mo) species.

[0032] In some embodiments, the molybdenum-containing film comprises one or more of molybdenum metal (elemental molybdenum), molybdenum carbide (MoC_x), molybdenum carbonitride (MoC_xN_y), molybdenum silicide (MoSi_x), molybdenum carbo-silicide (MoC_xSi_y), molybdenum sulfide (MoS_x), molybdenum carbosulfide

(MoC_xS_y), molybdenum nitride (MoN_x), molybdenum phosphide (MoP_x), or molybdenum carbophosphide (MoC_xP_y).

[0033] The skilled artisan will recognize that the use of molecular formula, e.g., molybdenum carbide (MoC_x), molybdenum carbonitride (MoC_xN_y), molybdenum silicide (5 MoSi_x), molybdenum carbosilicide (MoC_xSi_y), molybdenum sulfide (MoS_x), molybdenum carbosulfide (MoC_xS_y), molybdenum nitride (MoN_x), molybdenum phosphide (MoP_x), or molybdenum carbophosphide (MoC_xP_y), does not imply a specific stoichiometric relationship between the elements but merely the identity of the major components of the film. For example, MoC_x refers to a film whose major composition 10 comprises molybdenum (Mo) atoms and carbon (C) atoms. In some embodiments, the major composition of the specified film (i.e., the sum of the atomic percent of the specified atoms) is greater than or equal to about 95%, 98%, 99% or 99.5% of the film, on an atomic basis.

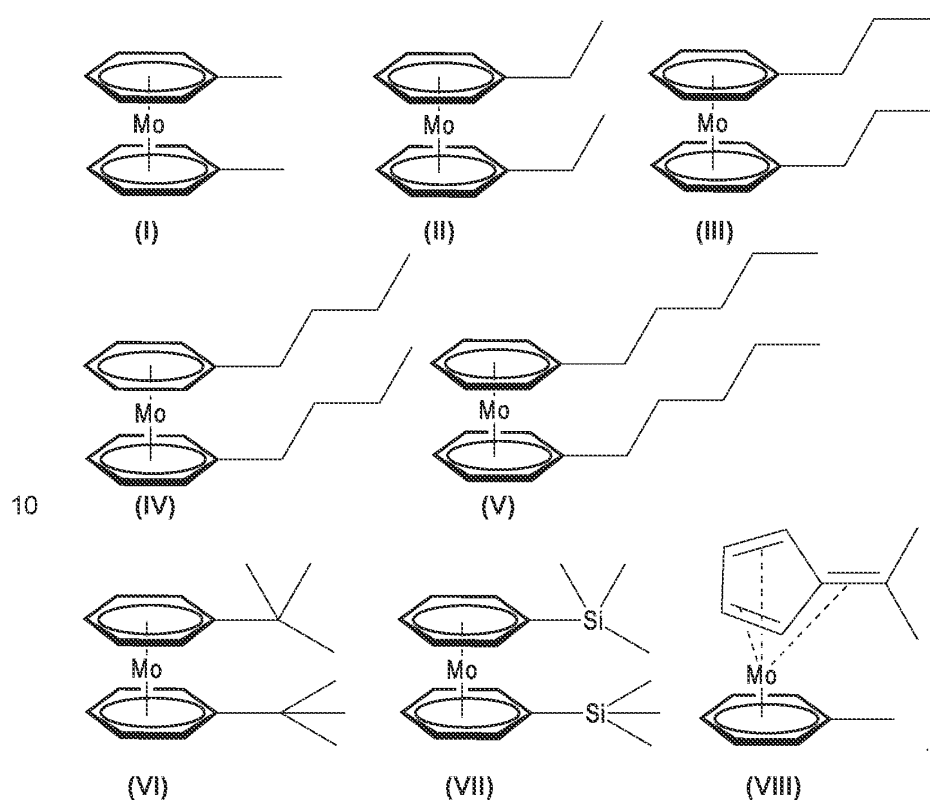
[0034] With reference to FIG. 1, one or more embodiments of the disclosure are 15 directed to method 100 of depositing a molybdenum-containing film. The method illustrated in FIG. 1 is representative of an atomic layer deposition (ALD) process in which the substrate or substrate surface is exposed sequentially to the reactive gases in a manner that prevents or minimizes gas phase reactions of the reactive gases. In some embodiments, the method comprises a chemical vapor deposition (CVD) process 20 in which the reactive gases are mixed in the processing chamber to allow gas phase reactions of the reactive gases and deposition of the thin film.

[0035] In some embodiments, the method 100 optionally includes a pre-treatment operation 105. The pre-treatment can be any suitable pre-treatment known to the skilled artisan. Suitable pre-treatments include, but are not limited to, pre-heating, cleaning, 25 soaking, native oxide removal, or deposition of an adhesion layer (e.g., titanium nitride (TiN)). In one or more embodiments, an adhesion layer, such as titanium nitride, is deposited at operation 105. In other embodiments, an adhesion layer is not deposited.

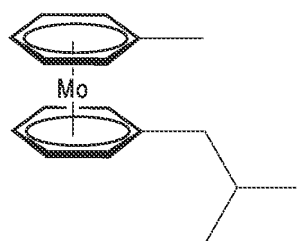
[0036] At deposition 110, a process is performed to deposit a molybdenum-containing film on the substrate (or substrate surface). The deposition process can 30 include one or more operations to form the molybdenum-containing film on the substrate. In operation 112, the substrate (or substrate surface) is exposed to a molybdenum precursor to deposit a film on the substrate (or substrate surface). The

molybdenum precursor can be any suitable molybdenum-containing compound that can react with (i.e., adsorb or chemisorb onto) the substrate surface to leave a molybdenum-containing species on the substrate surface.

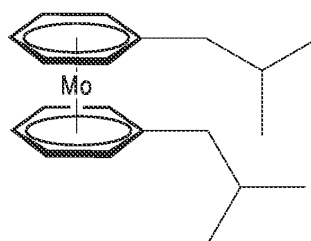
[0037] In one or more embodiments, the molybdenum(0) precursor comprises a structure of Formula (I), Formula (II), Formula (III), Formula (IV), Formula (V), Formula (VI), Formula (VII), or Formula (VIII):



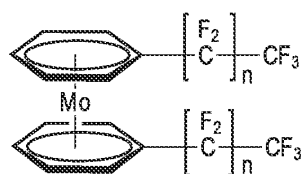
[0038] In other embodiments, the molybdenum(0) precursor comprises a structure of Formula (IX), Formula (X), Formula (XI), or Formula (XII):



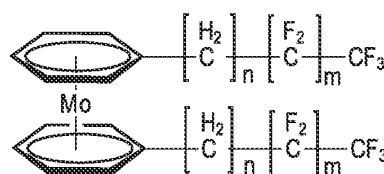
(IX)



(X)



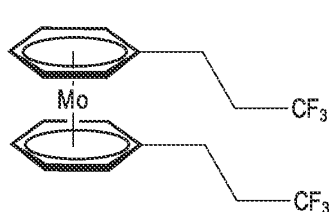
(XI)



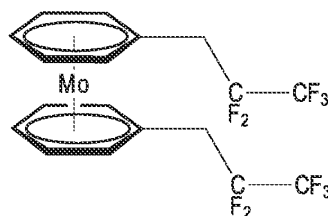
(XII)

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wherein n is in a range of from 0 to 10 and m is in a range of from 0 to 10. In one or more embodiments, n is in a range of from 1 to 9, 2 to 8, 3 to 7, or 4 to 6, and m is in a range of from 1 to 9, 2 to 8, 3 to 7, or 4 to 6. In one or more specific embodiments, the molybdenum(0) precursor comprises a structure of Formula (XII-A) or Formula (XII-B):



(XII-A)



(XII-B)

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[0039] As used herein, a "substrate surface" refers to any substrate surface upon which a layer may be formed. The substrate surface may have one or more features formed therein, one or more layers formed thereon, and combinations thereof. The substrate (or substrate surface) may be pretreated prior to the deposition of the molybdenum-containing layer, for example, by polishing, etching, reduction, oxidation, halogenation, hydroxylation, annealing, baking, or the like.

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[0040] The substrate may be any substrate capable of having material deposited thereon, such as a silicon substrate, a III-V compound substrate, a silicon germanium (SiGe) substrate, an epi-substrate, a silicon-on-insulator (SOI) substrate, a display substrate such as a liquid crystal display (LCD), a plasma display, an electro luminescence (EL) lamp display, a solar array, solar panel, a light emitting diode (LED) substrate, a semiconductor wafer, or the like. In some embodiments, one or more additional layers may be disposed on the substrate such that the molybdenum-containing layer may be at least partially formed thereon. For example, in some embodiments, a layer comprising a metal, a nitride, an oxide, or the like, or combinations thereof may be disposed on the substrate and may have the molybdenum-containing layer formed upon such layer or layers.

[0041] At operation 114, the processing chamber is optionally purged to remove unreacted molybdenum precursor, reaction products and by-products. As used in this manner, the term "processing chamber" also includes portions of a processing chamber adjacent the substrate surface without encompassing the complete interior volume of the processing chamber. For example, in a sector of a spatially separated processing chamber, the portion of the processing chamber adjacent the substrate surface is purged of the molybdenum precursor by any suitable technique including, but not limited to, moving the substrate through a gas curtain to a portion or sector of the processing chamber that contains none or substantially none of the molybdenum precursor. In one or more embodiments, purging the processing chamber comprises applying a vacuum. In some embodiments, purging the processing chamber comprises flowing a purge gas over the substrate. In some embodiments, the portion of the processing chamber refers to a micro-volume or small volume process station within a processing chamber. The term "adjacent" referring to the substrate surface means the physical space next to the surface of the substrate which can provide sufficient space for a surface reaction (e.g., precursor adsorption) to occur. In one or more embodiments, the purge gas is selected from one or more of nitrogen (N₂), helium (He), and argon (Ar).

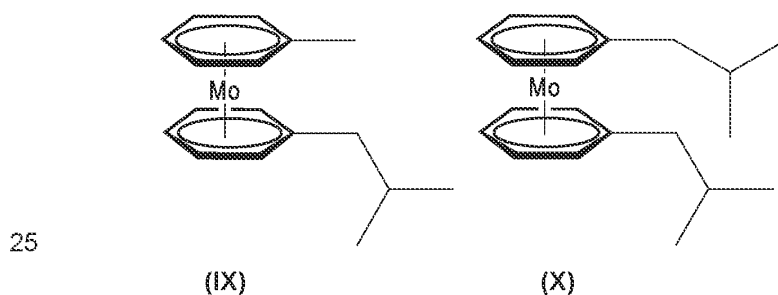
[0042] At operation 116, the substrate (or substrate surface) is exposed to a reactant to form the molybdenum-containing film on the substrate. The reactant can react with the molybdenum-containing species on the substrate surface to form the molybdenum-containing film. In some embodiments, the reactant comprises a reducing agent. In one

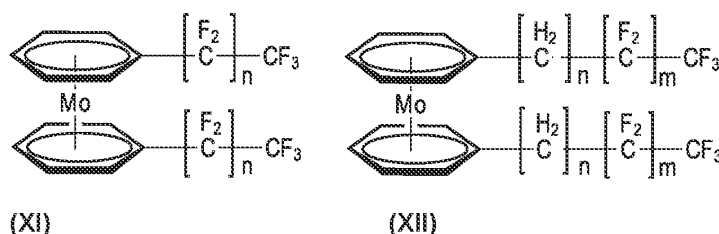
or more embodiments, the reducing agent can comprise any reducing agent known to one of skill in the art. In one or more embodiments, the reducing agent comprises one or more of tetrahydrofuran (THF), acetonitrile (MeCN), triethylamine (NEt₃), pyridine (C₅H₅N), dimethylsulfide ((CH₃)₂S), dimethyl disulfide (C₂H₆S₂), trimethylphosphine (PMe₃), hydrogen sulfide (H₂S), ammonia (NH₃), 1-Azabicyclo[2.2.2]octane (quinuclidine), or 1,4-diazabicyclo[2.2.2]octane (DABCO).

[0043] In some embodiments, the reactant is selected from one or more of 1,1-dimethylhydrazine (DMH), alkyl amine, hydrazine, alkyl hydrazine, allyl hydrazine, hydrogen (H₂), ammonia (NH₃), and plasmas thereof. In some embodiments, the alkyl amine is selected from one or more of tert-butyl amine (tBuNH₂), isopropyl amine (iPrNH₂), ethylamine (CH₃CH₂NH₂), diethylamine ((CH₃CH₂)₂NH), or butyl amine (BuNH₂). In some embodiments, the reactant comprises one or more of compounds with the formula R'NH₂, R'₂NH, R'₃N, R'₂SiNH₂, (R'₃Si)₂NH, (R'₃Si)₃N; where each R' is independently H or an alkyl group having 1-12 carbon atoms. In some embodiments, the alkyl amine consists essentially of one or more of tert-butyl amine (tBuNH₂), isopropyl amine (iPrNH₂), ethylamine (CH₃CH₂NH₂), diethylamine ((CH₃CH₂)₂NH), butyl amine (BuNH₂).

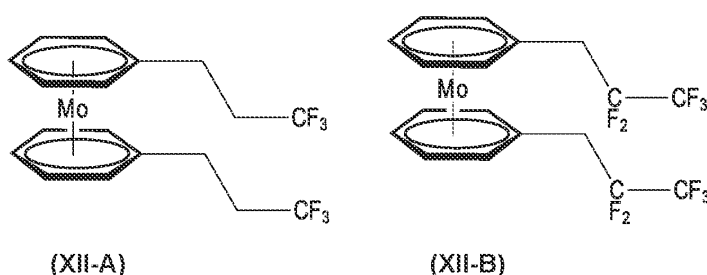
[0044] The molybdenum(0) precursors comprising the structure of Formula (I), Formula (II), Formula (III), Formula (IV), Formula (V), Formula (VI), Formula (VII), or Formula (VIII) can advantageously be prepared as a single compound in a single step via ligand exchange reaction starting from a commercially available molybdenum(0) precursor.

[0045] In other embodiments, the molybdenum(0) precursor comprises a structure of Formula (IX), Formula (X), Formula (XI), or Formula (XII):





wherein n is in a range of from 0 to 4 and m is in a range of from 0 to 4. In one or more embodiments, n is in a range of from 1 to 9, 2 to 8, 3 to 7, or 4 to 6, and m is in a range of from 1 to 9, 2 to 8, 3 to 7, or 4 to 6. In one or more specific embodiments, the molybdenum(0) precursor comprises a structure of Formula (XII-A) or Formula (XII-B):



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[0046] In specific embodiments where the molybdenum(0) precursor comprises a structure of Formula (IX), Formula (X), Formula (XI), or Formula (XII) [including Formula (XII-A) and (XII-B)], a 2-step reaction is performed to form the stated molybdenum(0) precursor. In one or more embodiments, the 2-step reaction includes starting from a commercially available molybdenum(0) precursor and using a co-reagent to form the molybdenum(0) precursor comprising a structure of Formula (IX), Formula (X), Formula (XI), or Formula (XII) [including Formula (XII-A) and (XII-B)]. In one or more embodiments, the co-reagent is a reducing agent comprising one or more of tetrahydrofuran (THF), acetonitrile (MeCN), triethylamine (NEt₃), pyridine (C₅H₅N), dimethylsulfide ((CH₃)₂S), dimethyl disulfide (C₂H₆S₂), trimethylphosphine (PMe₃), hydrogen sulfide (H₂S), ammonia (NH₃), 1-Azabicyclo[2.2.2]octane (quinuclidine), or 1,4-diazabicyclo[2.2.2]octane (DABCO). In one or more embodiments, the 2-step reaction forms a molybdenum(0) precursor comprising a structure of Formula (IX), Formula (X), Formula (XI), or Formula (XII) [including Formula (XII-A) and (XII-B)] in the

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form of a black precipitate comprising a purity of greater than or equal to 80 % molybdenum (Mo) on a molar basis.

[0047] At operation 118, the processing chamber is optionally purged after exposure to the reactant. Purging the processing chamber in operation 118 can be the same process or different process than the purge in operation 114. Purging the processing chamber, portion of the processing chamber, area adjacent the substrate surface, etc., removes unreacted reactant, reaction products and by-products from the area adjacent the substrate surface.

[0048] At decision 120, the thickness of the deposited film, or number of cycles of molybdenum(0) precursor and reactant is considered. If the deposited film has reached a predetermined thickness or a predetermined number of process cycles have been performed, the method 100 moves to an optional post-processing operation 130. If the thickness of the deposited film or the number of process cycles has not reached the predetermined threshold, the method 100 returns to operation 110 to expose the substrate surface to the molybdenum precursor again in operation 112 and continuing.

[0049] In specific embodiments, the method 100 comprises a pulse of a molybdenum(0) precursor using a carrier gas comprising a mixture of argon (Ar) and hydrogen (H₂) for about 3 seconds, purging the substrate using a purge gas comprising a mixture of argon (Ar) and hydrogen (H₂), a pulse of a reactant comprising hydrogen sulfide (H₂S) using a carrier gas comprising a mixture of argon (Ar), hydrogen (H₂), and hydrogen sulfide (H₂S) for about 1 second, and purging the substrate using a purge gas comprising a mixture of argon (Ar) and hydrogen (H₂). In some embodiments, the molybdenum(0) precursor ampoule is maintained a temperature of about 130 °C. It has been advantageously found that performing method 100 in accordance with one or more embodiments, such as in specific embodiments, yields a molybdenum-containing film that forms selectively on a metal surface relative to a dielectric surface.

[0050] The optional post-processing operation 130 can be, for example, a process to modify film properties (e.g., annealing) 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 130 can be a process that modifies a property of the deposited film. In some embodiments, the optional post-processing operation 130 comprises annealing the as-deposited film. 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 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 the as-deposited film increases the density, decreases the resistivity and/or increases the purity of the film.
- 5 [0051] The method 100 can be performed at any suitable temperature depending on, for example, the molybdenum precursor, reactant, or thermal budget of the device. In one or more embodiments, the use of high temperature processing may be undesirable for temperature-sensitive substrates, such as logic devices. In some embodiments, exposure to the molybdenum precursor (operation 112) and the reactant (operation
- 10 116) occur at the same temperature. In some embodiments, the substrate is maintained at a temperature in a range of about 20 °C to about 400 °C, or about 50 °C to about 650 °C.
- 15 [0052] In some embodiments, exposure to the molybdenum(0) precursor (operation 112) occurs at a different temperature than the exposure to the reactant (operation 116).
- 20 In some embodiments, the substrate is maintained at a first temperature in a range of about 20 °C to about 400 °C, or about 50 °C to about 650 °C, for the exposure to the molybdenum(0) precursor, and at a second temperature in the range of about 20 °C to about 400 °C, or about 50 °C to about 650 °C, for exposure to the reactant.
- 25 [0053] In the embodiment illustrated in FIG. 1, at deposition operation 110 the substrate (or substrate surface) is exposed to the molybdenum(0) precursor and the reactant sequentially. In another, un-illustrated, embodiment, the substrate (or substrate surface) is exposed to the molybdenum precursor(0) and the reactant simultaneously in a CVD reaction. In a CVD reaction, the substrate (or substrate surface) can be exposed to a gaseous mixture of the molybdenum precursor and reactant to deposit a
- 30 molybdenum-containing film having a predetermined thickness. In the CVD reaction, the molybdenum-containing film can be deposited in one exposure to the mixed reactive gas or can be multiple exposures to the mixed reactive gas with purges between.

[0054] In some embodiments, the molybdenum-containing film formed comprises elemental molybdenum. Stated differently, in some embodiments, the molybdenum-containing film comprises a metal film comprising molybdenum. In some embodiments, the metal film consists essentially of molybdenum. As used in this manner, the term "consists essentially of molybdenum" means that the molybdenum-containing film is greater than or equal to about 80%, 85%, 90%, 95%, 98%, 99% or 99.5% molybdenum, on an atomic basis. Measurements of the composition of the molybdenum-containing film refer to the bulk portion of the film, excluding interface regions where diffusion of elements from adjacent films may occur.

[0055] The deposition operation 110 can be repeated to form a molybdenum-containing film having a predetermined thickness. In some embodiments, the deposition operation 110 is repeated to provide one or more of a molybdenum-containing film, such as a film comprising molybdenum metal (elemental molybdenum), molybdenum carbide (MoC_x), molybdenum carbonitride (MoC_xN_y), molybdenum silicide (MoSi_x), molybdenum carbosilicide (MoC_xSi_y), molybdenum sulfide (MoS_x), molybdenum carbosulfide (MoC_xS_y), molybdenum nitride (MoN_x), molybdenum phosphide (MoP_x), or molybdenum carbophosphide (MoC_xP_y), having a thickness in the range of about 0.3 nm to about 100 nm, or in the range of about 30 Å to about 10 μm.

[0056] One or more embodiments of the disclosure are directed to methods of depositing molybdenum-containing films in high aspect ratio features. A high aspect ratio feature is a trench, via or pillar having a height:width ratio greater than or equal to about 10, 20, or 50, or more. In some embodiments, the molybdenum-containing film is deposited conformally on the high aspect ratio feature. As used in this manner, a conformal film has a thickness near the top of the feature that is in the range of about 80-120% of the thickness at the bottom of the feature.

[0057] Some embodiments of the disclosure are directed to methods for bottom-up gapfill of a feature. A bottom-up gapfill process fills the feature from the bottom versus a conformal process which fills the feature from the bottom and sides. In some embodiments, the feature has a first material at the bottom (e.g., a nitride) and a second material (e.g., an oxide) at the sidewalls. The molybdenum-containing film deposits selectively on the first material relative to the second material so that the molybdenum film fills the feature in a bottom-up manner.

[0058] According to one or more embodiments, the substrate is subjected to processing prior to and/or after forming the layer. This processing can be performed in the same chamber or in one or more separate processing chambers. In some embodiments, the substrate is moved from the first chamber to a separate, second
5 chamber for further processing. The substrate can be moved directly from the first chamber to the separate processing chamber, or it can be moved from the first chamber to one or more transfer chambers, and then moved to the separate processing chamber. Accordingly, the processing apparatus may comprise multiple chambers in communication with a transfer station. An apparatus of this sort may be referred to as
10 a "cluster tool" or "clustered system," and the like.

[0059] Generally, a cluster tool is a modular system comprising multiple chambers which perform various functions including substrate center-finding and orientation, degassing, annealing, deposition and/or etching. According to one or more embodiments, a cluster tool includes at least a first chamber and a central transfer
15 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 one chamber to another and/or to a load lock chamber positioned at a front end of the cluster tool. Two well-known cluster tools which
20 may be adapted for the present disclosure are the Centura® and the Endura®, both available from Applied Materials, Inc., of Santa Clara, Calif. 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
25 deposition (ALD), chemical vapor deposition (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 a chamber on a cluster tool, surface contamination of the substrate with atmospheric impurities can be avoided without oxidation prior to depositing a
30 subsequent film.

[0060] 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, an inert gas is used as a purge gas to remove some or all of the reactants (e.g., reactant). According to one or
5 more embodiments, a purge gas is injected at the exit of the deposition chamber to prevent reactants (e.g., reactant) from moving from the deposition 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.

[0061] The substrate can be processed in single substrate deposition chambers,
10 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
15 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.

[0062] 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,
20 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
25 temperature. In some embodiments, a heater/cooler is positioned within the chamber adjacent the substrate surface to convectively change the substrate temperature.

[0063] 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
30 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.

[0064] The disclosure is now described with reference to the following examples. Before describing several exemplary embodiments of the disclosure, it is to be understood that the disclosure is not limited to the details of construction or process steps set forth in the following description. The disclosure is capable of other
5 embodiments and of being practiced or being carried out in various ways.

[0065] EXAMPLES

[0066] Example 1: Preparation of Formula (I)

10 [0067] The molybdenum(0) precursor comprising the structure of Formula (I) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with 30 equivalents toluene at 170 °C for 3 days. The removal of volatiles under vacuum provided the target precursor comprising the structure of Formula (I) as a single compound solid in 88% yield with a purity of 90% and a melting point of 67 °C. As used
15 herein, the term "removal of volatiles" refers to the removal of any compound, unreacted precursor, and/or byproducts from the stated reaction other than the target precursor. As used herein, the stated purity is expressed on a percentage (%) molar basis, which refers to a percentage of molecules in the stated molybdenum(0) precursor (e.g., the target precursor) that include a molybdenum (Mo) species.

20 [0068] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.65-4.58 (m, 8H, CH), 4.52 (t, 2H, CH *J*_{HH} = 4Hz), 1.86 (s, 6H, CH₃)

[0069] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 89.5, 78.4, 75.7, 74.8, 21.3

[0070] Example 2A: Preparation of Formula (II) Using Formula (I)

[0071] The molybdenum(0) precursor comprising the structure of Formula (II) was
25 prepared by reacting the molybdenum(0) precursor comprising the structure of Formula (I) with 70 equivalents of ethylbenzene at 170 °C for 4 days. The removal of volatiles under vacuum provided the target precursor comprising the structure of Formula (II) as a single compound semi-liquid in 78% yield with a purity of 99% and a melting point in a range of from 28 °C to 31 °C.

30 [0072] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.66-4.52 (m, 10H, CH), 2.10 (q, 4H, CH₂ *J*_{HH} = 7Hz), 1.07 (t, 6H, CH₃, *J*_{HH} = 7Hz)

[0073] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 97.5, 77.1, 75.4, 74.7, 29.0, 16.3

[0074] Example 2B: Preparation of Formula (II) Using Commercially Available Bis(Ethylbenzene)Molybdenum

[0075] The molybdenum(0) precursor comprising the structure of Formula (II) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with 76 equivalents of ethylbenzene at 170 °C for 3 days. This reaction forms intermediate compounds including a mixture of the molybdenum(0) precursor comprising the structure of Formula (II) and unreacted compounds from the commercially available bis(ethylbenzene)molybdenum. The mixture of the molybdenum(0) precursor comprising the structure of Formula (II) and unreacted compounds from the commercially available bis(ethylbenzene)molybdenum were reacted with 76 equivalents of ethylbenzene at 170 °C for 2 days to form the molybdenum(0) precursor comprising the structure of Formula (II). The removal of volatiles under vacuum provided the target precursor comprising the structure of Formula (II) as a single compound semi-liquid in 84% yield with a purity of 99% and a melting point in a range of from 28 °C to 31 °C.

[0076] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.66-4.52 (m, 10H, CH), 2.10 (q, 4H, CH₂ J_{HH} = 7Hz), 1.07 (t, 6H, CH₃, J_{HH} = 7Hz)

[0077] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 97.5, 77.1, 75.4, 74.7, 29.0, 16.3

[0078] Example 3A: Preparation of Formula (III) Using Formula (I)

[0079] The molybdenum(0) precursor comprising the structure of Formula (III) was prepared by reacting the molybdenum(0) precursor comprising the structure of Formula (I) with n-propylbenzene at 195 °C for 2 days. The reaction provided the target precursor comprising the structure of Formula (III) as a single compound solid in 64% yield with a purity of 95% and a melting point of 36 °C.

[0080] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.69-4.50 (m, 10H, CH), 2.02 (t, 4H, CH₂ J_{HH} = 7Hz), 1.49 (h, 4H, CH₂ J_{HH} = 7Hz), 0.91 (t, 6H, CH₃, J_{HH} = 7Hz)

[0081] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 95.0, 77.8, 75.7, 74.9, 38.1, 26.1, 13.2

[0082] Example 3B: Preparation of Formula (III) Using Commercially Available Bis(Ethylbenzene)Molybdenum

[0083] The molybdenum(0) precursor comprising the structure of Formula (III) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with 30 equivalents of n-propylbenzene at 170 °C for 3 days. The removal of volatiles under

vacuum provided the target precursor comprising the structure of Formula (III) as a single compound solid in 64% yield with a purity of 95% and a melting point of 36 °C.

[0084] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.69-4.50 (m, 10H, CH), 2.02 (t, 4H, CH₂ J_{HH} = 7Hz), 1.49 (h, 4H, CH₂ J_{HH} = 7Hz), 0.91 (t, 6H, CH₃, J_{HH} = 7Hz)

5 [0085] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 95.0, 77.8, 75.7, 74.9, 38.1, 26.1, 13.2

[0086] Example 4: Preparation of Formula (IV)

[0087] The molybdenum(0) precursor comprising the structure of Formula (IV) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with 30 equivalents of n-butylbenzene at 170 °C for 3 days. The removal of volatiles under vacuum provided the target precursor comprising the structure of Formula (IV) as a single compound liquid in 60% yield with a purity of 95%.

[0088] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.70-4.54 (m, 10H, CH), 2.10 (t, 4H, CH₂ J_{HH} = 7Hz), 1.52-1.44 (m, 4H, CH₂), 1.36-1.26 (m, 4H, CH₂), 0.87 (t, 6H, CH₃, J_{HH} = 7Hz)

15 [0089] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 95.2, 77.8, 75.6, 74.8, 36.2, 35.1, 22.6, 13.9

[0090] Example 5: Preparation of Formula (V)

[0091] The molybdenum(0) precursor comprising the structure of Formula (V) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with n-pentylbenzene at 170 °C for 3 days. The removal of volatiles under vacuum provided the target precursor comprising the structure of Formula (V) as a single compound liquid in 61% yield with a purity of 95%.

20 [0092] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.72-4.54 (m, 10H, CH), 2.12 (t, 4H, CH₂ J_{HH} = 7Hz), 1.55-1.49 (m, 4H, CH₂), 1.35-1.23 (m, 8H, CH₂), 0.88 (t, 6H, CH₃, J_{HH} = 7Hz)

25 [0093] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 95.2, 77.8, 75.6, 74.8, 36.5, 32.6, 31.7, 22.7, 14.0

[0094] Example 6: Preparation of Formula (VI)

30 [0095] The molybdenum(0) precursor comprising the structure of Formula (VI) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with 30 equivalents of t-butylbenzene at 170 °C for 3 days. The removal of volatiles under

vacuum provided the target precursor comprising the structure of Formula (VI) as a solid in 88% yield with a purity of 95% and a melting point of 96 °C.

[0096] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.74-4.66 (m, 4H, CH), 4.58-4.54 (m, 2H, CH), 4.54-4.49 (m, 4H, CH), 1.16 (s, 18H, CH₃)

5 [0097] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 73.8, 73.7, 73.6, 33.0, 30.7

[0098] Example 7: Preparation of Formula (VII)

[0099] The molybdenum(0) precursor comprising the structure of Formula (VII) was prepared by reacting commercially available bis(ethylbenzene)molybdenum with 10 equivalents of (trimethylsilyl)benzene at 170 °C for 3 days. The removal of volatiles under vacuum provided the target precursor comprising the structure of Formula (VII) as a single compound solid in 81% yield with a purity of 95% and a melting point of 85 °C.

[00100] ¹H NMR (C₆D₆, 500 MHz, ppm): δ 4.72-4.65 (m, 2H, CH), 4.59-4.53 (m, 4H, CH), 4.50-4.44 (m, 4H, CH), 0.16 (s, 18H, CH₃)

15 [00101] ¹³C NMR (C₆D₆, 500 MHz, ppm): δ 79.4, 77.3, 75.0, -0.9

[00102] Example 8: Preparation of Formula (VIII)

[00103] The molybdenum(0) precursor comprising the structure of Formula (VIII) was prepared by reacting the molybdenum(0) precursor comprising the structure of Formula (I) with 3.5 equivalents of 6,6-dimethylfulvene in the presence of toluene at 50 °C for 3 days. The reaction provided the target precursor comprising the structure of Formula (VIII) as a solid in 90% yield with a purity of 95% and a melting point of 70 °C.

[00104] ¹H NMR (toluene-d₈, 500 MHz, ppm): δ 4.98 (s, 2H, C₅H₄), 4.54 (s, 2H, C₅H₄), 3.93 (m, 1H, C₆H₅), 3.83 (m, 2H, C₆H₅), 3.80 (m, 2H, C₆H₅), 1.78 (s, 3H, C₆H₅CH₃), 1.68 (s, 6H, CMe₂).

25 [00105] ¹³C NMR (toluene-d₈, 500 MHz, ppm): δ 90.1, 82.3, 78.3, 76.1, 75.9, 75.6, 74.7, 24.8, 20.8

[00106] Example 9: Atomic Layer Deposition (ALD) of Molybdenum-Containing Films

[00107] General procedure: A semiconductor substrate was placed in a processing chamber. A molybdenum(0) precursor having a purity of greater than or equal to 90% molybdenum (Mo) on a molar basis was flowed into the processing chamber in an atmosphere of nitrogen (N₂) gas over the semiconductor substrate leaving a molybdenum-precursor terminated surface. Unreacted precursor and byproducts were

then purged out of the chamber. Next, a co-reactant was then introduced into the chamber that reacted with the surface-bound molybdenum species. Again, excess coreactant and byproducts were removed from the chamber. The resultant material on the substrate was a molybdenum-containing film comprising greater than or equal to 80
5 % molybdenum (Mo) on an atomic basis.

[00108] Spatially relative terms, such as "beneath," "below," "lower," "above," "upper" and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. It will be understood that the spatially relative terms are intended to encompass different
10 orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, if the device in the figures is turned over, elements described as "below" or "beneath" other elements or features would then be oriented "above" the other elements or features. Thus, the exemplary term "below" may encompass both an orientation of above and below. The device may be otherwise oriented (rotated 90
15 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly.

[00109] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the materials and methods discussed herein (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless
20 otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any
25 suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the materials and methods and does not pose a limitation on the scope unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential
30 to the practice of the disclosed materials and methods.

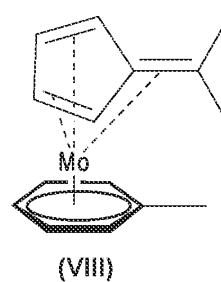
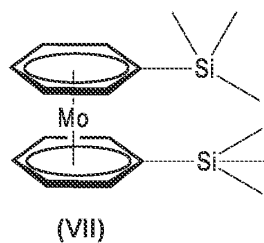
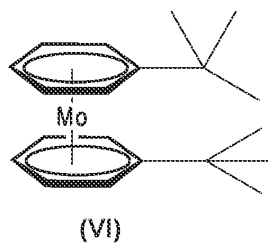
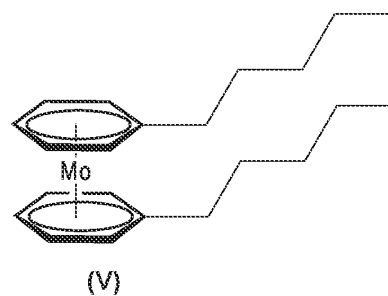
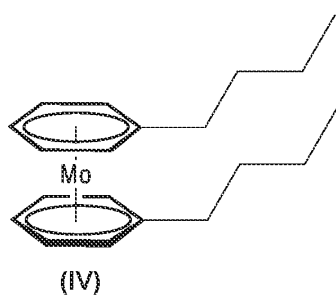
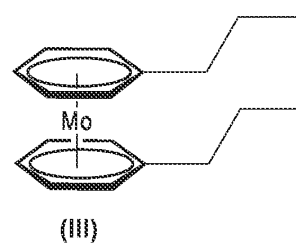
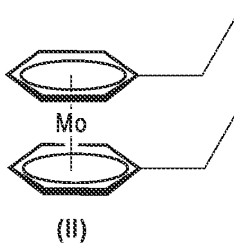
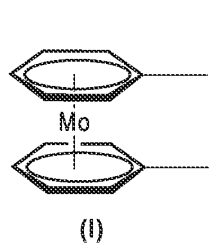
[00110] Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments" or "an embodiment" means that a particular

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
5 throughout this specification are not necessarily referring to the same embodiment of the disclosure. In one or more embodiments, the particular features, structures, materials, or characteristics are combined in any suitable manner.

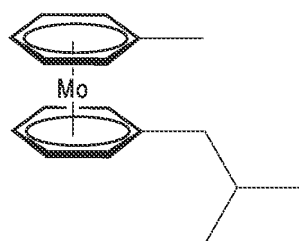
[00111] Although the disclosure herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely
10 illustrative of the principles and applications of the present disclosure. It will be apparent to those skilled in the art that various modifications 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
15 equivalents.

What is claimed is:

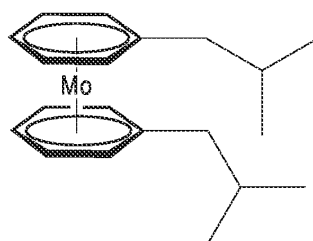
1. A molybdenum(0) precursor comprising a structure of Formula (I), Formula (II), Formula (III), Formula (IV), Formula (V), Formula (VI), Formula (VII), Formula (VIII), Formula (IX), Formula (X), Formula (XI), Formula (XII), Formula (XII-A), or Formula (XII-B):
- 5



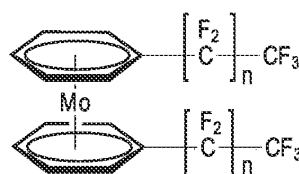
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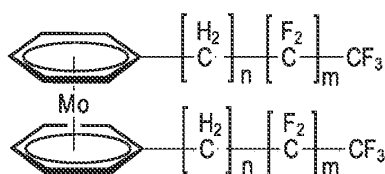
(IX)



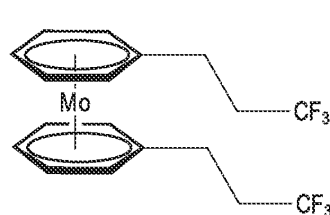
(X)



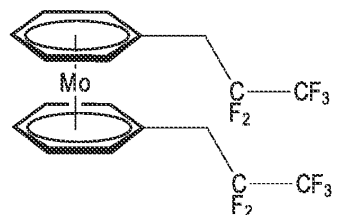
(XI)



(XII)



(XII-A)



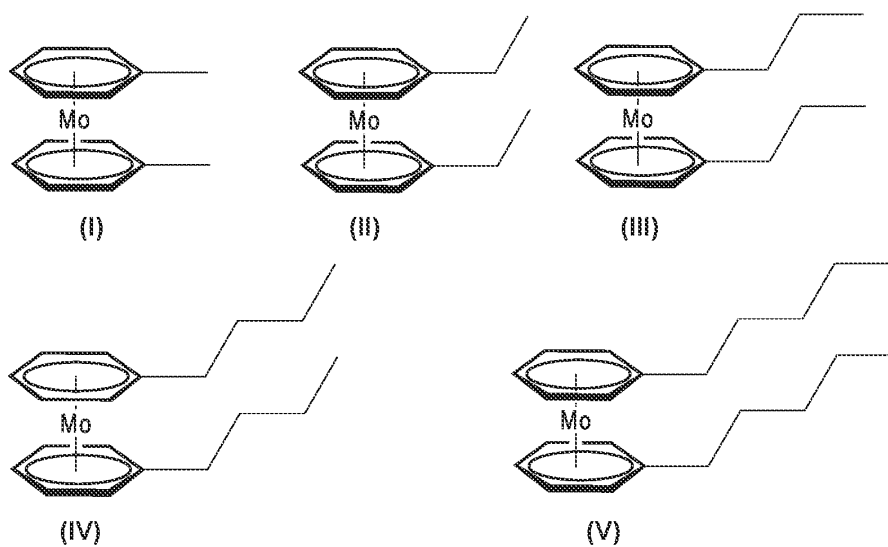
(XII-B)

wherein n is in a range of from 0 to 10 and m is in a range of from 0 to 10, the molybdenum(0) precursor having a purity of greater than or equal to 90% molybdenum (Mo) on a molar basis.

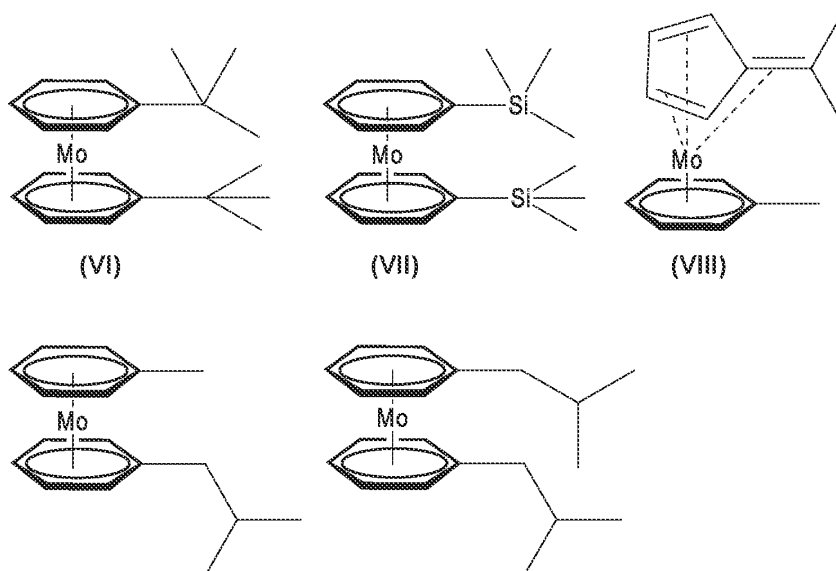
2. The molybdenum(0) precursor of claim 1, substantially free of halogen, oxygen, and a Mo-O bond.
3. A method of forming a molybdenum-containing film, the method comprising:
 - exposing a substrate surface to a molybdenum(0) precursor; and
 - exposing the substrate surface to a reactant to form the molybdenum-containing film on the substrate surface.

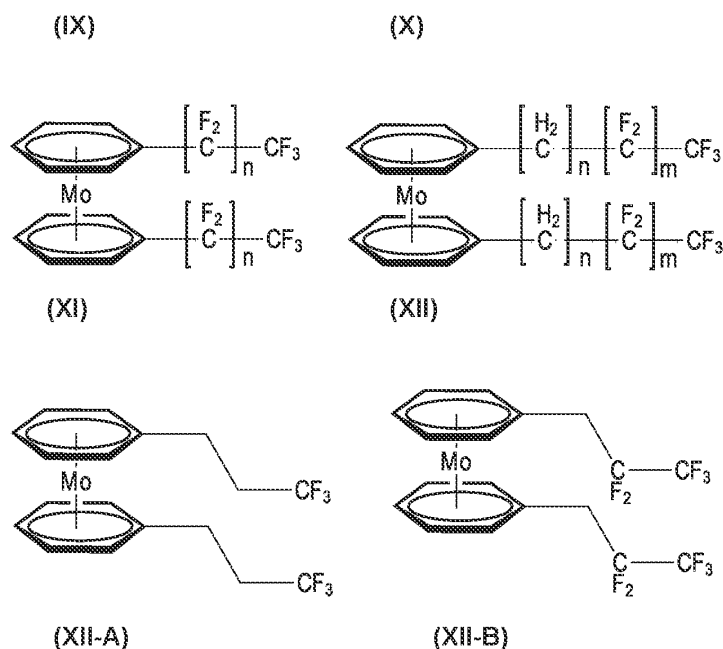
4. The method of claim 3, wherein the molybdenum(0) precursor has a structure of Formula (I), Formula (II), Formula (III), Formula (IV), Formula (V), Formula (VI), Formula (VII), Formula (VIII), Formula (IX), Formula (X), Formula (XI), Formula (XII), Formula (XII-A), or Formula (XII-B):

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wherein n is in a range of from 0 to 10 and m is in a range of from 0 to 10, and the molybdenum(0) precursor has a purity of greater than or equal to 90% molybdenum (Mo) on a molar basis.

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5. The method of claim 4, wherein the molybdenum(0) precursor is a liquid precursor.
6. The method of claim 3, wherein the reactant comprises a reducing agent, the reducing agent comprising one or more of tetrahydrofuran (THF), acetonitrile (MeCN), triethylamine (NEt_3), pyridine (C_5H_5N), dimethylsulfide ($(CH_3)_2S$), dimethyl disulfide ($C_2H_6S_2$), trimethylphosphine (PMe_3), hydrogen sulfide (H_2S), ammonia (NH_3), 1-Azabicyclo[2.2.2]octane (quinuclidine), or 1,4-diazabicyclo[2.2.2]octane (DABCO).
7. The method of claim 3, wherein the molybdenum-containing film comprises one or more of molybdenum metal (elemental molybdenum), molybdenum carbide

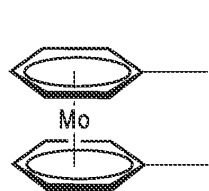
(MoC_x), molybdenum carbonitride (MoC_xN_y), molybdenum silicide (MoSi_x), molybdenum carbosilicide (MoC_xSi_y), molybdenum sulfide (MoS_x), molybdenum carbosulfide (MoC_xS_y), molybdenum nitride (MoN_x), molybdenum phosphide (MoP_x), or molybdenum carbophosphide (MoC_xP_y).

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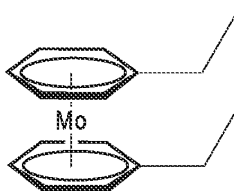
8. The method of claim 3, wherein the substrate surface is exposed to the molybdenum(0) precursor and the reactant sequentially.
9. The method of claim 3, wherein the substrate surface is exposed to the molybdenum(0) precursor and the reactant simultaneously.
10. The method of claim 3, further comprising purging the substrate surface of the molybdenum(0) precursor prior to exposing the substrate surface to the reactant.
11. The method of claim 10, wherein purging comprises one or more of applying a vacuum or flowing a purge gas over the substrate surface.
12. The method of claim 11, wherein the purge gas comprises one or more of nitrogen (N₂), helium (He), or argon (Ar).
13. The method of claim 3, wherein the molybdenum-containing film comprises greater than or equal to 80 % molybdenum (Mo) on an atomic basis.
14. A method of forming a molybdenum-containing film, the method comprising:
performing a process cycle comprising sequential exposure of a substrate surface to a molybdenum(0) precursor, purge gas, reactant, and purge gas.
15. The method of claim 14, wherein the molybdenum(0) precursor has a structure of Formula (I), Formula (II), Formula (III), Formula (IV), Formula (V), Formula (VI), Formula (VII), Formula (VIII), Formula (IX), Formula (X), Formula (XI), Formula (XII), Formula (XII-A), or Formula (XII-B):

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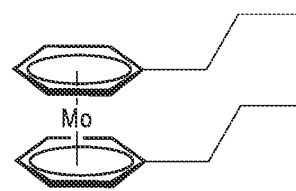
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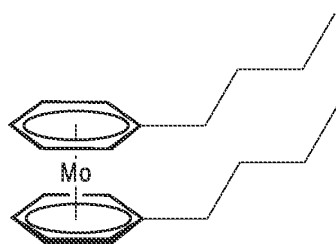
(I)



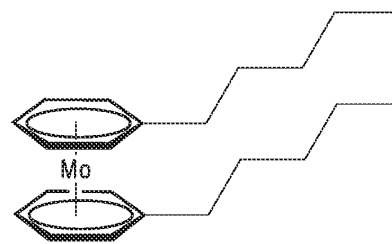
(II)



(III)

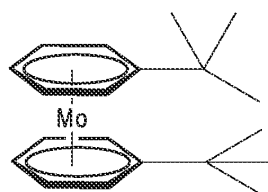


(IV)

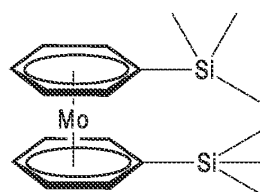


(V)

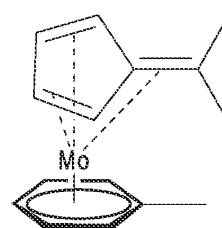
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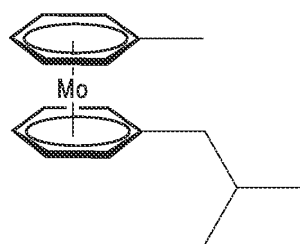
(VI)



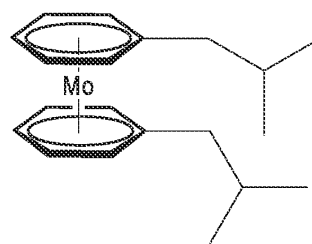
(VII)



(VIII)

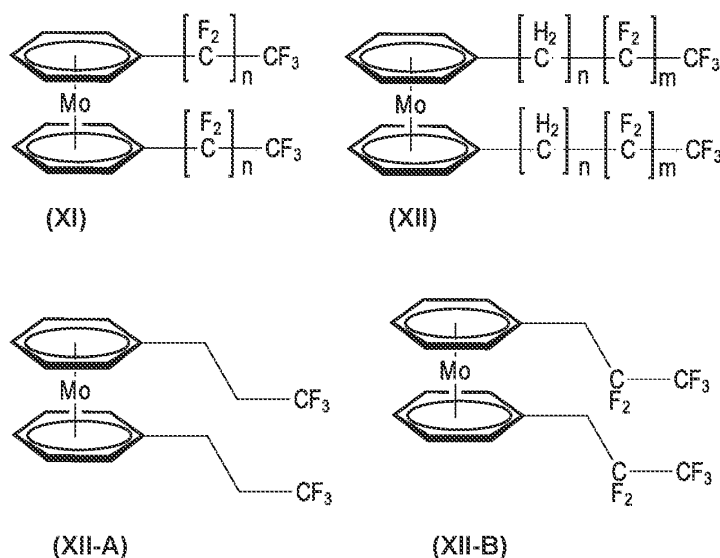


(IX)



(X)

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wherein n is in a range of from 0 to 10 and m is in a range of from 0 to 10, and the molybdenum(0) precursor has a purity of greater than or equal to 90% molybdenum (Mo) on a molar basis.

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16. The method of claim 15, wherein the molybdenum(0) precursor is substantially free of halogen, oxygen, and a Mo-O bond.
17. The method of claim 14, wherein the reactant comprises a reducing agent, the reducing agent comprising one or more of tetrahydrofuran (THF), acetonitrile (MeCN), triethylamine (NEt₃), pyridine (C₅H₅N), dimethylsulfide ((CH₃)₂S), dimethyl disulfide (C₂H₆S₂), trimethylphosphine (PMe₃), hydrogen sulfide (H₂S), ammonia (NH₃), 1-Azabicyclo[2.2.2]octane (quinuclidine), or 1,4-diazabicyclo[2.2.2]octane (DABCO).
18. The method of claim 14, wherein the purge gas comprises one or more of nitrogen (N₂), helium (He), and argon (Ar).

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19. The method of claim 14, wherein the molybdenum-containing film comprises one or more of molybdenum metal (elemental molybdenum), molybdenum carbide (MoC_x), molybdenum carbonitride (MoC_xN_y), molybdenum silicide (MoSi_x), molybdenum carbosilicide (MoC_xSi_y), molybdenum sulfide (MoS_x), molybdenum carbosulfide (MoC_xS_y), molybdenum nitride (MoN_x), molybdenum phosphide (MoP_x), or molybdenum carbophosphide (MoC_xP_y).
20. The method of claim 14, wherein the molybdenum-containing film comprises greater than or equal to 80 % molybdenum (Mo) on an atomic basis.