

## DINUCLAR MOLYBDENUM PRECURSORS FOR DEPOSITION OF MOLYBDENUM-CONTAINING FILMS

### TECHNICAL FIELD

5   **[0001]** Embodiments of the disclosure relate to molybdenum precursors and methods for depositing molybdenum-containing films. More particularly, embodiments of the disclosure are directed to dinuclear molybdenum precursors containing sterically and electronically adapted phosphine ligands and methods of use thereof.

### 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]** Chemical vapor deposition (CVD) is one of the most common deposition  
20 processes employed for depositing layers on a substrate. CVD is a flux-dependent 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  
25 technique to maintain adequate uniformity.

**[0004]** A variant of CVD that demonstrates excellent step coverage is cyclical deposition or atomic layer deposition (ALD). Cyclical deposition is based upon atomic layer epitaxy (ALE) and employs chemisorption techniques to deliver precursor molecules on a substrate surface in sequential cycles. The cycle exposes the  
30 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 product compound as a film on the substrate surface. The cycle is repeated to form the layer to a desired thickness.

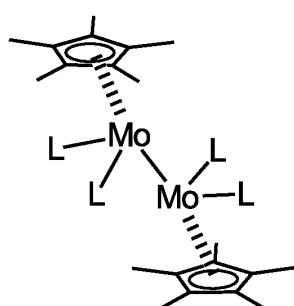
**[0005]** The advancing complexity of advanced microelectronic devices is placing stringent demands on currently used deposition techniques. Unfortunately, there is a limited number of viable chemical precursors available that have the requisite properties of robust thermal stability, high reactivity, 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. However, molybdenum precursors often have halogens, oxygen and carbonyl groups. The halogens and oxygen contamination may affect device performance and hence require additional removal procedures. Carbonyl group binds strongly to metals, requiring higher thermal budget, or the use of additional reagents for its removal. Further, carbonyl group can redeposit and poison other metal surface as well. The use of high temperature processes are not desirable for temperature-sensitive substrates (e.g. logic devices). There is, therefore, a need in the art for molybdenum precursors that are free of oxygen, halogen and carbonyl groups that react to form molybdenum metal and molybdenum based films.

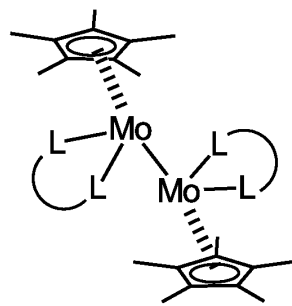
## SUMMARY

**[0007]** One or more embodiments of the disclosure are directed to metal coordination complexes. In one or more embodiments, a metal coordination complex comprises a dinuclear molybdenum and a sterically or electronically adapted phosphine ligand or derivative thereof, the metal coordination complex substantially free of oxygen, halogen, and carbonyl.

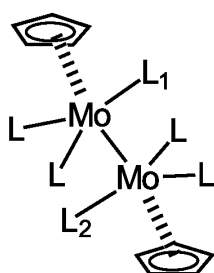
**[0008]** One or more embodiments of the disclosure are directed to a method of depositing a film. In one or more embodiments, a method of depositing a film comprises: exposing a substrate to a dinuclear molybdenum coordination complex having a structure of Formula (I), Formula (II), Formula (III), or Formula (IV)



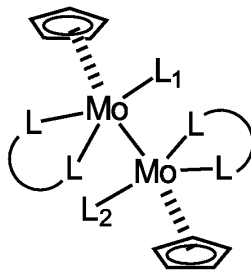
(I)



(II)



(III)



(IV)

wherein Mo-Mo is dinuclear

molybdenum, L and  are independently a sterically or electronically adapted phosphine ligand or derivative thereof, and one or more of L<sub>1</sub> and L<sub>2</sub> are independently a sterically or electronically adapted phosphine ligand or derivative thereof, or a carbonyl ligand or derivative thereof; and exposing the substrate to a reactant to form a molybdenum-containing film on the substrate.

**[0009]** Further embodiments of the disclosure are directed to methods of depositing a film. In one or more embodiments, a method of depositing a film comprises: forming a molybdenum-containing film in a process cycle comprising sequential exposure of a substrate to a dinuclear molybdenum coordination complex precursor, purge gas, reactant, and purge gas.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]** 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 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.

**[0011]** FIG. 1 illustrates a process flow diagram of a method in accordance with one or more embodiments of the disclosure.

#### DETAILED DESCRIPTION

**[0012]** 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 set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

**[0013]** Embodiments of the disclosure provide precursors and processes for depositing molybdenum-containing films. The precursor comprises a dinuclear molybdenum coordination complex. In one or more embodiments, the dinuclear molybdenum coordination complex comprises dinuclear molybdenum and one or more ligands coordinated to the dinuclear molybdenum. In some embodiments, the ligand comprises a phosphine ligand. In some embodiments, the phosphine ligand is sterically and electronically adapted to stabilize and deliver highly reactive and thermally-sensitive molybdenum(VI) species under ALD and CVD conditions. 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 dinuclear molybdenum precursors of one or more embodiments are volatile and thermally stable, and, thus, suitable for vapor deposition.

**[0014]** The dinuclear molybdenum coordination complexes of one or more embodiments are substantially free of oxygen, halogen and carbonyl groups. As used herein, the term "substantially free" means that there is 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 carbonyl groups, and there is 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 carbonyl group, on an atomic basis, in the molybdenum-containing film.

**[0015]** 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 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 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 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 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.

**[0016]** According to one or more embodiments, the method uses an atomic layer deposition (ALD) process. In such embodiments, the substrate surface is exposed to 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.

**[0017]** 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.

**[0018]** "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.

15 **[0019]** 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

20 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

25 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.

**[0020]** 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

30 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.

**[0021]** Without intending to be bound by theory, it is thought that the presence of halogens, carbonyls groups, and, in some case, oxygen, in the structure of molybdenum (Mo) precursors can pose challenges, as halogen and oxygen contamination may affect device performance and hence require additional removal  
5 procedures. Carbonyl (CO) binds strongly to metals, requiring higher thermal budget, or the use of additional reagents for its removal. Carbonyl (CO) can redeposit and poison other metal surfaces.

**[0022]** Molybdenum (Mo) can be grown by atomic layer deposition or chemical vapor deposition for many applications. One or more embodiments of the disclosure  
10 advantageously provide processes for atomic layer deposition or chemical vapor deposition to form molybdenum-containing films. As used in this specification and the appended claims, the term “molybdenum-containing film” refers to a film that comprises molybdenum atoms and has greater than or equal to about 1 atomic %  
15 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 %  
20 % 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, or greater than or equal to about 60 atomic % molybdenum. In some embodiments, the molybdenum-containing film comprises one or more of molybdenum metal (elemental  
25 molybdenum), molybdenum oxide ( $\text{MoO}_2$ ,  $\text{MoO}_3$ ), molybdenum carbide ( $\text{MoC}$ ,  $\text{Mo}_2\text{C}$ ), molybdenum silicide ( $\text{MoSi}_2$ ), or molybdenum nitride ( $\text{Mo}_2\text{N}$ ). The skilled artisan will recognize that the use of molecular formula like  $\text{MoSi}_x$  does not imply a specific stoichiometric relationship between the elements but merely the identity of the major components of the film. For example,  $\text{MoSi}_x$  refers to a film whose major composition  
30 comprises molybdenum and silicon atoms. In some embodiments, the major composition of the specified film (i.e., the sum of the atomic percents of the specified

atoms) is greater than or equal to about 95%, 98%, 99% or 99.5% of the film, on an atomic basis.

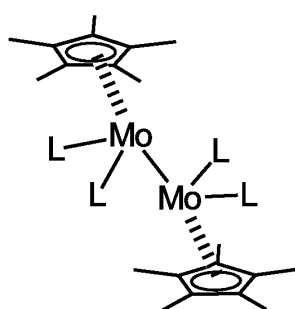
**[0023]** With reference to FIG. 1, one or more embodiments of the disclosure are directed to method 100 of depositing a film. The method illustrated in FIG. 1 is representative of an atomic layer deposition (ALD) process in which the substrate or substrate surface is exposed sequentially to the reactive 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 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.

**[0024]** In some embodiments, the method 100 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, 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.

**[0025]** At deposition 110, a process is performed to deposit a molybdenum-containing film on the substrate (or substrate surface). The deposition process can 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 precursor 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.

**[0026]** Current molybdenum precursors for ALD of metallic films use halogen and carbonyl-based ligands, which provide sufficient stability at the expense of reduced reactivity, increasing process temperature. Amide ligands can cause nitride impurities. Accordingly, one or more embodiments use the one or more sterically or electronically adapted phosphine ligands or derivatives thereof, and stabilize the resulting complexes. This combination provides the molybdenum precursors with improved thermal stability, while retaining high volatility.

**[0027]** In one or more embodiments, the molybdenum precursor comprises a dinuclear molybdenum coordination complex. In one or more embodiments, the dinuclear molybdenum coordination complex comprises one or more of cyclopentadienyl, pentamethyl cyclopentadienyl, or derivatives thereof. In one or more  
5       embodiments, the dinuclear molybdenum coordination complex has a structure of Formula (I), wherein Mo-Mo is dinuclear molybdenum, and wherein L is independently a sterically or electronically adapted phosphine ligand or derivative thereof.



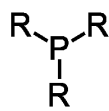
(I)

**[0028]** Unless otherwise indicated, the term "lower alkyl," "alkyl," or "alk" as used  
10       herein alone or as part of another group includes both straight and branched chain hydrocarbons, containing 1 to 20 carbons, or 1 to 10 carbons, 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  
15       include up to 1 to 4 substituents. The alkyl may be substituted or unsubstituted.

**[0029]** Without intending to be bound by theory, it is thought that bulky alkyl groups, such as, but not limited to, methyl, ethyl, propyl, isopropyl, butyl, t-butyl, CH<sub>2</sub>-t-butyl, and the like, provide steric protection and prevent "pi-pi stacking" of aromatic rings in the ligands, L, thus increasing the volatility of the dinuclear molybdenum  
20       precursor.

**[0030]** In one or more embodiments, to prevent ligand dissociation (as a potential decomposition pathway) and enhance the thermal stability of molybdenum precursors, phosphine based ligands, L, are used.

**[0031]** Accordingly, in one or more embodiments, L comprises a phosphine ligand  
25       or derivative thereof. In some embodiments, L is independently represented by

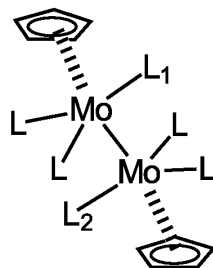


, where R is independently a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl group.

In one or more embodiments, R is independently selected from the group consisting of

Me-, Et-, iPr-, tBu-, and  substituents.

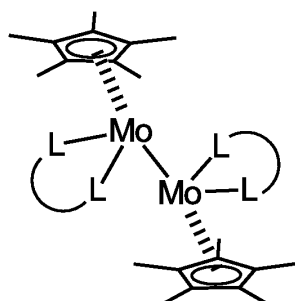
- [0032]** In one or more embodiments, to form the dinuclear molybdenum coordination complex of Formula (I), a molybdenum dimer complex having one or more first ligands is exposed to one or more phosphine based ligands. In some embodiments, the first ligand comprises a carbonyl ligand or derivative thereof. In some embodiments, the molybdenum dimer complex has a structure of Formula (III), wherein Mo-Mo is dinuclear molybdenum, L is independently a sterically or electronically adapted phosphine ligand or derivative thereof, and one or more of L<sub>1</sub> and L<sub>2</sub> is independently a sterically or electronically adapted phosphine ligand or derivatives thereof or a carbonyl ligand or derivative thereof.



(III)

**[0033]** In some embodiments, the dinuclear molybdenum precursor has a structure

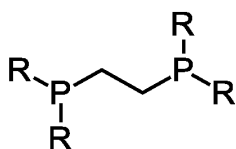
- of Formula (II), wherein Mo-Mo is dinuclear molybdenum and  is independently a sterically or electronically adapted phosphine ligand or derivative thereof.



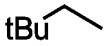
(II)



**[0034]** In some embodiments, is independently represented by



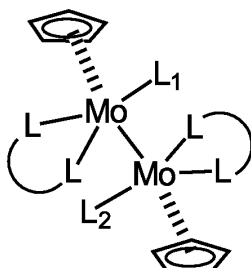
, where R is independently a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl group. In some embodiments, R is independently selected from the group

5 consisting of Me-, Et-, iPr-, tBu-, and  substituents.

**[0035]** In one or more embodiments, to form the dinuclear molybdenum coordination complex of Formula (II), a molybdenum dimer complex having one or more first ligands is exposed to one or more phosphine based ligands. In some embodiments, the first ligand comprises a carbonyl ligand or derivative thereof. In  
10 some embodiments, the molybdenum dimer complex has a structure of Formula (IV),



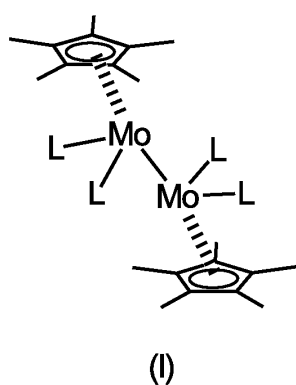
wherein Mo-Mo is dinuclear molybdenum, is independently a sterically or electronically adapted phosphine ligand or derivative thereof, and one or more of L<sub>1</sub> and L<sub>2</sub> is independently a sterically or electronically adapted phosphine ligand or derivative thereof, or a carbonyl ligand or derivative thereof.



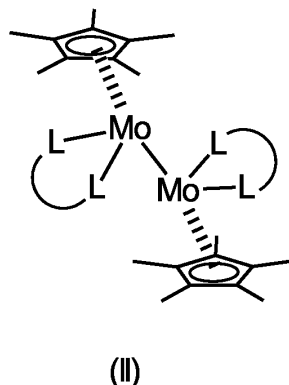
(IV)

**[0036]** In one or more embodiments, the dinuclear molybdenum precursor has a structure of Formula (I) or Formula (II), wherein Mo-Mo is dinuclear molybdenum, and

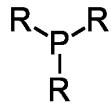
one or more of L and  are independently a sterically or electronically adapted phosphine ligand or derivative thereof.

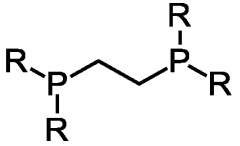


(I)



(II)

**[0037]** In some embodiments, L is independently represented by  and

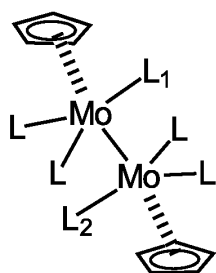
 is independently represented by , where R is independently a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl group. In some embodiments, R is independently selected from the group consisting of Me-, Et-, iPr-, tBu-, and tBu- substituents.

**[0038]** In one or more embodiments, to form the dinuclear molybdenum precursors of Formula (I) or Formula (II), the molybdenum dimer complex having one or more first ligands is exposed to one or more phosphine based ligands. In some embodiments, the first ligand comprises a carbonyl ligand or derivative thereof. In some

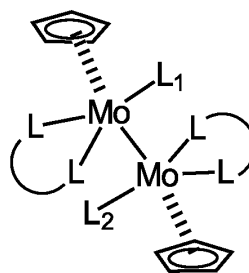
5       embodiments, the molybdenum dimer complex has the structure of Formula (III) or

Formula (IV), wherein Mo-Mo is dinuclear molybdenum, one or more of L and , and are independently a sterically or electronically adapted phosphine ligand or derivative thereof, and one or more of L<sub>1</sub> and L<sub>2</sub> are independently a sterically or electronically adapted phosphine ligand or derivative thereof, or a carbonyl ligand or derivative thereof.

10       thereof.



(III)



(IV)

**[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

15       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.

**[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

20       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.

5 **[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  
10 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  
15 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  
20 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 (N<sub>2</sub>), helium (He), and argon (Ar).

**[0042]** At operation 116, the substrate (or substrate surface) is exposed to a reactant to form one or more of a molybdenum-containing film on the substrate. The  
25 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 other embodiments, the reactant comprises an oxidizing agent. In one or more embodiments, the oxidizing  
30 agent can comprise any oxidizing agent known to one of skill in the art. In further embodiments, the reactant comprises one or more of oxidizing agent and a reducing agent.

**[0043]** In specific embodiments, the reactant is selected from one or more of 1,1-dimethylhydrazine (DMH), alkyl amine, hydrazine, alkyl hydrazine, allyl hydrazine, hydrogen (H<sub>2</sub>), ammonia (NH<sub>3</sub>), alcohols, water (H<sub>2</sub>O), oxygen (O<sub>2</sub>), ozone (O<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), nitrogen dioxide (NO<sub>2</sub>), peroxides, and plasmas thereof. In some  
5 embodiments, the alkyl amine is selected from one or more of tert-butyl amine (tBuNH<sub>2</sub>), isopropyl amine (iPrNH<sub>2</sub>), ethylamine (CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>), diethylamine ((CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH), or butyl amine (BuNH<sub>2</sub>). In some embodiments, the reactant comprises one or more of compounds with the formula R'<sup>1</sup>NH<sub>2</sub>, R'<sup>2</sup>NH, R'<sup>3</sup>N, R'<sup>2</sup>SiNH<sub>2</sub>, (R'<sup>3</sup>Si)<sub>2</sub>NH, (R'<sup>3</sup>Si)<sub>3</sub>N; where each R' is independently H or an alkyl group having 1-12  
10 carbon atoms. In some embodiments, the alkyl amine consists essentially of one or more of tert-butyl amine (tBuNH<sub>2</sub>), isopropyl amine (iPrNH<sub>2</sub>), ethylamine (CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>), diethylamine ((CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NH), butyl amine (BuNH<sub>2</sub>).

**[0044]** At operation 118, the processing chamber is optionally purged after exposure to the reactant. Purging the processing chamber in operation 118 can be the  
15 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.

**[0045]** At decision 120, the thickness of the deposited film, or number of cycles of  
20 molybdenum-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. In some embodiments, the process cycle comprises sequential exposure of the substrate to the molybdenum precursor, purge gas, reactant and purge gas. If the  
25 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.

**[0046]** The optional post-processing operation 130 can be, for example, a process  
30 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 (N<sub>2</sub>), argon (Ar)) or a reducing gas (e.g., molecular hydrogen (H<sub>2</sub>) or ammonia (NH<sub>3</sub>)) or an oxidant, such as, but not limited to, oxygen (O<sub>2</sub>), ozone (O<sub>3</sub>), 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.

**[0047]** 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 116) occur at the same temperature. In some embodiments, the substrate is maintained at a temperature in a range of from 20 °C to 650 °C, from 20 °C to 500 °C, from 20 °C to 400 °C, from 20 °C to 300 °C, from 50 °C to 650 °C, from 50 °C to 500 °C, from 50 °C to 400 °C, from 50 °C to 300 °C, from 100 °C to 650 °C, from 100 °C to 500 °C, from 100 °C to 400 °C or from 100 °C to 300 °C. In some embodiments, the substrate is maintained at a temperature in a range of from 20 °C to <650 °C, from 20 °C to <500 °C, from 20 °C to <400 °C, from 20 °C to <300 °C, from 50 °C to <650 °C, from 50 °C to <500 °C, from 50 °C to <400 °C, from 50 °C to <300 °C, from 100 °C to <650 °C, from 100 °C to <500 °C, from 100 °C to <400 °C or from 100 °C to <300 °C.

**[0048]** In some embodiments, exposure to the molybdenum precursor (operation 112) occurs at a different temperature than the exposure to the reactant (operation 116). In some embodiments, the substrate is exposed to the molybdenum precursor (operation 112) at a first temperature in a range of from 20 °C to 650 °C, from 20 °C to 500 °C, from 20 °C to 400 °C, from 20 °C to 300 °C, from 50 °C to 650 °C, from 50 °C

to 500 °C, from 50 °C to 400 °C, from 50 °C to 300 °C, from 100 °C to 650 °C, from 100 °C to 500 °C, from 100 °C to 400 °C or from 100 °C to 300 °C. In some embodiments, the substrate is exposed to the molybdenum precursor (operation 112) at a first temperature in a range of from 20 °C to <650 °C, from 20 °C to <500 °C, from 20 °C to <400 °C, from 20 °C to <300 °C, from 50 °C to <650 °C, from 50 °C to <500 °C, from 50 °C to <400 °C, from 50 °C to <300 °C, from 100 °C to <650 °C, from 100 °C to <500 °C, from 100 °C to <400 °C or from 100 °C to <300 °C. In some embodiments, the reactant is reacted with the precursor film (operation 116) at a temperature in a range of from 20 °C to 650 °C, from 20 °C to 500 °C, from 20 °C to 400 °C, from 20 °C to 300 °C, from 50 °C to 650 °C, from 50 °C to 500 °C, from 50 °C to 400 °C, from 50 °C to 300 °C, from 100 °C to 650 °C, from 100 °C to 500 °C, from 100 °C to 400 °C or from 100 °C to 300 °C. In some embodiments, the reactant is reacted with the precursor film (operation 116) at a temperature in a range of from 20 °C to <650 °C, from 20 °C to <500 °C, from 20 °C to <400 °C, from 20 °C to <300 °C, from 50 °C to <650 °C, from 50 °C to <500 °C, from 50 °C to <400 °C, from 50 °C to <300 °C, from 100 °C to <650 °C, from 100 °C to <500 °C, from 100 °C to <400 °C or from 100 °C to <300 °C.

**[0049]** In the embodiment illustrated in FIG. 1, at deposition operation 110 the substrate (or substrate surface) is exposed to the molybdenum precursor and the reactant sequentially. In another, un-illustrated, embodiment, the substrate (or substrate surface) is exposed to the molybdenum precursor 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 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.

**[0050]** 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.

5   **[0051]** In other embodiments, the molybdenum-containing film comprises molybdenum oxide ( $\text{MoO}_x$ ) with an oxygen content of greater than or equal to about 5%, 7.5%, 10%, 12.5 or 15%, on an atomic basis. In some embodiments, the molybdenum-containing film comprises an oxygen content in the range of about 2% to about 30%, or in the range of about 3% to about 25%, or in the range of about 4% to about 20%, on an atomic basis.

10   **[0052]** In other embodiments, the molybdenum-containing film comprises molybdenum carbide ( $\text{MoC}_x$ ) with a carbon content of greater than or equal to about 5%, 7.5%, 10%, 12.5 or 15%, on an atomic basis. In some embodiments, the molybdenum-containing film comprises a carbon content in the range of about 2% to about 30%, or in the range of about 3% to about 25%, or in the range of about 4% to about 20%, on an atomic basis.

15   **[0053]** The deposition operation 110 can be repeated to form one or more of a molybdenum oxide film, a molybdenum carbide film, a molybdenum silicide film, and a molybdenum nitride film, having a predetermined thickness. In some embodiments, the deposition operation 110 is repeated to provide one or more of a molybdenum oxide film, a molybdenum carbide film, a molybdenum silicide film, and a molybdenum nitride film 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 3000 Å.

20   **[0054]** 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.

30   **[0055]** 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-containing film fills the feature in a bottom-up manner.

**[0056]** 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 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 a "cluster tool" or "clustered system," and the like.

**[0057]** 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 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 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 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 subsequent film.

**[0058]** 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 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.

**[0059]** 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 substrate 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.

**[0060]** 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.

**[0061]** 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  
5 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.

**[0062]** The disclosure is now described with reference to the following examples. Before describing several exemplary embodiments of the disclosure, it is to be  
10 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 embodiments and of being practiced or being carried out in various ways.

**[0063]** EXAMPLES

**[0064]** Example 1: Preparation of Phosphine-Substituted Dinuclear Molybdenum  
15 Complexes

**[0065]** The target compounds bearing mono or bidentate phosphine ligands were prepared by dissolving the starting Cp-based Mo precursors in acetonitrile followed by addition of the corresponding alkylphosphine. The resulting mixture was heated under reflux and the reaction progress was monitored by <sup>31</sup>P NMR Spectroscopy. Upon  
20 completion, all volatiles were removed under vacuum to yield molybdenum dinuclear systems in good to moderate yields.

**[0066]** Example 2: Atomic Layer Deposition of Molybdenum Containing Films

**[0067]** General procedure: A silicon substrate is placed in a processing chamber. A molybdenum precursor is flowed into the processing chamber in an atmosphere of  
25 nitrogen (N<sub>2</sub>) gas over the silicon substrate leaving a molybdenum-precursor terminated surface. Unreacted precursor and byproducts are then purged out of the chamber. Next, a co-reactant is then introduced into the chamber that reacts with the surface-bound molybdenum species. Again, excess coreactant and byproducts are removed from the chamber. The resultant material on the substrate is a molybdenum-  
30 containing film.

**[0068]** 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 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  
5 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 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly.

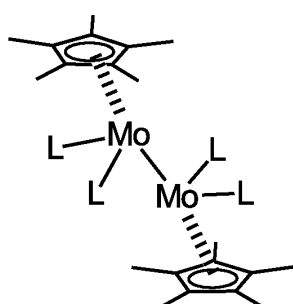
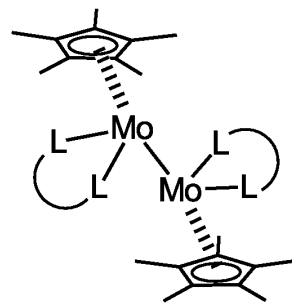
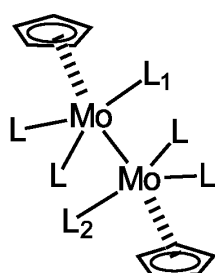
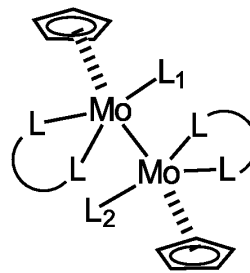
10 **[0069]** The use of the terms "a" and "an" and "the" and similar referents in the context of describing the materials and methods discussed herein (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation  
15 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 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")  
20 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 to the practice of the disclosed materials and methods.

**[0070]** Reference throughout this specification to "one embodiment," "certain  
25 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  
30 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.

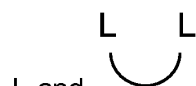
**[0071]** Although the disclosure herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present disclosure. It will be apparent to those skilled in the art that various modifications 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 metal coordination complex comprising a dinuclear molybdenum and a sterically or electronically adapted phosphine ligand or derivative thereof, the metal coordination complex substantially free of oxygen, halogen, and carbonyl.
2. The metal coordination complex of claim 1 having a structure of Formula (I), Formula (II), Formula (III), or Formula (IV):

**(I)****(II)****(III)****(IV)**

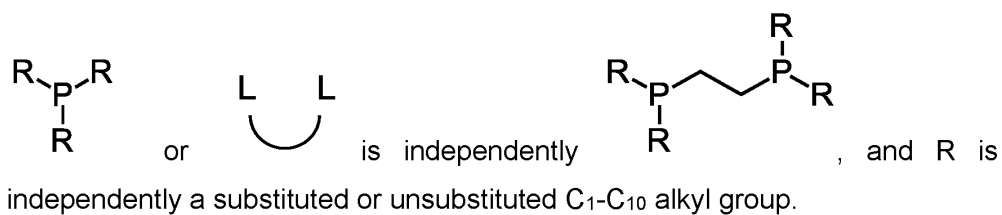
wherein Mo-Mo is dinuclear molybdenum,



L and  are independently the sterically or electronically adapted phosphine ligand or derivative thereof, and

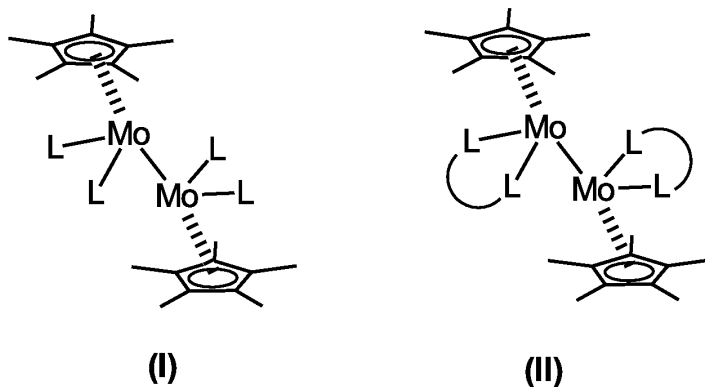
one or more of L<sub>1</sub> and L<sub>2</sub> are independently the sterically or electronically adapted phosphine ligand or derivative thereof, or a carbonyl ligand or derivative thereof.

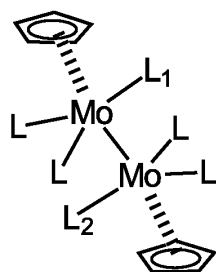
5        3. The metal coordination complex of claim 2, wherein L is independently



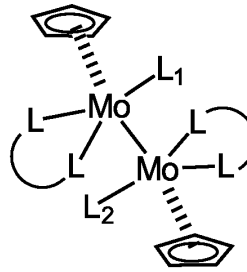
4. The metal coordination complex of claim 3, wherein R is independently  
10 selected from Me-, Et-, iPr-, tBu-, and  substituents.

5. A method of depositing a film, the method comprising:  
 exposing a substrate to a dinuclear molybdenum coordination complex  
 15 having a structure of Formula (I), Formula (II), Formula (III), or Formula (IV)





(III)



(IV)

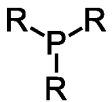
wherein Mo-Mo is dinuclear molybdenum,

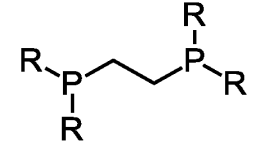
L and  are independently a sterically or electronically adapted phosphine ligand or derivative thereof, and

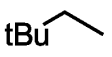
5 one or more of L<sub>1</sub> and L<sub>2</sub> are independently a sterically or electronically adapted phosphine ligand or derivative thereof, or a carbonyl ligand or derivative thereof; and

exposing the substrate to a reactant to form a molybdenum-containing film on the substrate.

10

6. The method of claim 5, wherein L is independently  and  is

independently , R is independently a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl group.

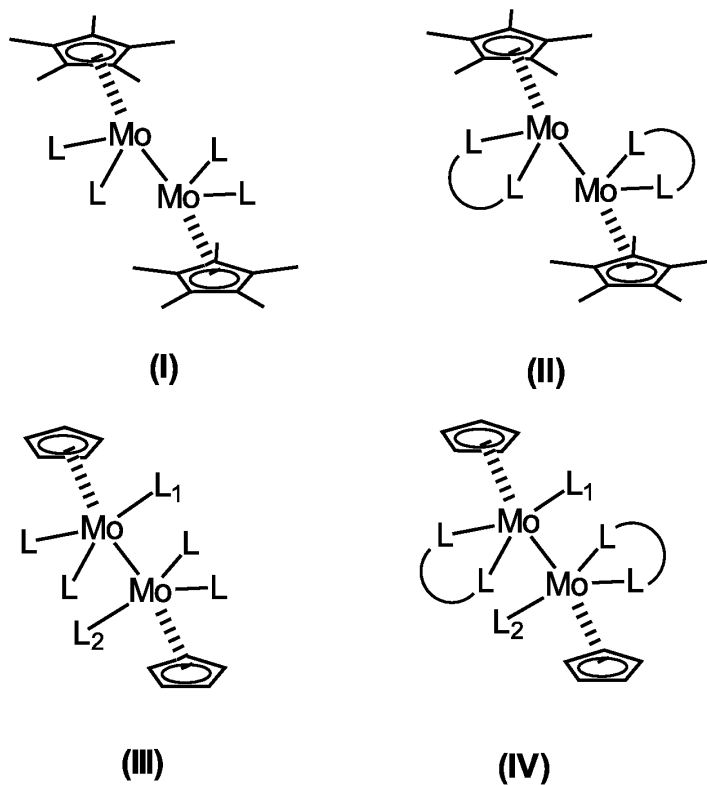
15 7. The method of claim 6, wherein R is independently selected from Me-, Et-, iPr-, tBu-, and .

8. The method of claim 5, wherein the method is one or more of chemical vapor deposition or atomic layer deposition.

9. The method of claim 5, wherein the reactant is reacted with the film at a temperature in a range of from 100°C to <400°C.
- 5 10. The method of claim 5, wherein the reactant comprises one or more of an oxidizing agent and a reducing agent.
- 10 11. The method of claim 5, wherein the molybdenum-containing film comprises one or more of a molybdenum metal (elemental Mo) film, a molybdenum oxide film, a molybdenum carbide film, a molybdenum silicide film, and a molybdenum nitride film.
- 15 12. The method of claim 5, wherein the substrate is exposed to the dinuclear molybdenum coordination complex and the reactant sequentially.
13. The method of claim 5, wherein the substrate is exposed to the dinuclear molybdenum coordination complex and the reactant simultaneously.
- 20 14. The method of claim 5, further comprising purging the substrate of the dinuclear molybdenum coordination complex prior to exposing the substrate to the reactant.
- 25 15. The method of claim 14, wherein purging comprises one or more of applying a vacuum or flowing a purge gas over the substrate.
16. The method of claim 5, further comprising repeating the method to provide a molybdenum-containing film having a thickness of about 0.3 to about 100 nm.
- 30 17. The method of claim 15, wherein the purge gas comprises one or more of nitrogen (N<sub>2</sub>), helium (He), and argon (Ar).
18. A method of depositing a film, the method comprising:

forming a molybdenum-containing film in a process cycle comprising sequential exposure of a substrate to a dinuclear molybdenum coordination complex precursor, purge gas, reactant, and purge gas.

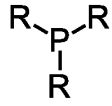
- 5 19. The method of claim 18, wherein the dinuclear molybdenum coordination complex has a structure of Formula (I), Formula (II), Formula (III), or Formula (IV):

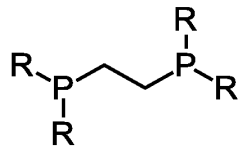


wherein Mo-Mo is dinuclear molybdenum,

L and  are independently a sterically or electronically adapted phosphine ligand or derivative thereof, and

one or more of L<sub>1</sub> and L<sub>2</sub> are independently the sterically or electronically adapted phosphine ligand or derivative thereof, or a carbonyl ligand or derivative thereof.

20. The method claim 19, wherein L is independently ,  is

independently , and R is independently a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl group.