

**SUBSTANTIALLY CARBON-FREE MOLYBDENUM-CONTAINING AND
TUNGSTEN-CONTAINING FILMS IN SEMICONDUCTOR DEVICE
MANUFACTURING**

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INCORPORATION BY REFERENCE

A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claims benefit of or priority to as identified in the concurrently filed PCT Request Form is incorporated by reference herein in its entirety and for all purposes.

FIELD OF THE INVENTION

This invention pertains to methods of semiconductor device manufacturing. Specifically, embodiments of this invention pertain to deposition of molybdenum-containing films and tungsten-containing films in semiconductor processing.

BACKGROUND

In integrated circuit (IC) fabrication, deposition and etching techniques are used for forming patterns of materials, such as for forming metal lines embedded in dielectric layers. Some patterning schemes require conformal deposition of materials, where the deposited layer should follow the contour of protrusions and/or recessed features on the surface of the substrate. Atomic layer deposition (ALD) is often a preferred method of forming conformal films on a substrate, because ALD relies on adsorption of one or more reactants (precursors) to the surface of the substrate, and on subsequent chemical transformation of the adsorbed layer to the desired material. Because ALD uses sequential reactions that occur on the surface of the substrate, that are separated in time, and that are typically limited by the amount of the adsorbed reactant, this method can provide thin conformal layers having excellent step coverage.

Chemical vapor deposition (CVD) is another deposition method widely used in semiconductor processing. In CVD, the reaction occurs in the volume of the

process chamber, and is not limited by the amount of reactants adsorbed to the substrate. As a result, CVD-deposited films are often less conformal than ALD-deposited films. CVD is typically used in applications where step coverage is less important.

ALD and CVD may employ plasma to promote the reactions of the deposition precursors resulting in the formation of the desired films. The methods that make use of the plasma are known as plasma enhanced ALD (PEALD) and plasma enhanced CVD (PECVD). The methods that do not employ plasma are referred to as thermal ALD and thermal CVD.

10 While ALD and CVD are most commonly used for deposition of silicon-containing films, such as silicon oxide, silicon nitride, and silicon carbide, these methods are also suitable for deposition of some metals, most notably tungsten and cobalt.

The background description provided herein is for the purposes of generally presenting the context of the disclosure. Work of the presently named inventor, to the extent it is described in this background section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are neither expressly nor impliedly admitted as prior art against the present disclosure.

20 SUMMARY

Methods for depositing substantially carbon-free molybdenum-containing and tungsten-containing films, such as metallic molybdenum, molybdenum nitride (MoN), molybdenum boride (MoB), molybdenum silicide (MoSi), and combinations thereof, such as (MoON) are provided. Semiconductor device structures containing such films (e.g., as liner layers, diffusion barrier layers, or electrode layers) are also provided.

In one aspect, a method of forming a substantially carbon-free metal-containing layer on a semiconductor substrate is provided. The method includes introducing a metal-containing precursor into a processing chamber housing the semiconductor substrate, wherein the precursor is a halide-free, carbonyl-free compound that comprises at least one ligand, bound to a metal selected from the group consisting of molybdenum and tungsten, wherein the halide-free, carbonyl-free

compound does not include metal-carbon bonds and metal-oxygen double bonds. The method further involves reacting the metal-containing precursor with at least one reactant in an absence of plasma to form a metal-containing layer on the semiconductor substrate, wherein the formed metal-containing layer is a substantially carbon-free molybdenum-containing or tungsten-containing layer that has a carbon content of less than about 5 atomic % (such as less than about 2 atomic %), wherein the layer is selected from the group consisting of Mo, W, MoN, WN, MoON, WON, MoB, WB, MoSi, WSi and combinations thereof. The combinations, for example, may include MoNB, or WONSi layers. In some embodiments the molybdenum-containing or tungsten-containing precursor does not include beta-hydrogen atoms. In some embodiments, the formed layer is post-treated (e.g., by a plasma treatment) to modify electrical properties of the layer. In some embodiments the formed layer is an electrode layer in a pMOS (p-type metal-oxide-semiconductor) device.

In another aspect, a semiconductor device is provided, where the semiconductor device includes a substantially carbon-free metal-containing liner layer, wherein the metal is selected from the group consisting of molybdenum and tungsten, and wherein carbon content in the substantially carbon-free metal containing layer is less than about 3 atomic %, wherein the substantially carbon-free metal liner layer has a thickness of less than about 50 Å, a resistivity of less than about 3,000 $\mu\cdot\text{cm}^{-1}$, and is positioned between a dielectric layer and a conductive layer. In some embodiments the substantially carbon-free liner layer is a diffusion barrier layer.

In another aspect, a semiconductor device comprising a gate electrode is provided, where the gate electrode comprises a substantially carbon-free metal-containing layer, wherein carbon content in the substantially carbon-free metal-containing layer is less than about 3 atomic %, and wherein the substantially carbon-free metal-containing layer has a work function of greater than 4.9 eV, and comprises a metal selected from the group consisting of molybdenum and tungsten. In some embodiments the substantially carbon-free metal-containing layer is a MoN layer.

In another aspect, an apparatus for forming a substantially carbon-free metal-containing layer on a semiconductor substrate is provided, where the apparatus includes: (a) a deposition processing chamber having a substrate support, an inlet for an introduction of a metal-containing precursor and a second inlet for an introduction

of at least one reactant; (b) a plasma treatment processing chamber, different from the deposition processing chamber, wherein the plasma treatment processing chamber comprises a substrate support and an inlet for introducing a plasma treatment reactant; and (c) a controller comprising program instructions for: (i) causing a surface-limited
5 reaction between the metal-containing precursor and at least one reactant in the deposition process chamber in an absence of plasma to form a layer of a substantially carbon-free metal-containing material, wherein the metal is selected from the group consisting of molybdenum and tungsten; (ii) causing transfer of the semiconductor substrate from the deposition processing chamber to the plasma treatment processing
10 chamber without exposing the semiconductor substrate to an ambient atmosphere; and (iii) causing treatment of the substantially carbon-free metal-containing material by a plasma-activated plasma treatment reactant.

In another aspect, a flow mixer for mixing a carrier gas and a metal-containing precursor is provided. The flow mixer includes: (a) an outer fluidic conduit
15 comprising an inlet for admitting the carrier gas into the outer fluidic conduit, a mixing zone for mixing the carrier gas with the metal-containing precursor and an outlet for removing the carrier gas mixed with the metal-containing precursor from the outer fluidic conduit; (b) an inner fluidic conduit positioned at least partially inside the outer fluidic conduit, wherein the inner fluidic conduit comprises an inlet
20 for admitting the metal-containing precursor into the inner fluidic conduit, and an outlet configured to release the metal-containing precursor into the outer fluidic conduit, wherein a distance from the inlet of the inner fluidic conduit to the inlet of the outer fluidic conduit is greater than a distance from the outlet of the inner fluidic conduit to the inlet of the outer fluidic conduit, thereby supporting opposing flows of
25 the carrier gas and of the metal-containing precursor in the flow mixer, wherein the distances refer to distances in a z-direction.

In another aspect, a method of depositing a metal-containing layer on a semiconductor substrate is provided, wherein the method includes: (a) mixing a metal-containing precursor with a carrier gas in the flow mixer provided herein;
30 and (b) delivering the formed mixture to a processing chamber and reacting the metal-containing precursor with a reactant to form the metal-containing layer on the semiconductor substrate.

In another aspect, a multi-plenum showerhead for delivery of a plurality of reactants to a processing chamber is provided, where the multi-plenum showerhead includes: (a) a showerhead faceplate comprising a first plurality of conduits for delivery of a first reactant and a second plurality of conduits for delivery of a second reactant, wherein the first plurality of conduits is configured to be fluidically isolated from the second plurality of conduits; and (b) a showerhead housing positioned about the perimeter of the showerhead faceplate, wherein the showerhead faceplate is releasably attached to the showerhead housing.

In another aspect, a faceplate for a showerhead for a deposition apparatus is provided, wherein the faceplate comprises a first plurality of conduits for delivery of a first reactant and a second plurality of conduits for delivery of a second reactant, wherein the first plurality of conduits is configured to be fluidically isolated from the second plurality of conduits, and wherein the faceplate is configured to be releasably attachable to a showerhead housing.

In another aspect, a deposition apparatus for depositing a metal-containing layer on a semiconductor substrate is provided, wherein the deposition apparatus includes a multi-plenum showerhead provided herein.

These and other aspects of implementations of the subject matter described in this specification are set forth in the accompanying drawings and the description below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A provides examples of molybdenum precursors that can be used in the deposition methods according to embodiments provided herein.

Figure 1B provides several specific examples of molybdenum precursors that can be used in the methods according to embodiments provided herein.

Figure 2 is a process flow diagram for a method of forming metal-containing films according to an embodiment provided herein.

Figure 3 is a process flow diagram for a method of forming metal-containing films according to an embodiment provided herein.

Figure 4A is a process flow diagram for a method of treating metal-containing films according to an embodiment provided herein.

Figure 4B is a process flow diagram for a method of treating metal-containing films according to an embodiment provided herein.

- 5 Figure 5 is a schematic cross-sectional view of a pMOS device structure containing a layer of substantially carbon-free metal-containing material, in accordance with an embodiment provided herein.

Figures 6A-6C are schematic cross-sectional views of a semiconductor device during fabrication, in accordance with an embodiment provided herein.

- 10 Figure 7 is a schematic presentation of an apparatus that is suitable for depositing molybdenum-containing films, according to an embodiment provided herein.

Figure 8 shows a schematic view of a multi-station processing system according to an embodiment provided herein.

- 15 Figure 9 shows a schematic view of a multi-station processing system according to an embodiment provided herein.

Figure 10 shows a schematic side view with a cross-sectional insert of a flow mixer in accordance with an embodiment provided herein.

- 20 Figure 11A shows a view of a portion of a dual-plenum showerhead assembly according to an embodiment provided herein.

Figure 11B shows a view of a portion of a showerhead faceplate detached from the showerhead housing according to an embodiment provided herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- 25 Methods for depositing substantially carbon-free molybdenum-containing films and tungsten-containing films on semiconductor substrates are provided. These methods can be used, for example, for depositing a blanket substantially carbon-free metal-containing layer on a planar substrate, for depositing a conformal metal-

containing layer on a substrate having one or more recessed or protruding features, and for filling recessed features with substantially carbon-free metal-containing materials. In some embodiments, methods are provided for forming substantially carbon-free metal-containing layers as liners or diffusion barrier layers on semiconductor substrates. In some embodiments, methods are provided for forming substantially carbon-free metal-containing layers as electrode layers in pMOS devices.

The methods can be used for deposition of a variety of molybdenum-containing and tungsten-containing materials including, but not limited to molybdenum metal (Mo), molybdenum nitride (MoN), molybdenum boride (MoB), molybdenum silicide (MoSi), and molybdenum oxynitride (MoON), tungsten metal (W), tungsten nitride (WN), tungsten boride (WB), tungsten silicide (WSi), and tungsten oxynitride (WON), where the stoichiometry of these compounds may vary, and the listed formulas are not indicative of stoichiometry. For example, MoN can include, in various embodiments, between about 10 – 70 atomic % of nitrogen.

The term “substantially carbon-free” refers to materials with carbon content of less than about 5 atomic %, where hydrogen (if present) is excluded from the calculations. In some embodiments, provided substantially carbon-free films include less than about 3 atomic % carbon, such as less than about 2 atomic % carbon.

“Metal”, e.g. “metallic molybdenum” or “metallic tungsten” as used herein, refers to material that consists essentially of metal (e.g., Mo or W). Other elements (e.g., B, Si, N, or O) can be present in the metal in small quantities (e.g., with a total content of less than about 15 atomic %, or less than about 10%, where hydrogen is not included in the calculation).

Molybdenum nitride (MoN), molybdenum boride (MoB), molybdenum silicide (MoSi), molybdenum oxynitride (MoON), tungsten nitride (WN), tungsten boride (WB), tungsten silicide (WSi), tungsten oxynitride (WON), refer to materials that consist essentially of the listed elements, where the stoichiometry of these compounds may vary and is not determined by the listed formulas (e.g., MoN does not necessarily indicate 1:1 Mo:N stoichiometry). Other elements may be present in

these compounds in small quantities, e.g., in an amount of less than about 10% atomic, where hydrogen is excluded from the calculation.

5 The term “semiconductor substrate” as used herein refers to a substrate at any stage of semiconductor device fabrication containing a semiconductor material anywhere within its structure. It is understood that the semiconductor material in the semiconductor substrate does not need to be exposed. Semiconductor wafers having a plurality of layers of other materials (e.g., dielectrics) covering the semiconductor material, are examples of semiconductor substrates. The following detailed description assumes the disclosed implementations are implemented on a
10 semiconductor wafer, such as on a 200 mm, 300 mm, or 450 mm semiconductor wafer. However, the disclosed implementations are not so limited. The work piece may be of various shapes, sizes, and materials. In addition to semiconductor wafers, other work pieces that may take advantage of the disclosed implementations include various articles such as printed circuit boards and the like.

15 The term “about” when used in reference to numerical values includes a range of $\pm 10\%$ of the recited numerical value, unless otherwise specified.

The term “alkyl”, as used herein, refers to saturated substituents containing exclusively carbon and hydrogen atoms. Alkyls include both linear, branched and cyclic groups. Examples of linear alkyl groups include without limitation, methyl
20 groups, ethyl groups, *n*-propyl groups, *n*-butyl groups, etc. Examples of branched alkyls groups include without limitation, isopropyl, isobutyl, *sec*-butyl, and *t*-butyl. Examples of cycloalkyls include without limitation, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, etc.

The term “fluoroalkyl”, as used herein, refers alkyl groups containing one or
25 more fluorine substituents. In some implementations fluoroalkyls contain exclusively fluorine substituents, such as in CF_3 , C_2F_5 , C_3F_7 . Fluoroalkyls may be linear, branched and cyclic.

The term “alkylsilyl”, as used herein, refers to SiR_3 group, wherein at least one R is an alkyl, and each R is independently selected from H and an alkyl. Alkylsilyls

include mono, bis, and tris alkylsilyls. Examples of alkylsilyls include trimethylsilyl, dimethylsilyl, methylsilyl, triethylsilyl, diethylsilyl, and ethylsilyl.

The term “alkylamino”, as used herein, refers to NR_2 group, wherein at least one R is an alkyl, and each R is independently selected from H and an alkyl.

5 Examples of alkylamino substituents include dimethylamino and diethylamino substituents.

The term “alkoxy”, refers to an OR, group, where R is an alkyl. Examples of alkoxy groups include methoxy, ethoxy, propoxy groups.

The term “independently selected”, when referring to R substituent selection
10 in a molecule containing multiple R groups, means that the selection of R substituents at different atoms of a molecule is independent and that the selection of R substituents at one atom having multiple R substituents is also independent.

The term “metalorganic precursors” as used herein refer to metal-containing compounds that include at least one carbon-containing ligand, where the compounds
15 do not contain metal-carbon bonds.

The embodiments of the invention are described primarily making reference to molybdenum-containing precursors and films, as examples. It is understood that the general descriptions and principles also apply to tungsten-containing precursors and films.

20 Deposition of molybdenum-containing and tungsten-containing films with desirable properties on semiconductor substrates presented several problems, which hindered integration of these films in many of the device fabrication process flows. Specifically, the use of halide-containing molybdenum and tungsten CVD and ALD precursors can lead to inadvertent etching of the substrate. Metalorganic and
25 organometallic precursors can eliminate the integration problems in semiconductor processing caused by halide-containing precursors, but because molybdenum and tungsten form very stable carbide phases, the use of carbon-containing precursors often leads to incorporation of large amounts of carbon into the formed films. Carbon-

containing films are not desired for many applications, as presence of carbon may increase the resistivity of the films and lower the work function of the films.

Methods for deposition of substantially carbon-free molybdenum-containing and tungsten-containing films are provided. These methods are useful for depositing
5 molybdenum-containing and tungsten-containing materials such as nitrides, borides, silicides, oxynitrides, and combinations thereof. Some materials deposited by these methods are used as MOSFET (metal-oxide-semiconductor field-effect transistor) gate electrode materials. Since carbon has a negative impact on effective work function in early transition metal films, these methods are advantageous for producing
10 films which have a high work function (e.g., greater than about 5 eV) suitable for pMOS structures. Some materials deposited by these methods are also useful as ultrathin low resistivity liner and/or barrier materials. In some embodiments, these methods are carried out in an integrated multi-chamber apparatus including, for example, a deposition chamber and a plasma treatment chamber, where the
15 substantially carbon-free film is deposited by CVD or ALD in an absence of plasma in a deposition chamber, and is treated with a plasma in a plasma treatment chamber. The plasma treatment can be used to tune the film composition, densify the formed film, and/or to tune the effective work function of the formed material.

The provided methods utilize a halide-free molybdenum-containing or
20 tungsten-containing metalorganic compound as a CVD or ALD precursor, where the metalorganic compound does not include metal-carbon (molybdenum-carbon or tungsten-carbon) bonds and does not include carbonyl (CO) ligands. Further, in some embodiments the precursor does not include beta hydrogen atoms. The deposition is carried out by reacting the precursor with a reactant, preferably in an absence of
25 plasma. In some embodiments the reaction is carried out at a temperature of less than about 450 °C, such as less than about 420 °C in an absence of plasma. The careful selection of the precursor advantageously allows to avoid substantial incorporation of carbon into the formed film, and films with carbon content of less than about 5 atomic %, such as less than about 3 atomic % can be formed.

30 This result is unexpected, because the metalorganic precursors contain carbon, and it can be expected that due to high affinity of molybdenum and tungsten to carbon, carbon incorporation in the films would necessarily occur at high levels.

However, it was discovered that when metals in the precursors do not form direct bonds with carbon and when the precursors do not include carbonyl ligands, incorporation of carbon into the films can be avoided, particularly if plasma is not used during the deposition reactions. Another factor that can significantly reduce carbon incorporation into the films is an absence of beta-hydrogens in the ligands of the metal-containing precursor. It is believed that beta-hydrogen can lead to a low-energy reaction pathway leading to incorporation of carbon into the film even at low temperature deposition conditions. The absence of beta hydrogens may stabilize the ligands against decomposition and allow for the ligands to be removed intact during the subsequent reactant gas exposure.

In some embodiments the metal-containing precursors, used herein include a metal (e.g., molybdenum or tungsten) that forms bonds only to elements selected from the group consisting of N, O, and S. In some embodiments the precursors preferably do not include beta hydrogen atoms. For example, in some embodiments the precursors include carbon bonded to three alkyl groups at beta positions. In some embodiments, the precursor does not include metal-oxygen double bonds ($M=O$).

In some embodiments precursors which can be used for deposition include halide-free molybdenum and tungsten complexes bearing at least one of a monodentate ligand such as an amine, a nitrile, an imide, a nitride, an alkoxide, or a thiolate, or halide-free molybdenum and tungsten complexes bearing multidentate ligands which bond to the metal through N, O, or S atoms. The ligands preferentially do not contain β -hydrogen atoms.

Examples of suitable molybdenum-containing precursors 1-16 are shown in Figure 1, where each L is a carbon-containing ligand that does not form metal-carbon bonds, and where m is an integer between 1-4, and n is an integer between 1-4. Each R and R1 is independently selected from the group consisting of an alkyl, fluoroalkyl, and alkylsilyl. In some embodiments, each R1 is selected such that it does not provide beta hydrogen atoms. Examples of such R1 substituents include t-butyl and trialkylsilyl substituents. It is noted that in some embodiments, R substituents at the O and S atoms, may provide beta hydrogen atoms, as at these positions the beta hydrogens are not readily eliminated and are not expected to lead to carbon contamination of the resulting films. Further, in compounds 7, 8, and 14, beta

hydrogens at the alkyl-substituted carbon atoms adjacent to anionic nitrogen are also stabilized, and these stabilized compounds are also suitable for deposition of provided films.

5 In some embodiments, both R and R1 do not provide beta hydrogen atoms. In some embodiments the precursor does not include beta hydrogen atoms. For example, in some embodiments the precursor is any of the compounds 1, 2, 3, 4, 5, 6, 15, and 16, where each of R, R1 and L does not provide beta hydrogen atoms.

10 More specific examples of molybdenum-containing precursors are shown in Figure 1B, which depicts structures 17-20. It can be seen that molybdenum forms bonds only to N and O atoms, and that the precursors do not include any hydrogen atoms at beta positions. The precursors can be synthesized by reacting a molybdenum starting material, such as a halide-containing molybdenum starting material with the deprotonated ligands. Exemplary synthetic routes are described in the US Patent Application Publication No. 2018/0355484.

15 The precursors used for deposition are amenable to vaporization and are stable at target temperatures and pressures. For example, in some embodiments the precursors are used in deposition reactions at temperatures of less than about 450 °C, such as less than about 420 °C. In order to maintain appropriate volatility, in many embodiments discussed herein, the precursors having molecular weights of less than about 450 g/mol, such as less than about 400 g/mol are selected.

25 Substantially carbon-free molybdenum-containing and tungsten-containing materials can be deposited using the precursors described herein by a variety of deposition methods, such as CVD, and ALD. An exemplary method for deposition of a molybdenum-containing or tungsten-containing layer is illustrated by a process flow diagram shown in Figure 2. The process starts in 201 by introducing a halide-free molybdenum-containing or tungsten-containing precursor into a process chamber housing the semiconductor substrate. The precursor does not include metal-carbon bonds, and, preferably does not include beta hydrogen atoms. The precursor can be introduced in a vaporized form in a flow of inert gas such as argon, helium, or nitrogen (N₂). In operation 203 (which can occur before, after, or during introduction of the molybdenum-containing precursor 201) a reactant is introduced into the process

chamber housing the substrate. In some embodiments, introduction of the metal-containing precursor and of the reactant is sequential. The chemistry of the reactant depends on the chemistry of the target molybdenum-containing or tungsten-containing film. For example, for deposition of metal (Mo or W), the second reactant
5 is typically a reducing reactant (e.g., H_2). Deposition of metal nitride can be carried out using a nitrogen-containing reactant (e.g., NH_3 , or N_2H_4). In some embodiments, metal nitrides are deposited using H_2 as a reactant, and the requisite nitrogen can be supplied by the ligand. Deposition of metal boride can be performed using a boron-containing reactant (e.g., B_2H_6). Metal silicides can be formed using a silicon-
10 containing reactant (e.g., SiH_4 or Si_2H_6).

In some embodiments the precursor and the reactant are allowed to mix in the body of the processing chamber. In other embodiments, after the metal-containing precursor has been introduced and has been adsorbed on the surface of the substrate, the processing chamber is purged with an inert gas and/or evacuated to remove the
15 unadsorbed precursor from the process chamber. In some embodiments the layer of the precursor on the substrate is adsorption-limited. In other embodiments a thicker layer of precursor can be formed on the surface of the substrate prior to purging and/or evacuation of the process chamber. It is noted that when the precursor and the reactant are introduced sequentially, the sequence of introduction of the precursor and
20 of the reactant may be reversed. In some embodiments the reactant is introduced first and is allowed to adsorb on the surface of the substrate. Then the process chamber is purged and/or evacuated to remove the second reactant from the volume of the process chamber, and the precursor is then introduced.

Referring to operation 205, the precursor is reacted with the reactant to form a
25 layer of a substantially carbon-free molybdenum-containing material on the substrate, where the reaction occurs on the surface of the substrate and/or in the body of the processing chamber, and is preferably performed in an absence of plasma. For example, in CVD processes the precursor and reactant may be introduced simultaneously into the body of the processing chamber, where reaction occurs
30 continuously either the body of the processing chamber or on the surface. In ALD processes the reaction occurs only on the surface and is limited by the amount of the adsorbed material on the surface (by the amount of precursor and/or by the amount of

adsorbed reactant). The temperature during the reaction process can be, for example, between about 20 – 600 °C. Low temperature deposition at about 450 °C or less such as about 420 °C or less, e.g., between about 200 – 400 °C is conducted in some embodiments and is particularly advantageous for deposition of substantially carbon-free films. The pressure in the process chamber can be in a range of between about 0.1 - 100 Torr, such as between about 1 – 60 Torr in thermal ALD, such as about 10 Torr

After the reaction is completed, the formed molybdenum-containing or tungsten-containing layer can be optionally treated with a second reactant to modify the layer, as shown in operation 207. The treatment may be performed in order to tune the properties of the layer, such as to densify the layer, modify the composition or electrical properties of the layer, reduce the resistivity of the layer, etc. The treatment is, in some embodiments, plasma-assisted. For example, the substrate may be treated with a direct plasma (formed in the compartment housing the substrate), or a remote plasma (formed away from the substrate and introduced into the compartment housing the substrate). The use of remote plasma is preferred in some cases as it reduces the damage to the substrate. In one of preferred embodiments, the substantially carbon-free molybdenum-containing or tungsten-containing layer is deposited in an absence of plasma. The substrate is then transferred to a plasma treatment process chamber without exposing the substrate to an ambient atmosphere, where the substrate is treated with a plasma treatment reactant. The choice of plasma treatment reactant depends on the desired properties of the final layer. The substrate may be treated for example with plasma-activated H₂, NH₃, N₂, BH₃, SiH₄, Ar, He, and mixtures thereof.

An example of a surface-based deposition process for forming a molybdenum-containing or tungsten-containing film on a substrate is illustrated by a process flow diagram shown in Figure 3. In operation 301, a layer of a metal-containing precursor and/or of a reactant is formed on a surface of a substrate. In some embodiments the layer is an adsorption-limited layer. Next in operation 303, the processing chamber is purged and/or evacuated. This step ensures that the precursor and/or reactant are present only on the surface of the substrate and not in the volume of the processing chamber. Next, in 305 the precursor is reacted with the reactant on the surface of the substrate. For example, if only a metal-containing precursor is adsorbed on the surface of the substrate in 301, a reactant may be introduced into the processing chamber and

allowed to react with the precursor on the surface. If both the metal-containing precursor and the reactant layers are formed on the surface of the substrate in 301, in 313 the process conditions can be adjusted (e.g., using a temperature increase) to activate the reaction. Next, in 307 the processing chamber is purged and/or evacuated, and in 309 operations 301-307 are repeated to form more metal-containing material. In some embodiments each cycle of operations 301-307 deposits about 0.1-5 Å of metal-containing material on average. In some embodiments, 1-100, such as 2-100 cycles are performed. For example, 1-20, such as 2-20 cycles can be performed. Substantially carbon-free molybdenum-containing and tungsten-containing layers with thicknesses of between about 5 – 500 Å, such as 5 – 50 Å can be formed with high level of control over layer thickness. This method can be used to form conformal layers with excellent step coverage.

In some embodiments the as-deposited substantially carbon-free molybdenum-containing and tungsten-containing films are treated with a second reactant to modify the properties of the film, such as density, resistivity, or effective work function.

Figure 4A provides a process flow diagram for one example of a film modifications. The process starts in 401 by reacting a molybdenum-containing precursor with a reactant to form a substantially carbon-free molybdenum-containing films on a substrate in an absence of plasma. For example, a MoN layer can be formed using several cycles of reacting a halide-free metalorganic molybdenum-containing precursor with NH_3 or H_2 in an absence of plasma on a surface of the substrate. Next, in operation 403, the film is treated with a plasma-activated nitrogen-containing reactant to increase the nitrogen content in the film. For example, the MoN film can be treated with a plasma formed in a process gas containing N_2 to increase the nitrogen content in the MoN layer. In some embodiments nitrogen content is increased by such treatment by at least 5%, such as by at least 10%. Increase of nitrogen content in the MoN layer is associated with an increase in work function. In some embodiments the work function increase due to this treatment is at least 30 meV, such as 50-200 meV. In some embodiments, the MoN material obtained after the treatment has a nitrogen content of at least 25 atomic % and a work function of at least about 5.0 eV, such as at least 5.2 eV.

Another example of a post-treatment is illustrated by the process diagram shown in Figure 4B. In this example, the process starts as in Figure 4A by reacting a molybdenum-containing precursor with a reactant to form a substantially carbon-free molybdenum-containing layer in 411. Next, in 413, the formed layer is treated with a plasma-activated hydrogen-containing reactant to decrease resistivity of the layer. For example, a substantially carbon-free molybdenum nitride layer may be treated with a plasma formed in a process gas that contains H₂, resulting in substantial decrease of the films' resistivity. In some embodiments the resistivity can be decreased by this treatment by at least 20%, such as at least 50%, or even at least 80 %. In some embodiments, the H₂ plasma treatment decreases the resistivity of the film at least two-fold, three-fold, or five-fold. In some embodiments, films with resistivities of less than about 1,000 $\mu\Omega\cdot\text{cm}$, such as less than about 800 $\mu\Omega\cdot\text{cm}$ are obtained after H₂ plasma treatment. In some embodiments, plasma treatment (e.g., plasma treatment using hydrogen-containing reactants, such as H₂) is further used to densify the as-deposited films. For example, density of the film can be increased by at least 20%, such as by at least 40% by H₂ plasma post-treatment.

The provided substantially carbon-free molybdenum-containing and tungsten-containing films can be deposited on a variety of surfaces including on metals (e.g., copper, nickel, cobalt, tungsten, etc.), dielectrics (e.g., silicon oxide based dielectrics, silicon nitride, silicon carbide, metal oxides, metal nitrides, etc.), and on amorphous and crystalline silicon. In some embodiments the films are deposited as liners or diffusion barrier layers.

In one implementation, provided substantially carbon-free metal-containing films are used as MOSFET gate electrode materials. In one example, the provided films are integrated into a pMOS device structure. A schematic cross-sectional view of a pMOS device is shown in Figure 5. The device (e.g., a transistor) includes a semiconductor layer 501, a source region 501, a drain region 503, and a gate dielectric layer 505 formed over the semiconductor layer 501, and defining a channel region 515 in the semiconductor layer 501 between the source region 501 and a drain region 503. The semiconductor layer 501 includes a semiconductor material, such as silicon (Si), germanium (Ge), or silicon germanium (SiGe). The gate dielectric layer 505 includes, in one embodiment, a high-k dielectric having a dielectric constant of

greater than about 3.9. For example, the gate dielectric layer 505 may include high-k materials, such as HfO, HfSiO, HfSiON, and the like. The gate dielectric layer is typically very thin, e.g., between about 10 – 15 Å thick. Layers 509, 511 and 513 are disposed over the gate dielectric layer 505, and collectively form the gate electrode.

5 Layer 509 is an optional capping layer formed directly over and in contact with the gate dielectric layer 505. The capping layer 509 includes, in some embodiments TiN, TaN and/or WN, and has a thickness of between about 10 – 20 Å. The layer 511 over the capping layer 509 is referred to a work function metal-containing layer. The layer 511 includes a substantially carbon-free molybdenum-containing or tungsten-

10 containing material provided herein, where the material has a high work function, such as a work function of greater than about 4.9 eV, greater than about 5.0 eV, or greater than about 5.1 eV. In some embodiments, the layer 511 is a substantially carbon-free MoN layer having an effective work function of greater than about 5.0. The substantially carbon-free layer is deposited by ALD or CVD methods described

15 herein, and in some embodiments, is additionally treated with a plasma treatment reactant, to increase its work function. For example, in some embodiments, the as-deposited substantially carbon-free molybdenum-containing or tungsten-containing material is treated with a plasma-activated nitrogen-containing reactant (e.g., N₂) to increase nitrogen content, and work function of the formed layer. The layer 511, in

20 some embodiments, has a thickness of between about 5 – 50 Å, or 5 – 15 Å. In one implementation the work function metal-containing layer 511 has a thickness of about 30 Å. In some embodiments the substantially carbon-free metal-containing layer 511 is deposited directly onto the capping layer 509. When capping layer 509 is absent, the layer 511 may be deposited directly onto the gate dielectric layer 507. Finally, the

25 device optionally may include one or more conductive layers 513 formed over the substantially carbon-free metal-containing layer 511. In some embodiments the conductive layer 513 includes one or more of TiAl, TiAlC, TiAlON, and/or a conductive metal fill, such as Mo, Co, or W. The device shown in Figure 5 is a schematic view of a partially fabricated device that does not depict contacts formed to

30 source and drain regions, which can be formed after formation of the electrode layers.

The provided substantially carbon-free molybdenum-containing and tungsten-containing layers may be used in a planar pMOS device, a FinFET pMOS device or in

a gate all-around (GAA) pMOS device. Films with work functions of greater than 5.0 eV, such as between about 5.0 – 5.5 eV, can be obtained.

In another application, the substantially carbon-free films are deposited as diffusion barrier layers on a substrate containing recessed features, such as vias and trenches. Schematic cross-sectional views of an exemplary substrate during fabrication are shown in Figures 6A-6B. Referring to Figure 6A, a substrate containing a dielectric layer 601 is provided, where the dielectric may be a silicon oxide based inter layer dielectric, e.g., a low-k dielectric, having a recessed feature 603 formed therein. Referring to Figure 6B, a substantially carbon-free molybdenum-containing or tungsten-containing film 605 is deposited conformally over the dielectric 601, where the film lines the recessed features. Conformal films are preferably deposited by ALD using the precursors as described herein. In some embodiments the film 605 is deposited directly onto the dielectric. In other embodiments, one or more additional layers, such as adhesion layers may be formed on the dielectric before film 605 is deposited. Next, referring to Figure 6B, the recessed feature 603 is filled with metal, such as with copper or cobalt. Copper or cobalt may be deposited, for example, by electrodeposition onto a thin conformal metal seed layer (not shown). The formed structure includes a thin layer of substantially carbon-free molybdenum-containing or tungsten-containing layer positioned between a dielectric layer and a metal-filled via or a trench. In some embodiments, the film 605 has a thickness of between about 5-50 Å, such as between about 10-30 Å. In some embodiments the film 605 is a diffusion barrier layer, which prevents diffusion of copper into the dielectric. Examples of suitable diffusion barrier materials include MoN, and WN. In some embodiments the film 605 is an adhesion layer that may promote adhesion of a conventional diffusion barrier layer (e.g., TaN, TiN) to a conductive seed layer. Examples of suitable adhesion layer materials include Mo, and MoN with a relatively low nitrogen content. In many embodiments it is preferable that the film 605 is a low-resistivity film, such as a film with a resistivity of less than about 1000 $\mu\Omega\cdot\text{cm}$, such as less than about 500 $\mu\Omega\cdot\text{cm}$. In some embodiments, these films are formed using a plasma post-treatment of as-deposited substantially carbon-free films, where the post-treatment reduces the resistivity of the as-deposited film. For example, in some embodiments deposited films (e.g., MoN or

WN films) are post treated with a plasma formed in a hydrogen-containing gas (e.g., H₂), as described with reference to Figure 4B.

It is noted that while the description provided herein uses molybdenum deposition as an example, tungsten-containing layers can be deposited using similar precursors and conditions. For example, tungsten-containing precursors having the same structures as shown in Figures 1A and 1B (with molybdenum substituted for tungsten) can be used.

Experimental Examples

Example 1. Substantially carbon-free MoN films were deposited on SiO₂ substrates using bis(tert-butylimido)bis(tert-butoxy)molybdenum (compound 19) shown in Figure 1B, as a molybdenum-containing precursor. The substrates were exposed to the precursor 19 in an ALD process chamber; then the process chamber was purged to remove the nonsurface-bound precursor, and the substrates were then contacted with a reactant (NH₃, H₂ or a combination of NH₃ and H₂, either in a mixture or sequentially) to react the precursor on the surface of the substrate. The process chamber was purged, and the precursor and reactant dosing were repeated. Between 1 and 500 ALD cycles was used. The depositions were performed in an absence of plasma at temperatures of between 300-400 °C.

Composition analysis of deposited MoN films by both x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) showed carbon contents of between 0.2-2 atomic %. Film resistivities were 500-4,000 μΩ·cm for film thicknesses between 2-10 nm.

A 2 nm thick film was subjected to a H₂ plasma treatment for 60 seconds. The film was treated at 400 °C with a remotely generated plasma (13.56 MHz, 2kW) in a process gas comprising H₂. The resulting 1 nm film, as measured by TEM, had a resistivity of about 600 μΩ·cm illustrating a 6-fold reduction in resistivity compared to the initial 3600 μΩ·cm resistivity for the as-deposited film.

Example 2 (comparative). Substantial carbon incorporation was demonstrated to occur when molybdenum precursor is treated with a reactant in a plasma. MoC films were deposited on SiO₂ substrates using bis(tert-butylimido)bis(tert-

5 butoxy)molybdenum (compound 19) shown in Figure 1B as a molybdenum-containing precursor. The substrate was exposed to the precursor 19 in an ALD process chamber; then the process chamber was purged to remove the non-surface bound precursor, and the substrate was then contacted with a plasma formed in H₂ to react the precursor on the surface of the substrate. The process chamber was purged, and the precursor and reactant dosing were repeated. 200 ALD cycles was used. The deposition was performed at a temperature of 250 °C. Composition analysis of a 15 nm film by X-ray photoelectron spectroscopy showed 58 atomic % Mo and 41 atomic % C. It is believed that the energetic plasma reactant induces uncontrolled decomposition of organic ligands, which enables ready formation of highly thermodynamically stable Mo carbide films. Thus, it is difficult to achieve substantially carbon-free metallic Mo-containing films using a plasma reactant.

15 Example 3. A plasma treatment with a mixture of N₂ and argon was performed on a 3 nm substantially carbon-free MoN film at 400 °C for 150 seconds. The plasma was generated remotely at a power of 3 kW. MOS capacitors were fabricated and the effective work function was obtained by extrapolating the plot of flat-band voltage versus effective oxide thickness to zero. The plasma-treated film showed an effective work function increase of approximately 0.08 eV versus the untreated film. Separate experiments to determine the composition change due to the plasma treatment showed approximately 10% higher nitrogen content after plasma treatment.

APPARATUS

25 The deposition methods described herein can be carried out in a variety of apparatuses. A suitable apparatus includes a processing chamber having one or more inlets for introduction of reactants, a substrate holder in the process chamber configured to hold the substrate in place during deposition, and, optionally, a plasma generating mechanism configured for generating a plasma in a process gas. The apparatus may include a controller having program instructions for causing any of the method steps described herein. The deposition methods described herein may be carried out in corresponding ALD and CVD apparatuses

available from Lam Research Corp. of Fremont, CA, such as Altus[®], Vector[®], and Striker[®] tools.

For example, in some embodiments the apparatus includes a controller having program instructions that include instructions for: causing an introduction of a molybdenum or tungsten precursor to the processing chamber, wherein the precursor
5 is any of the precursors described herein; and causing a reaction between the precursor and a reactant to form a layer of substantially carbon-free molybdenum-containing or tungsten-containing material on a substrate. The controller may include program instructions for causing any of the methods described herein.

10 An example of a deposition apparatus suitable for depositing molybdenum-containing films using provided methods is shown in Figure 7. Figure 7 schematically shows an embodiment of a process station 700 that may be used to deposit material using atomic layer deposition (ALD) and/or chemical vapor deposition (CVD), either of which may be optionally plasma enhanced. It is noted that in many embodiments
15 plasma-enhancement of deposition reaction is avoided to prevent incorporation of carbon into the films. For simplicity, the process station 700 is depicted as a standalone process station having a process chamber body 702 for maintaining a low-pressure environment. However, it will be appreciated that a plurality of process stations 700 may be included in a common process tool environment. Further, it will
20 be appreciated that, in some embodiments, one or more hardware parameters of process station 700, including those discussed in detail below, may be adjusted programmatically by one or more computer controllers.

Process station 700 fluidly communicates with reactant delivery system 701 for delivering process gases to a distribution showerhead 706. Reactant delivery
25 system 701 includes a mixing vessel 704 for blending and/or conditioning process gases for delivery to showerhead 706. One or more mixing vessel inlet valves 720 may control introduction of process gases to mixing vessel 704. Similarly, a showerhead inlet valve 705 may control introduction of process gasses to the showerhead 706.

30 Some metal-containing precursors may be stored in solid or liquid form prior to vaporization and subsequent delivery to the process station. For example, the

embodiment of Figure 7 includes a vaporization point 703 for vaporizing solid reactant to be supplied to mixing vessel 704. In some embodiments, vaporization point 703 may be a heated vaporizer. In some embodiments a flow of an inert gas is passed over the heated solid molybdenum or tungsten precursor, or bubbled through the heated liquid molybdenum or tungsten precursor, under subatmospheric pressure, and carries the precursor vapor to the process chamber. The precursor vapor produced from such vaporizers may condense in downstream delivery piping. Exposure of incompatible gases to the condensed reactant may create small particles. These small particles may clog piping, impede valve operation, contaminate substrates, etc. Some approaches to addressing these issues involve sweeping and/or evacuating the delivery piping to remove residual reactant. However, sweeping the delivery piping may increase process station cycle time, degrading process station throughput. Thus, in some embodiments, delivery piping downstream of vaporization point 703 may be heat traced. In some examples, mixing vessel 704 may also be heat traced. In one non-limiting example, piping downstream of vaporization point 703 has an increasing temperature profile extending from approximately 100°C to approximately 200°C at mixing vessel 704.

Showerhead 706 distributes process gases toward substrate 712. In the embodiment shown in Figure 7, substrate 712 is located beneath showerhead 706, and is shown resting on a pedestal 708. It will be appreciated that showerhead 706 may have any suitable shape, and may have any suitable number and arrangement of ports for distributing processes gases to substrate 712. While not explicitly shown, in some embodiments the showerhead 706 is a dual plenum showerhead that includes at least two types of conduits, where the first type of conduit is dedicated to delivery of molybdenum-containing or tungsten-containing precursor vapor, and the second type of conduit is dedicated to delivery of the reactant (e.g., H₂, NH₃, etc.). In these embodiments the molybdenum-containing precursor and the reactant are not allowed to mix in the conduits prior to entry to the process chamber, and do not share the conduits if delivered to the chamber consecutively.

In some embodiments, a microvolume 707 is located beneath showerhead 706. Performing an ALD and/or CVD process in a microvolume rather than in the entire volume of a process station may reduce reactant exposure and sweep times,

may reduce times for altering process conditions (e.g., pressure, temperature, etc.), may limit an exposure of process station robotics to process gases, etc. Example microvolume sizes include, but are not limited to, volumes between 0.1 liter and 2 liters. This microvolume also impacts productivity throughput. While deposition rate
5 per cycle drops, the cycle time also simultaneously reduces. In certain cases, the effect of the latter is dramatic enough to improve overall throughput of the module for a given target thickness of film.

In some embodiments, pedestal 708 may be raised or lowered to expose substrate 712 to microvolume 707 and/or to vary a volume of microvolume 707. For
10 example, in a substrate transfer phase, pedestal 708 may be lowered to allow substrate 712 to be loaded onto pedestal 708. During a deposition process phase, pedestal 708 may be raised to position substrate 712 within microvolume 707. In some embodiments, microvolume 707 may completely enclose substrate 712 as well as a portion of pedestal 708 to create a region of high flow impedance during a deposition
15 process.

Optionally, pedestal 708 may be lowered and/or raised during portions the deposition process to modulate process pressure, reactant concentration, etc., within microvolume 707. In one scenario where process chamber body 702 remains at a base pressure during the deposition process, lowering pedestal 708 may allow
20 microvolume 707 to be evacuated. Example ratios of microvolume to process chamber volume include, but are not limited to, volume ratios between 1:700 and 1:10. It will be appreciated that, in some embodiments, pedestal height may be adjusted programmatically by a suitable computer controller.

While the example microvolume variations described herein refer to a
25 height-adjustable pedestal, it will be appreciated that, in some embodiments, a position of showerhead 706 may be adjusted relative to pedestal 708 to vary a volume of microvolume 707. Further, it will be appreciated that a vertical position of pedestal 708 and/or showerhead 706 may be varied by any suitable mechanism within the scope of the present disclosure. In some embodiments, pedestal 708 may include a
30 rotational axis for rotating an orientation of substrate 712. It will be appreciated that, in some embodiments, one or more of these example adjustments may be performed programmatically by one or more suitable computer controllers.

Returning to the embodiment shown in Figure 7, showerhead 706 and pedestal 708 electrically communicate with RF power supply 714 and matching network 716 for powering a plasma. In other embodiments apparatuses without a plasma generator are used for depositing molybdenum-containing and tungsten-containing films using provided methods. In some embodiments, the plasma energy may be controlled by controlling one or more of a process station pressure, a gas concentration, a radio frequency (RF) source power, an RF source frequency, and a plasma power pulse timing. For example, RF power supply 714 and matching network 716 may be operated at any suitable power to form a plasma having a desired composition of radical species. Likewise, RF power supply 714 may provide RF power of any suitable frequency. In some embodiments, RF power supply 714 may be configured to control high- and low-frequency RF power sources independently of one another. Example low-frequency RF frequencies may include, but are not limited to, frequencies between 50 kHz and 700 kHz. Example high-frequency RF frequencies may include, but are not limited to, frequencies between 1.8 MHz and 2.45 GHz. It will be appreciated that any suitable parameters may be modulated discretely or continuously to provide plasma energy for the surface reactions. In one non-limiting example, the plasma power may be intermittently pulsed to reduce ion bombardment with the substrate surface relative to continuously powered plasmas. In some embodiments the plasma is used for post-treatment of deposited substantially carbon-free films.

In some embodiments, the plasma may be monitored in-situ by one or more plasma monitors. In one scenario, plasma power may be monitored by one or more voltage, current sensors (e.g., VI probes). In another scenario, plasma density and/or process gas concentration may be measured by one or more optical emission spectroscopy sensors (OES). In some embodiments, one or more plasma parameters may be programmatically adjusted based on measurements from such in-situ plasma monitors. For example, an OES sensor may be used in a feedback loop for providing programmatic control of plasma power. It will be appreciated that, in some embodiments, other monitors may be used to monitor the plasma and other process characteristics. Such monitors may include, but are not limited to, infrared (IR) monitors, acoustic monitors, and pressure transducers.

In some embodiments, the plasma may be controlled via input/output control (IOC) sequencing instructions. In one example, the instructions for setting plasma conditions for a plasma process phase may be included in a corresponding plasma activation recipe phase of a deposition process recipe. In some cases, process recipe phases may be sequentially arranged, so that all instructions for a deposition process phase are executed concurrently with that process phase. In some embodiments, instructions for setting one or more plasma parameters may be included in a recipe phase preceding a plasma process phase. For example, a first recipe phase may include instructions for setting a flow rate of an inert and/or a reactant gas, instructions for setting a plasma generator to a power set point, and time delay instructions for the first recipe phase. A second, subsequent recipe phase may include instructions for enabling the plasma generator and time delay instructions for the second recipe phase. A third recipe phase may include instructions for disabling the plasma generator and time delay instructions for the third recipe phase. It will be appreciated that these recipe phases may be further subdivided and/or iterated in any suitable way within the scope of the present disclosure.

In some embodiments, pedestal 708 may be temperature controlled via heater 710. Further, in some embodiments, pressure control for deposition process station 700 may be provided by butterfly valve 718. As shown in the embodiment of Figure 7, butterfly valve 718 throttles a vacuum provided by a downstream vacuum pump (not shown). However, in some embodiments, pressure control of process station 700 may also be adjusted by varying a flow rate of one or more gases introduced to process station 700.

Figure 8 shows a schematic view of an embodiment of a multi-station processing tool 800 with an inbound load lock 802 and an outbound load lock 804, either or both of which may comprise a remote plasma source. Such tool may be used for processing the substrates using the methods provided herein. A robot 806, at atmospheric pressure, is configured to move wafers from a cassette loaded through a pod 808 into inbound load lock 802 via an atmospheric port 810. A wafer is placed by the robot 806 on a pedestal 812 in the inbound load lock 802, the atmospheric port 810 is closed, and the load lock is pumped down. Where the inbound load lock 802 comprises a remote plasma source, the wafer may be exposed to a remote plasma

treatment in the load lock prior to being introduced into a processing chamber 814. Further, the wafer also may be heated in the inbound load lock 802 as well, for example, to remove moisture and adsorbed gases. Next, a chamber transport port 816 to processing chamber 814 is opened, and another robot (not shown) places the wafer
5 into the reactor on a pedestal of a first station shown in the reactor for processing. While the embodiment depicted in Figure 8 includes load locks, it will be appreciated that, in some embodiments, direct entry of a wafer into a process station may be provided.

The depicted processing chamber 814 comprises four process stations,
10 numbered from 1 to 4 in the embodiment shown in Figure 8. Each station has a heated pedestal (shown at 818 for station 1), and gas line inlets. It will be appreciated that in some embodiments, each process station may have different or multiple purposes. While the depicted processing chamber 814 comprises four stations, it will be understood that a processing chamber according to the present disclosure may have
15 any suitable number of stations. For example, in some embodiments, a processing chamber may have five or more stations, while in other embodiments a processing chamber may have three or fewer stations.

Figure 8 also depicts an embodiment of a wafer handling system 890 for transferring wafers within processing chamber 814. In some embodiments, wafer
20 handling system 890 may transfer wafers between various process stations and/or between a process station and a load lock. It will be appreciated that any suitable wafer handling system may be employed. Non-limiting examples include wafer carousels and wafer handling robots. Figure 8 also depicts an embodiment of a system controller 850 employed to control process conditions and hardware states of process
25 tool 800. System controller 850 may include one or more memory devices 856, one or more mass storage devices 854, and one or more processors 852. Processor 852 may include a CPU or computer, analog and/or digital input/output connections, stepper motor controller boards, etc.

In some embodiments, system controller 850 controls all of the activities of
30 process tool 800. System controller 850 executes system control software 858 stored in mass storage device 854, loaded into memory device 856, and executed on processor 852. System control software 858 may include instructions for controlling

the timing, mixture of gases, chamber and/or station pressure, chamber and/or station temperature, purge conditions and timing, wafer temperature, RF power levels, RF frequencies, substrate, pedestal, chuck and/or susceptor position, and other parameters of a particular process performed by process tool 800. System control software 858
5 may be configured in any suitable way. For example, various process tool component subroutines or control objects may be written to control operation of the process tool components necessary to carry out various process tool processes in accordance with the disclosed methods. System control software 858 may be coded in any suitable computer readable programming language.

10 In some embodiments, system control software 858 may include input/output control (IOC) sequencing instructions for controlling the various parameters described above. For example, each phase of an ALD process may include one or more instructions for execution by system controller 850. The instructions for setting process conditions for an ALD process phase may be included in a
15 corresponding ALD recipe phase. In some embodiments, the ALD recipe phases may be sequentially arranged, so that all instructions for a ALD process phase are executed concurrently with that process phase.

Other computer software and/or programs stored on mass storage device 854 and/or memory device 856 associated with system controller 850 may be employed in
20 some embodiments. Examples of programs or sections of programs for this purpose include a substrate positioning program, a process gas control program, a pressure control program, a heater control program, and a plasma control program.

A substrate positioning program may include program code for process tool components that are used to load the substrate onto pedestal 818 and to control the
25 spacing between the substrate and other parts of process tool 800.

A process gas control program may include code for controlling gas composition and flow rates and optionally for flowing gas into one or more process stations prior to deposition in order to stabilize the pressure in the process station. The process gas control program may include code for controlling gas composition and
30 flow rates within any of the disclosed ranges. A pressure control program may include code for controlling the pressure in the process station by regulating, for

example, a throttle valve in the exhaust system of the process station, a gas flow into the process station, etc. The pressure control program may include code for maintaining the pressure in the process station within any of the disclosed pressure ranges.

5 A heater control program may include code for controlling the current to a heating unit that is used to heat the substrate. Alternatively, the heater control program may control delivery of a heat transfer gas (such as helium) to the substrate. The heater control program may include instructions to maintain the temperature of the substrate within any of the disclosed ranges.

10 A plasma control program may include code for setting RF power levels and frequencies applied to the process electrodes in one or more process stations, for example using any of the RF power levels disclosed herein. The plasma control program may also include code for controlling the duration of each plasma exposure.

15 In some embodiments, there may be a user interface associated with system controller 850. 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.

20 In some embodiments, parameters adjusted by system controller 850 may relate to process conditions. Non-limiting examples include process gas composition and flow rates, temperature, pressure, plasma conditions (such as RF power levels, frequency, and exposure time), etc. These parameters may be provided to the user in the form of a recipe, which may be entered utilizing the user interface.

25 Signals for monitoring the process may be provided by analog and/or digital input connections of system controller 850 from various process tool sensors. The signals for controlling the process may be output on the analog and digital output connections of process tool 800. Non-limiting examples of process tool sensors that may be monitored include mass flow controllers, pressure sensors (such as manometers), thermocouples, etc. Appropriately programmed feedback and control algorithms may be used with data from these sensors to maintain process conditions.

30 Any suitable chamber may be used to implement the disclosed

embodiments. Example deposition apparatuses include, but are not limited to, apparatus from the Altus[®] product family, available from Lam Research Corp., of Fremont, California, or any of a variety of other commercially available processing systems. Two or more of the stations may perform the same functions. Similarly,
5 two or more stations may perform different functions. Each station can be designed/configured to perform a particular function/method as desired.

In some embodiments, the apparatus includes a process chamber for deposition of substantially carbon-free films, and a different process chamber configured for treating these films with a remote plasma to densify the films, to
10 decrease the resistivity of the films or to increase their work function. In some embodiments the apparatus is programmed or configured to transfer the substrate from a deposition process chamber to a plasma treatment process chamber without exposing the substrate to an ambient atmosphere, moisture or oxygen.

Figure 9 is a block diagram of a processing system suitable for conducting
15 thin film deposition processes in accordance with certain embodiments. The system 900 includes a transfer module 903. The transfer module 903 provides a clean, pressurized environment to minimize risk of contamination of substrates being processed as they are moved between various reactor modules. Mounted on the transfer module 903 are two multi-station reactors 909 and 910, each capable of
20 performing atomic layer deposition (ALD) and/or chemical vapor deposition (CVD) according to certain embodiments. Reactors 909 and 910 may include multiple stations 911, 913, 915, and 917 that may sequentially or non-sequentially perform operations in accordance with disclosed embodiments. The stations may include a heated pedestal or substrate support, one or more gas inlets or showerhead or
25 dispersion plate.

Also mounted on the transfer module 903 may be one or more single or multi-station modules 907 capable of performing plasma or chemical (non-plasma) pre-cleans, or any other processes described in relation to the disclosed methods. The module 907 may in some cases be used for various treatments to, for example, prepare
30 a substrate for a deposition process. The module 907 may also be designed/configured to perform various other processes such as etching or polishing. The system 900 also includes one or more wafer source modules 901, where wafers

are stored before and after processing. An atmospheric robot (not shown) in the atmospheric transfer chamber 919 may first remove wafers from the source modules 901 to loadlocks 921. A wafer transfer device (generally a robot arm unit) in the transfer module 903 moves the wafers from loadlocks 921 to and among the modules
5 mounted on the transfer module 903.

In various embodiments, a system controller 929 is employed to control process conditions during deposition. The controller 929 will typically include one or more memory devices and one or more processors. A processor may include a CPU or computer, analog and/or digital input/output connections, stepper motor controller
10 boards, etc.

The controller 929 may control all of the activities of the deposition apparatus. The system controller 929 executes system control software, including sets of instructions for controlling the timing, mixture of gases, chamber pressure, chamber temperature, wafer temperature, radio frequency (RF) power levels, wafer
15 chuck or pedestal position, and other parameters of a particular process. Other computer programs stored on memory devices associated with the controller 929 may be employed in some embodiments.

Typically there will be a user interface associated with the controller 929. 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,
20 keyboards, touch screens, microphones, etc.

System control logic may be configured in any suitable way. In general, the logic can be designed or configured in hardware and/or software. The instructions for controlling the drive circuitry may be hard coded or provided as software. The
25 instructions may be provided by "programming." Such programming is understood to include logic of any form, including hard coded logic in digital signal processors, application-specific integrated circuits, and other devices which have specific algorithms implemented as hardware. Programming is also understood to include software or firmware instructions that may be executed on a general purpose
30 processor. System control software may be coded in any suitable computer readable programming language.

The computer program code for controlling the precursor flows, and other processes in a process sequence 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. Also as indicated, the program code may be hard coded.

The controller parameters relate to process conditions, such as, for example, process gas composition and flow rates, temperature, pressure, cooling gas pressure, substrate temperature, and chamber wall temperature. These parameters are provided to the user in the form of a recipe, and may be entered utilizing the user interface. Signals for monitoring the process may be provided by analog and/or digital input connections of the system controller 929. The signals for controlling the process are output on the analog and digital output connections of the deposition apparatus 900.

The system software may be designed or configured in many different ways. For example, various chamber component subroutines or control objects may be written to control operation of the chamber components necessary to carry out the deposition processes (and other processes, in some cases) in accordance with the disclosed embodiments. Examples of programs or sections of programs for this purpose include substrate positioning code, process gas control code, pressure control code, and heater control code.

In some implementations, a controller 929 is part of a system, which may be part of the above-described examples. Such systems can include semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be referred to as the "controller," which may control various components or subparts of the system or systems. The controller 929, depending on the processing requirements and/or the type of system, may be programmed to control any of the processes disclosed herein, including the delivery of processing gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings in

some systems, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool and other transfer tools and/or load locks connected to or interfaced with a specific system.

5 Broadly speaking, the controller may be defined as electronics having various integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips
10 defined as application specific integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the controller in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to
15 a system. The operational parameters may, in some embodiments, be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

 The controller, in some implementations, may be a part of or coupled to a
20 computer that is integrated with, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the controller may be in the “cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past
25 fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer
30 may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system from the remote computer. In some examples, the controller receives instructions in the form of data, which specify

parameters for each of the processing steps to be performed during one or more operations. It should be understood that the parameters may be specific to the type of process to be performed and the type of tool that the controller is configured to interface with or control. Thus as described above, the controller may be distributed, such as by comprising one or more discrete controllers that are networked together and working towards a common purpose, such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a chemical vapor deposition (CVD) chamber or module, an atomic layer deposition (ALD) chamber or module, an atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

As noted above, depending on the process step or steps to be performed by the tool, the controller might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

FLOW MIXER

In another aspect, a flow mixer for mixing a carrier gas and a metal-containing precursor prior to delivery to the processing chamber is provided. The described flow mixer is adapted to improve uniformity of delivery of the metal-containing precursor to the showerhead, and can be used for any metal-containing

precursors, including, but not limited to molybdenum and tungsten precursors described herein.

Examples of Mo-containing precursors for ALD or CVD of molybdenum or molybdenum-containing materials include MoF_6 , MoCl_5 , molybdenum dichloride dioxide (MoO_2Cl_2), molybdenum tetrachloride oxide (MoOCl_4), and molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$). Other Mo oxyhalides of the formula $\text{Mo}_x\text{O}_y\text{H}_z$ and H is a halogen (fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)) and x, y, and z being any number greater than zero that can form a stable molecule. These include molybdenum tetrafluoride oxide (MoOF_4), molybdenum dibromide dioxide (MoO_2Br_2), and molybdenum oxyiodides MoO_2I and $\text{Mo}_4\text{O}_{11}\text{I}$. Organo-metallic precursors may also be used with examples including Mo precursors having cyclopentadienyl ligands. Further examples include precursors of the formula Mo_2L_n , wherein each L is independently selected from an amidate ligand, an amidinate ligand, and a guanidinate ligand, where n is 2-5. The Mo_2L_n precursor includes a multiple molybdenum-molybdenum bond (such as a double bond or any multiple bond with a bond order of 2-5). Further examples include halide-containing heteroleptic molybdenum compounds (i.e., compounds having different types of ligands). Particular examples of such precursors are compounds that include molybdenum, at least one halide forming a bond with molybdenum, and at least one organic ligand having any of the N, O, and S elements, where an atom of any of these elements forms a bond with molybdenum. Examples of suitable organic ligands that provide nitrogen or oxygen bonding include amidinates, amidates, iminopyrrolidines, diazadienes, beta-imino amides, alpha-imino alkoxides, beta-amino alkoxides, beta-diketiminates, beta-ketoiminates, beta-diketonates, amines, and pyrazolates. Examples of suitable organic ligands that provide sulfur bonding include thioethers, thiolates, dithiolenes, dithiolates, and alpha-imino thiolenes. These ligands may be substituted or unsubstituted. In some embodiments, these ligands include one or more substituents independently selected from the group consisting of H, alkyl, fluoroalkyl, alkylsilyl, alkylamino, and alkoxy substituents. The organic ligands can be neutral or anionic (e.g., monoanionic or dianionic), and molybdenum can be in a variety of oxidation states, such as +1, +2, +3, +4, +5, and +6.

When metal precursor vapor is delivered to the showerhead, it is typically mixed with a flow of a carrier gas, such as N_2 , argon, helium, and the like, to provide

a desired concentration of the precursor. This mixing is typically performed in a flow mixer, which has an outlet that is connected to the showerhead. It is noted that in many embodiments the metal precursor vapor is delivered to the mixing tube with a first flow of a carrier gas, and is then diluted with a second flow of a carrier gas. For clarity, this more concentrated flow of metal-containing precursor in a carrier gas will be referred to as metal precursor flow and the flow of carrier gas that does not include a precursor will be referred to as a carrier gas flow.

One of the problems that can be encountered during mixing of these flows is non-uniform delivery of the metal precursor to the showerhead. For example, peripheral regions near the edge of the showerhead may receive a flow with a lower concentration of metal precursor than more central portions of the showerhead. This, in turn, may lead to non-uniform distribution of the metal precursor in the processing chamber. A flow mixer that is configured for improving uniformity of mixing of the metal precursor with a carrier gas is provided. In some embodiments, the flow mixer delivers the metal precursor such that the concentration of the metal precursor at all showerhead outlets differs by no more than 2% by volume. In the described implementation, the flow mixer includes: (a) an outer fluidic conduit comprising an inlet for admitting the carrier gas into the outer fluidic conduit, a mixing zone for mixing the carrier gas with the metal-containing precursor and an outlet for removing the carrier gas mixed with the metal-containing precursor from the outer fluidic conduit; (b) an inner fluidic conduit positioned at least partially inside the outer conduit, wherein the inner fluidic conduit comprises an inlet for admitting the metal-containing precursor into the inner fluidic conduit, and an outlet configured to release the metal-containing precursor into the outer fluidic conduit, wherein a distance from the inlet of the inner fluidic conduit to the inlet of the outer fluidic conduit is greater than a distance from the outlet of the inner fluidic conduit to the inlet of the outer fluidic conduit, thereby supporting opposing flows of the carrier gas and of the metal-containing precursor in the flow mixer, wherein the distances refer to distances in a z-direction.

The described flow mixer is illustrated in Figure 10, which shows a schematic side view of the flow mixer 1001, and a cross-sectional view of a portion that illustrates the inlet of the inner fluidic conduit. Referring to Figure 10, the outer

fluidic conduit 1003 has a generally cylindrical shape, and has an inlet (not shown) for admitting a carrier gas at the top of the outer fluidic conduit 1003. The inlet of the outer fluidic conduit is connected to a source of a carrier gas. The flow of the carrier gas (without the metal precursor) is shown by downward arrows 1005. The outlet 1007 of the outer fluidic conduit 1003 is located opposite to the inlet at the bottom of the outer fluidic conduit 1003. The outlet is adapted to be connected to a showerhead (not shown) and to deliver the flow 1009 of mixed metal-containing precursor with the carrier gas to the showerhead. An inner fluidic conduit 1011 resides inside the outer fluidic conduit (at least partially) and has a portion that is coaxial with the outer fluidic conduit 1003. The inner fluidic conduit 1011 has an inlet 1013 configured to admit the metal precursor from a source of the metal precursor. The metal precursor is typically flowed into the inner fluidic conduit in a mixture with a carrier gas, but this flow has a higher metal precursor concentration than a target concentration for the showerhead, and needs to be further diluted with a carrier gas in the mixing tube. The metal precursor flow entering the inner fluidic conduit 1011 is shown by arrow 1015. The outlet 1017 of the inner fluidic conduit 1011 is configured to release the metal-containing precursor which flows upwards as shown by arrow 1019, into the outer fluidic conduit 1003, where the metal precursor flow is mixed with the carrier gas flow. Notably, the distance 1018 from the inlet 1013 of the inner fluidic conduit 1011 to the outlet 1017 of the inner fluidic conduit 1013 in z-direction (vertical direction) is smaller than the distance from the inlet 1013 of the inner fluidic conduit 1011 to the inlet (not shown) of the outer fluidic conduit 1003 located at the very top of the outer fluidic conduit 1003. This configuration is capable to support opposing flows of the carrier gas (illustrated by downward arrow 1005) and of the metal-containing precursor (illustrated by an upward arrow 1019), which makes the mixing of flows more efficient.

The outer fluidic conduit 1003 has a mixing zone 1021, where the metal-containing precursor and the carrier gas flows are allowed to mix without restrictions forming the mixed flow, illustrated by the downward arrow 1023. It is important to provide a mixing zone of adequate length, as mixing occurring in this zone affects the uniformity of precursor concentration in the showerhead. In some embodiments the length of the mixing zone L1 in the z-direction is at least about 102 mm, such as at least about 127 mm. For example at a flow of 1,000 sccm and an outer diameter of the

outer tube of about 41 mm, the 102 mm long mixing zone provides adequate mixing.. In some embodiments a ratio of a length L1 of the flow mixing zone in z-direction to an inner diameter of the outer fluidic conduit 1003 is at least about 2, such as at least about 3.

5 In some embodiments, such as in the embodiment shown in Figure 10, the outer fluidic conduit 1003 further has a restriction zone 1025, where the mixed flow 1023 is restricted into a plurality of more narrow channels located inside the outer fluidic conduit 1003. For example, in some embodiments the restriction zone contains six more narrow non-communicating channels, which carry the mixed flow to the
10 outlet 1007. The restriction zone has a length L2 (e.g., between about 1-5 mm) in z direction. The mixed flow in the restricted zone is shown by a downward arrow 1027.

In some embodiments, the flow mixer 1001 is designed, such that the outlet 1017 from the inner fluidic conduit 1013 includes a flow diverter 1029, configured to divert flow of the metal-containing precursor before the metal-containing precursor
15 flow mixes with the carrier gas flow in the outer fluidic conduit 1003, such that the diverted flow of the metal-containing precursor retains a velocity component opposing the velocity direction of the carrier gas flow in the outer fluidic conduit.

The flow diverter may include two parallel flow restrictor plates, configured to restrict the flow of the metal-containing precursor between the plates. For example,
20 the upward flow of the metal-containing precursor may be diverted in a lateral direction making a less than a 90 degree turn, thereby retaining a velocity component that opposes the downward direction of the carrier gas flow. Retaining this opposing velocity component is an important factor for improving efficiency of mixing. In some embodiments the flow diverter 1029 includes a delivery tee with a plurality (e.g.
25 six) evenly spaced radial openings.

In some implementations, a ratio of an inner diameter of the outer fluidic conduit to an inner diameter of the inner fluidic conduit is between about 1.5 -10, such as between about 1.5-5. In a specific example, an inner diameter of the outer fluidic conduit is about 40.5 mm, and an inner diameter of the inner fluidic conduit is
30 about 4.8 mm. In some implementations, the flow mixer has a total length in z-direction of between about 76-510 mm, such as between about 102-508 mm, such as

about 124.5 mm. The flow mixer can be made from a variety of materials that are compatible with the metal-containing precursors, including aluminum, stainless steel, and ceramic.

5 MULTI-PLENUM SHOWERHEAD

In another aspect, a multi-plenum showerhead for delivery of a plurality of reactants to a processing chamber, is provided. The showerhead may be used for delivery of any combination of reactants, including but not limited to molybdenum-containing and tungsten-containing precursors described herein. In some
10 embodiments, the multi-plenum showerhead includes (a) a showerhead faceplate having a first plurality of conduits for delivery of a first reactant and a second plurality of conduits for delivery of a second reactant, wherein the first plurality of conduits is configured to be fluidically isolated from the second plurality of conduits; and (b) a showerhead housing positioned about the perimeter of the showerhead
15 faceplate, wherein the showerhead faceplate is releasably attached to the showerhead faceplate. Because the showerhead is configured to have a removable faceplate, cleaning of the faceplate, which typically contains very small channels, can be performed with high efficiency. For example, the faceplate may be cleaned with the solvent, e.g., by immersion of the faceplate into the solvent and/or purging of channels
20 with a solvent. In some embodiments the faceplate includes openings with a diameter of about 1 mm or less, such as 0.5 mm or less, that can be efficiently cleaned after the faceplate is removed from the base.

In some embodiments, the multi-plenum showerhead is a dual-plenum showerhead, where the first plurality of conduits is configured for delivery of a
25 reactant (e.g., H_2 , NH_3 , SiH_4 , B_2H_6 , a hydrocarbon etc.) and the second plurality of conduits is configured for delivery of a metal-containing precursor (e.g., a molybdenum-containing or tungsten-containing precursor). Figure 11A shows a view of a portion of a dual-plenum showerhead 1101, which includes a faceplate 1103 and a housing 1105 attached to the faceplate 1103, where the housing 1105 is positioned
30 about the perimeter of the faceplate 1103. The top portion of the faceplate 1103 contains a large number of openings of conduits 1107, configured to deliver a metal-containing precursor through the faceplate. The metal-containing precursor is

delivered downward onto the faceplate, and is restricted by the showerhead housing on the sides. The faceplate 1103 also contains a plurality of fluidic conduits 1106, where fluidic conduits 1106 do not fluidically communicate with the metal precursor conduits 1107. The conduits 1106 are configured to receive a reactant (e.g., H₂, NH₃, etc.) from a reactant delivery annulus 1109 located in the housing 1105, and to laterally distribute the reactant through the showerhead faceplate 1103. The reactant conduits 1106 have a plurality of outlets on the bottom of the faceplate 1103 (not shown) configured for delivering the reactant to the processing chamber. These outlets, in some embodiments have diameters of about 1 mm or less or 0.5 mm or less. The outlets of both metal precursor conduits and reactant conduits open into the processing chamber. The conduits are designed such that the metal precursor and the reactant do not come into contact with each other in the body of the showerhead 1101.

While the showerhead faceplate 1103 serves to distribute and deliver the metal precursor and the reactant to the processing chamber without mixing them, the showerhead housing 1105 serves to confine a volume above the showerhead faceplate 1103 for the metal precursor, and to house a delivery annulus 1109 configured for delivery of the reactant to the reactant conduits 1106 of the showerhead faceplate 1103. The flow of the reactant through is shown by arrows 1110. The housing can further include a heater 1111, which may be annularly shaped, and embedded into a depression formed in the housing. The housing also typically includes a ledge 1113 for supporting an O-ring or another seal for sealing the showerhead to the metal precursor delivery line. Figure 11B shows a portion of the showerhead faceplate 1103 and of the showerhead housing 1105 after the faceplate 1103 has been released from the housing 1105 (e.g., for cleaning). This view illustrates removable fasteners 1115 which are fitted into the openings in the housing 1105, and are configured to releasably attach the housing 1105 to the faceplate 1103 using openings about a perimeter of the faceplate 1103.

The showerhead faceplate can be manufactured from any materials that are compatible with metal-containing precursors, such as aluminum, stainless steel and ceramic materials.

FURTHER IMPLEMENTATIONS

The apparatus and processes described herein may be used in conjunction with lithographic patterning tools or processes, for example, for the fabrication or manufacture of semiconductor devices, displays, LEDs, photovoltaic panels, and the like. Typically, though not necessarily, such apparatus and processes will be used or conducted together in a common fabrication facility. Lithographic patterning of a film typically comprises some or all of the following steps, each step enabled with a number of possible tools: (1) application of photoresist on a work piece, i.e., a substrate, using a spin-on or spray-on tool; (2) curing of photoresist using a hot plate or furnace or UV curing tool; (3) exposing the photoresist to visible or UV, or eUV or x-ray light with a tool such as a wafer stepper; (4) developing the resist so as to selectively remove resist and thereby pattern it using a tool such as a wet bench; (5) transferring the resist pattern into an underlying film or work piece by using a dry or plasma-assisted etching tool; and (6) removing the resist using a tool such as an RF or microwave plasma resist stripper.