defined herein); (15) heterocyclyloyl (e.g., -C(O)-R, in which R is heterocyclyl, as defined herein); (16) hydroxyl (e.g., -OH); (17) *N*-protected amino; (18) nitro (e.g., $-NO_2$); (19) oxo (e.g., =O); (20) $C_{1-6}$ thioalkyl (e.g., -S-R, in which R is alkyl); (21) thiol (e.g., -SH); (22) $-CO_2R^1$, where $R^1$ is selected from the group consisting of (a) hydrogen, (b) $C_{1-6}$ alkyl, (c) $C_{4-18}$ aryl, and (d) $C_{4-18}$ aryl-$C_{1-6}$ alkyl (e.g., -L-R, in which L is $C_{1-6}$ alkyl and R is $C_{4-18}$ aryl); (23) $-C(O)NR^1R^2$, where each of $R^1$ and $R^2$ is, independently, selected from the group consisting of (a) hydrogen, (b) $C_{1-6}$ alkyl, (c) $C_{4-18}$ aryl, and (d) $C_{4-18}$ aryl-$C_{1-6}$ alkyl (e.g., -L-R, in which L is $C_{1-6}$ alkyl and R is $C_{4-18}$ aryl); (24) $-SO_2R^1$, where $R^1$ is selected from the group consisting of (a) $C_{1-6}$ alkyl, (b) $C_{4-18}$ aryl, and (c) $C_{4-18}$ aryl-$C_{1-6}$ alkyl (e.g., -L-R, in which L is $C_{1-6}$ alkyl and R is $C_{4-18}$ aryl); (25) $-SO_2NR^1R^2$, where each of $R^1$ and $R^2$ is, independently, selected from the group consisting of (a) hydrogen, (b) $C_{1-6}$ alkyl, (c) $C_{4-18}$ aryl, and (d) $C_{4-18}$ aryl-$C_{1-6}$ alkyl (e.g., -L-R, in which L is $C_{1-6}$ alkyl and R is $C_{4-18}$ aryl); and (26) $-NR^1R^2$, where each of $R^1$ and $R^2$ is, independently, selected from the group consisting of (a) hydrogen, (b) an *N*-protecting group, (c) $C_{1-6}$ alkyl, (d) $C_{2-6}$ alkenyl, (e) $C_{2-6}$ alkynyl, (f) $C_{4-18}$ aryl, (g) $C_{4-18}$ aryl-$C_{1-6}$ alkyl (e.g., -L-R, in which L is $C_{1-6}$ alkyl and R is $C_{4-18}$ aryl), (h) $C_{3-8}$ cycloalkyl, and (i) $C_{3-8}$ cycloalkyl-$C_{1-6}$ alkyl (e.g., -L-R, in which L is $C_{1-6}$ alkyl and R is $C_{3-8}$ cycloalkyl), wherein in one embodiment no two groups are bound to the nitrogen atom through a carbonyl group or a sulfonyl group. The alkyl group can be a primary, secondary, or tertiary alkyl group substituted with one or more substituents (e.g., one or more halo or alkoxy). In some embodiments, the unsubstituted alkyl group is a $C_{1-3}$, $C_{1-6}$, $C_{1-12}$, $C_{1-16}$, $C_{1-18}$, $C_{1-20}$, or $C_{1-24}$ alkyl group.

**[0080]** By "alkylene," "alkenylene," or "alkynylene" is meant a multivalent (e.g., bivalent) form of an alkyl, alkenyl, or alkynyl group, respectively, as described herein. Exemplary alkylene groups include methylene, ethylene, propylene, butylene, etc. In some embodiments, the alkylene group is a $C_{1-3}$, $C_{1-6}$, $C_{1-12}$, $C_{1-16}$, $C_{1-18}$, $C_{1-20}$, $C_{1-24}$, $C_{2-3}$, $C_{2-6}$, $C_{2-12}$, $C_{2-16}$, $C_{2-18}$, $C_{2-20}$, or $C_{2-24}$ alkylene group. In other embodiments, the alkenylene or alkynylene group is a $C_{2-3}$, $C_{2-6}$, $C_{2-12}$, $C_{2-16}$, $C_{2-18}$, $C_{2-20}$, or $C_{2-24}$ alkenylene or alkynylene group. The alkylene, alkenylene, or alkynylene group can be branched or unbranched. The alkylene, alkenylene, or alkynylene group can also be substituted or unsubstituted. For example, the alkylene, alkenylene, or alkynylene group can be substituted with one or more substitution groups, as described herein for alkyl.

**[0081]** By "alkylsulfinyl" is meant an alkyl group, as defined herein, attached to the parent molecular group through an -S(O)- group. In some embodiments, the unsubstituted

heated to a temperature of about 300°C or lower, e.g., about 300°C to about 50°C. In some embodiments, the chamber may be pressurized to less than about 10 Torr. In some embodiments, the chamber pressure may be in the range of from about 0.1 to about 9.9 Torr. In some embodiments, the duration of exposure is from about 5 or 10 seconds to about 2 minutes.

**[0203]** In an operation 102, a substrate surface is exposed to a metal precursor. In some embodiments, the metal precursors may be molybdenum precursors, copper precursors, tungsten precursors, cobalt precursors or ruthenium precursors among others. Exemplary metal precursors are discussed in the following paragraphs.

***Copper Precursors***

**[0204]** Copper metal can be deposited using a variety of copper precursors, where copper may be in +1 or +2 oxidation states. The precursors may be cuprous (copper (I)) compounds such as acetylacetonates, ketoiminates, diiminates, cyclopentadienyl compounds, amidinates, guanidinates or amides; or cupric (copper (II)) compounds such as acetylacetonates, ketoiminates or aminoalkoxides as illustrated in **FIG. 2** and **FIG. 3**. In some embodiments the precursors are coordination complexes, where copper coordinates to a multiple bond such as a double or triple bond; or coordinates to the oxygen of a carbonyl group for example.

**[0205]** Examples of copper precursors include $Cu(acac)_2$ where acac = acetylacetonato; $Cu(thd)_2$ where thd = tetrahydrodionato); hexafluoroacetylacteonate-copper-trimethylsilane; cyclopentadienyl (Cp) compounds such as CpCu(CNMe), $CpCu(CNCMe_3)$, CpCuCO, $CPCuPR_3$ (where R = Me, Et or Ph) and $CpCu(CSiMe_3)_2$; alkyl or aryl compounds such as $MeCu(PPh_3)_3$, CuMe, CuCCH( ethynylcopper), CuCCMe (methylacetylide copper), $(H_2C{=}CMeCC)Cu$(3-methyl-3-buten-1ynylcopper), CuCCPh, $C_6H_5Cu$ (phenyl copper), $(Me)_3CCCCu$ (3,3-dimethyl-1-butynyl) copper, $Me_3SiCCCH_2Cu$; and other compounds such as CuCN, $[Cu(OAc]_n$ (where OAc = acetate), $Cu_2Cl_2$(butadiene), $C_7H_7CuO$(2-methoxyphenylcopper), $(MeCN)_4CuX$ (where X is a halide, an alkyl, an amine or a phenyl group), $Me_3SiOCu(PMe_3)_3$, $Cu(C_4H_4S)$ and Cu-carbene compounds such as those derived from imidazolium.

***Molybdenum-Containing Precursors***

**[0206]** Generally, molybdenum-containing precursors can include molybdenum in a wide range of oxidation states ranging from 0 to +6. In some embodiments, molybdenum

compounds have molybdenum in low oxidation states of +3, +4 and +5. Provided methods are particularly useful for depositing molybdenum containing materials from halogen-containing molybdenum-containing compounds, because silicon-containing reactants can assist in halogen scavenging, but halogen-free molybdenum-containing precursors can be used as well. Suitable molybdenum containing precursors include molybdenum halides and oxyhalides, such as fluorides, chlorides, bromides, oxyfluorides, oxychlorides, and oxybromides where molybdenum may be in any of the oxidation states from +2 to +6.

**[0207]** Molybdenum chloride precursors are given by the formula $MoCl_x$, where x is 2, 3, 4, 5, or 6, and include molybdenum dichloride ($MoCl_2$), molybdenum trichloride ($MoCl_3$), molybdenum tetrachloride ($MoCl_4$), molybdenum pentachloride ($MoCl_5$), and molybdenum hexachloride ($MoCl_6$). In some embodiments, $MoCl_5$ or $MoCl_6$ are used. While the description chiefly refers to $MoCl_x$ precursors, in other embodiments, other molybdenum halide precursors may be used. Molybdenum halide precursors are given by the formula $MoX_z$, where X is a halogen (fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)) and z is 2, 3, 4, 5, or 6. Examples of $MoX_z$ precursors include molybdenum fluoride ($MoF_6$). In some embodiments, a non-fluorine-containing $MoX_z$ precursor is used to prevent fluorine etch or incorporation. In some embodiments, a non-bromine-containing and/or a non-iodine-containing $MoX_z$ precursor is used to prevent etch or bromine or iodine incorporation.

**[0208]** Molybdenum oxyhalide precursors are given by the formula $MoO_yX_z$, where X is a halogen (fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)) and y and z are numbers greater than 0 such that $MoO_yX_z$ forms a stable compound. Examples of molybdenum oxyhalides include molybdenum dichloride dioxide ($MoO_2Cl_2$), molybdenum tetrachloride oxide ($MoOCl_4$), molybdenum tetrafluoride oxide ($MoOF_4$), molybdenum dibromide dioxide ($MoO_2Br_2$), and the molybdenum iodide dioxides $MoO_2I$, and $Mo_4O_{11}I$.

**[0209]** In some embodiments discussed herein, the precursors having molecular weights of less than about 450 g/mol, such as less than about 400 g/mol.

**[0210]** In some embodiments the molybdenum containing precursor has a formula $MoX_nY_m$, wherein X is a chalcogen (e.g., oxygen or sulfur), Y is a halogen (e.g., fluorine, chlorine, bromine, or iodine), n is 0, 1, or 2 and m is 2, 3, 4, 5, or 6. Examples of halogen-containing molybdenum-containing precursors include without limitation $MoCl_5$,

An example of an amidate is an amidate **3** shown in **FIG. 4**, where each R is independently selected from H, alkyl, and fluoroalkyl. Amidate **3** is a monoanionic ligand that can form one molybdenum-nitrogen, and one molybdenum-oxygen bond, serving as a bidentate ligand.

**[0217]** In some embodiments, at least one organic ligand in the precursor is a diazadiene. Examples of diazadienes are 1,4-diazabuta-1,3-dienes (DAD) **5**, **6**, and **7**, where each R is independently selected from H, alkyl, and fluoroalkyl. An interesting property of this ligand is that it can exist in neutral form **5**, monoanionic radical form **6**, and dianionic form **7**. Due to redox activity of monoanionic (radical) form **6**, it can be relatively easily removed during deposition making complexes of DAD **6** particularly useful for deposition of molybdenum metal and high purity molybdenum metal. DAD ligands **5**, **6**, and **7** can serve as bidentate ligands, each forming two molybdenum-nitrogen bonds. In some embodiments the molybdenum precursor includes DAD ligand **5**, **6**, or **7** as an organic ligand, where each R is independently selected from methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl and *t*-butyl.

**[0218]** In some embodiments, the at least one organic ligand is an iminopyrrolidinate (such as an iminopyrrolidinate **4**, where each R is independently selected from H, alkyl, and fluoroalkyl), a beta-imino amide (such as beta-imino amide **8**, where each R is independently selected from H, alkyl, and fluoroalkyl), an alpha-imino alkoxide (such as an alpha-imino alkoxide **9**, where each R is independently selected from H, alkyl, and fluoroalkyl), a beta-diketiminate (such as an beta-diketiminate **10**, where each R is independently selected from H, alkyl, and fluoroalkyl), a beta-ketoiminate (such as beta-ketoiminate **11**, where each R is independently selected from H, alkyl, and fluoroalkyl), a beta-diketonate **12** (such as beta-diketonate **12**, where each R is independently selected from H, alkyl, and fluoroalkyl), a pyrazolate (such as pyrazolate **13**, where each R is independently selected from H, alkyl, and fluoroalkyl), a beta-aminoalkoxide (such as betaaminoalkoxide **14**, where each R is independently selected from H, alkyl, and fluoroalkyl), or a guandinidate **15** (such as guandinidate **15**, where each R is independently selected from H, alkyl, and fluoroalkyl). These are monoanionic ligands that are capable of binding to molybdenum in bidentate manner.

**[0219]** In some embodiments, the at least one organic ligand is a sulfur containing ligand that is capable of forming molybdenum-sulfur bond. In some embodiments the at least one organic ligand in the precursor is a thioether. The term “thioether” is used herein

compared with conventional homoleptic molybdenum halides. These advantages are described for illustration purposes and do not limit the use of these compounds solely to molybdenum metal deposition or to deposition on etching-sensitive substrates.

**[0226]** In some embodiments, when deposition is conducted on fluorine-sensitive materials (e.g., silicon-containing materials) the precursors are selected to be fluorine free, e.g., include any of the Cl, Br, and I as the halides in the complex. Further, the use of compounds with fluoroalkyl substituents may be avoided in these embodiments.

***Sulfur-containing molybdenum compounds***

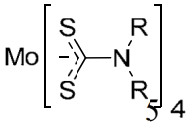
**[0227]** In one aspect, sulfur-containing molybdenum compounds are used as molybdenum-containing precursors for deposition of molybdenum-containing films, such as for deposition of molybdenum metal and molybdenum silicide. In some embodiments, the molybdenum compounds include molybdenum, and at least one sulfur-containing ligand providing molybdenum-sulfur bonding. Molybdenum precursors which are based on sulfur-containing ligands can be used to deposit molybdenum-containing films which are substantially free of impurities due to the ease of removal of sulfur impurities compared to oxygen, carbon, and nitrogen impurities. In some embodiments, the molybdenum compounds do not include molybdenum-carbon bonds and/or do not include molybdenum-oxygen double bonds.

**[0228]** In some embodiments the molybdenum compounds do not include molybdenum-nitrogen double bonds. In some embodiments in the provided molybdenum precursors molybdenum forms bonds only with sulfur atoms.

**[0229]** Examples of suitable sulfur-containing ligands that provide sulfur bonding include thioethers, thiolates, dithiolenes, dithiolates, thiocarbamates, and α-imino thiolenes. The ligands can include one or more substituents independently selected from the group consisting of H, alkyl, fluoroalkyl, alkylsilyl, alkylamino, and alkoxy substituents. The ligands can be neutral or anionic (e.g., monoanionic or dianionic), and molybdenum can be in a variety of oxidation states, such as 0, +1, +2, +3, +4, +5 and +6.

**[0230]** In some embodiments the sulfur-containing ligands are ligands **18-25** shown in **FIG. 5**, where R substituents are as previously described. Examples of suitable molybdenum precursors include molybdenum thiolates $Mo(SR)_4$, wherein R is an alkyl, e.g., methyl, ethyl propyl, butyl. In one specific example, the precursor is tetrakis(*tert*-butylthiolato)molybdenum(IV): $Mo(SR)_4$, wherein R is *t*-butyl. Another example of

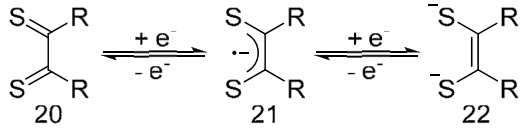
suitable molybdenum precursors are molybdenum thiocarbamates, such as tetrakis(diethyldithiocarbamato)molybdenum(IV):



where each R is independently selected from alkyl (e.g., ethyl, methyl, propyl, butyl), and fluoroalkyl (e.g., $CF_3$). In one specific example the precursor is tetrakis(diethyldithiocarbamato)molybdenum(IV).

**[0231]** In some embodiments dithiolene complexes of molybdenum are provided, where dithiolene may be in any of a neutral form **20**, anion-radical form **21**, and dianionic form **22**, where each R is independently H, alkyl or fluoroalkyl.

**[0232]** Dithiolene complexes are redox-active and can support molybdenum in a variety of oxidation states. Redox reactions of dithiolene ligands **20**, **21**, and **22** are shown in Equation 1:



(Equation 1)

**[0233]** In one implementation, the precursor is Mo(**21**)$_3$, where each R in **21** is independently selected from H, alkyl, and fluoroalkyl. For example, R may be methyl, ethyl, $CF_3$, etc. This is a homoleptic Mo(III) compound containing exclusively molybdenum-sulfur bonds.

**[0234]** In some embodiments, the ligands may provide nitrogen bonding in addition to sulfur bonding. One example of such ligand is alpha-iminothiolene **23**, which is a redox-active radical anion ligand that can exhibit behavior similar to that of thiolenes.

**[0235]** In some embodiments the precursor is Mo(III) compound Mo(**23**)$_3$, where each R in compound **23** is independently selected from H, alkyl, and fluoroalkyl.

**[0236]** In some embodiments, the precursor is $MoL_n$ compound, where n is from 2 to 6,

deposition can also lead to deposition of films with poor step coverage. A direct plasma (or plasma generated directly) is a plasma in which the plasma (electrons, neutral species, radicals, and positive ions at an appropriate concentration) resides in close proximity to the substrate surface during deposition, sometimes separated from the substrate surface by only a plasma sheath. Ions can play an important role in the direct plasma process. An apparatus for direct plasma treatment is described in **Fig. 8** below. In some embodiments, the plasma is generated remotely. A remote plasma (or plasma generated remotely) is one in which the plasma is generated at a distance from the substrate. The major reaction species may be radicals for plasma generated remotely. An apparatus for remote plasma treatment is described in **Fig. 7** below. Under some circumstances, there may be certain advantages of using a remote plasma instead of a direct plasma.

**[0260]** In some embodiments, a plasma of reactive species is formed. The plasma species could include electrons, positive ions, neutral species, radicals, and other plasma species. In some embodiments, the plasma may be a hydrogen-based plasma as the hydrogen-containing source including hydrogen atoms, hydrogen radicals, hydrogen reactive species, hydrogen plasma or combinations thereof. The plasma may be an oxygen-based plasma as the oxygen-containing source including oxygen atoms, oxygen radicals, oxygen reactive species, oxygen plasma or combinations thereof. In some embodiments, the plasma may also comprise noble gas species, for example argon, neon, krypton, xenon or helium species. In some instances, the plasma may comprise other species, for example, nitrogen atoms, nitrogen radicals, nitrogen plasma or combinations thereof.

**[0261]** In some embodiments the substrate is contacted with a reactant comprising hydrogen, oxygen, and helium plasma. The plasma may be formed in a reaction chamber or upstream of a reaction chamber, for example by flowing the hydrogen, oxygen and helium through a remote plasma generator, thereby generating plasma species that are introduced downstream to the reaction chamber. Alternatively, hydrogen and helium plasma may be fed into a reaction chamber separately from oxygen and helium plasma. In some embodiments, the hydrogen gas is supplied in a volume of from about 500 to about 5000 sccm (standard cubic centimeters/minute/one station chamber). In some embodiments of the plasma pre-treatment, the oxygen gas is supplied in a volume of from about 1 to about 150 sccm. In some embodiments, the oxygen gas is supplied in a volume of from about 15 to about 100 sccm. In some embodiments of the plasma pre-treatment,

with depositing a graded silicon carbide film and, optionally, other operations in a fabrication flow that includes the graded silicon carbide films. The controller 240 may execute system control software including sets of instructions for controlling the timing, gas composition, gas flow rates, chamber pressure, chamber temperature, RF power levels, substrate position, and/or other parameters. Other computer programs, scripts, or routines stored on memory devices associated with the controller 240 may be employed in some embodiments. To provide relatively mild reactive conditions at the environment adjacent to the substrate 230, parameters such as the RF power levels, gas flow rate to the remote plasma region, and timing of the plasma ignition can be adjusted and maintained by controller 240. Additionally, adjusting the substrate position may further reduce the presence of high-energy radical species at the environment adjacent to the substrate 230. In a multi-station reactor, the controller 240 may comprise different or identical instructions for different apparatus stations, thus allowing the apparatus stations to operate either independently or synchronously.

**[0274]** In some embodiments, the controller 240 may include instructions for performing operations such as flowing a metal-containing precursor through the first gas inlet 255 into the reaction chamber 210, providing one or more radical species of a source gas in a substantially low energy state from the remote plasma source 260, flowing a co-reactant gas through the second gas inlet 265 into the reaction chamber 210, changing a flow rate of the co-reactant gas over time, and flowing the one or more radical species through the second gas inlet 265 into the reaction chamber 210 to react with the metal-containing precursor to form the thin metal film on the substrate 230. In some implementations, the controller 240 may include instructions for changing a flow rate of the metal-containing precursor over time

**[0275]** In some embodiments, the apparatus may include a user interface associated with controller 240. The user interface may include a display screen, graphical software displays of the apparatus and/or process conditions, and user input devices such as pointing devices, keyboards, touch screens, microphones, etc.

**[0276]** The computer program code for controlling the above operations can be written in any conventional computer readable programming language: for example, assembly language, C, C++, Pascal, Fortran, or others. Compiled object code or script is executed by the processor to perform the tasks identified in the program.

## CLAIMS

1. A method for plasma-enhanced atomic layer deposition of a metal on a substrate comprising:

providing the substrate in a deposition chamber, wherein the substrate is at a temperature of about 300ºC or less;

exposing a surface of the substrate to a vapor phase metal precursor; and

exposing the substrate to plasma generated directly or plasma generated remotely from a hydrogen-containing gas source.

2. The method of claim 1, wherein the metal comprises vanadium, niobium, tantalum, chromium, cobalt, tungsten, iron, ruthenium, nickel, zinc, copper or molybdenum.

3. The method of claim 1, wherein the vapor phase metal precursor comprises vanadium-containing precursors, niobium-containing precursors, tantalum- containing precursors, chromium-containing precursors, cobalt-containing precursors, tungsten-containing precursors, iron-containing precursors, ruthenium- containing precursors, nickel-containing precursors, zinc-containing precursors, copper-containing precursors or molybdenum-containing precursors.

4. The method of claim 1, further comprising pre-treating the surface of the substrate with the plasma generated remotely from the hydrogen-containing gas source before exposing the surface of the substrate to the vapor phase metal precursor.

5. A method for plasma-enhanced atomic layer deposition of molybdenum on a substrate comprising:

providing the substrate in a deposition chamber, wherein the substrate is at a temperature of about 300ºC or less;

exposing a surface of the substrate to a vapor phase molybdenum precursor; and

exposing the substrate to plasma generated directly or plasma generated remotely from a hydrogen-containing gas source.

6. The method of claim 5, wherein the vapor phase molybdenum precursor comprises a structure of formula (I):

$$Mo(L\text{-}R^1)_6 \quad (I)$$

wherein each L is independently O, S or $NR^2$; and

$R^1$ and $R^2$ are independently hydrogen, optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted heteroaromatic, optionally substituted heteroaryl, optionally substituted heterocyclyl, optionally substituted aromatic, optionally substituted aryl, or optionally substituted arylalkylene; and

wherein two $R^1$ substituents can be taken together to form an optionally substituted cyclic group.

7. The method of claim 5, wherein the vapor phase molybdenum precursor comprises a structure of formula (II):

$$Mo(L\text{-}R^1)_2(Y)_4 \quad (II)$$

wherein each L is independently O, S, or $NR^2$;

$R^1$ and $R^2$ are independently hydrogen, optionally substituted aliphatic, optionally substituted alkyl, optionally substituted heteroaliphatic, optionally substituted heteroalkyl, optionally substituted heteroaromatic, optionally substituted heteroaryl, optionally substituted heterocyclyl, optionally substituted aromatic, optionally substituted aryl, or optionally substituted arylalkylene; and

wherein two $R^1$ substituents can be taken together to form an optionally substituted cyclic group; and

each Y is independently chlorine, fluorine, bromine or iodine.

8. The method of claim 5, wherein the vapor phase molybdenum precursor comprises $MoCl_5$, $Mo_2Cl_{10}$, $MoO_2Cl_2$, $MoOCl_4$ or any combination thereof.

9. The method of claim 5, wherein exposing the surface of the substrate to the vapor phase molybdenum precursor and exposing the substrate to plasma generated remotely from the hydrogen-containing gas source are performed in temporally separate pulses.

10. An apparatus for depositing a thin metal film on a substrate, the apparatus comprising:

at least one reaction chamber including a pedestal for holding the substrate;

at least one inlet port for delivering gas phase metal precursors to the reaction chamber;

a direct plasma generator or a remote plasma generator for providing plasma to the reaction chamber; and

a controller for controlling operations in the apparatus, including machine-readable instructions for

(a) causing the substrate to be at temperature of about 300ºC or less;

(b) causing introduction of a metal precursor in vapor phase into the at least one reaction chamber; and

(c) causing introduction of a plasma from the direct plasma generator or the remote plasma generator to form the thin metal film over the substrate, the plasma generated from a hydrogen-containing gas and from about 0.01% to about 1% of oxygen-containing gas.