Provided methods can be used for deposition of a variety of metal layers, such as a molybdenum layer, a cobalt layer, a ruthenium layer, or any combination thereof. In one implementation, the deposited metal layer is a molybdenum layer and the metal precursor is a molybdenum precursor comprising a molybdenum-halogen bond. For example, the molybdenum precursor may include $MoCl_5$, Mo_2Cl_{10}, MoO_2Cl_2, or $MoOCl_4$, or any combination thereof. In some embodiments organometallic molybdenum precursors, such as halogen-free organometallic molybdenum precursors are used. An example of a halogen-free organometallic molybdenum precursor is bis(ethylbenxene)molybdenum.

In some embodiments the deposition inhibitor modifies a surface on a field region and near an opening of the recessed feature to a greater degree than a surface of a bottom of the recessed feature. The modification can include, for example, at least one of physisorption and chemisorption. For example, in some embodiments the deposition inhibitor modifies the surface of the substrate by halogenating the surface of the substrate. The surface of the semiconductor substrate modified by the deposition inhibitor may include a metal, a metal nitride, a metal oxide, a metal carbide, metal silicide, amorphous silicon, polycristalline silicon, hydrogen-terminated silicon, silicon germanium, a silicon-containing dielectric, and any combination thereof. In one implementation the provided substrate comprises exposed metal nitride (e.g., titanium nitride), wherein the exposed metal nitride lines sidewalls of the recessed feature and a bottom of the recessed feature. The deposition inhibitor may modify the surface of the titanium nitride in the field region to a greater degree than at the bottom of the recessed feature.

In some embodiments the metal layer is deposited at a temperature of between about 250 ºC and 600 ºC (e.g. between about 350 ºC and 600 ºC) and a pressure of less than about 300 torr (e.g., less than about 200 torr).

In one implementation, after the semiconductor substrate has been exposed to the deposition inhibitor, the substrate is sequentially exposed to the metal precursor and a reducing agent, the sequential exposure to the metal precursor and the reducing agent is repeated to perform at least 10 inhibitor-free deposition cycles.

In another implementation the method comprses: (i) exposing the semiconductor substrate to the deposition inhibitor; (ii) after (i), exposing the semiconductor substrate to the metal precursor; (iii) after (ii) exposing the semiconductor substrate to a reducing agent to reduce the metal precursor to metal; and (iv) repeating steps (i) – (iii) to perform at least 10 inhibitor-assisted deposition cycles. In some embodiments each inhibitor-assisted deposition cycle includes a purging step after each of the exposure of the semiconductor substrate to the deposition inhibitor, exposure of the semiconductor substrate to the metal precursor, and the exposure of the semiconductor substrate to the reducing agent.

In some embodiments the metal layer is deposited conformally. In other embodiments the metal layer is deposited in a bottom-up deposition mode to fill the recessed feature.

In some embodiments the methods provided herein are integrated with photolithographic processing. For example, the methods may include the steps of: applying photoresist to the semiconductor substrate; exposing the photoresist to light; patterning the photoresist and transferring the pattern to the semiconductor substrate; and selectively removing the photoresist from the semiconductor substrate. For example, such photolithographic patterning may be used to form recessed features on the substrate prior to deposition of the metal layer.

In another aspect, an apparatus for processing a semiconductor substrate is provided, where the apparatus includes a controller having program instructions configured to cause performance of any of the methods provided herein. In some embodiments the apparatus includes: (a) a process chamber, having a substrate holder for holding a semiconductor substrate, and one or more inlets for introduction of reactants to the process chamber; and (b) a controller. The controller may include program instructions for: (i) causing contact of a semiconductor substrate having a recessed feature with a deposition inhibitor, wherein the deposition inhibitor is a halogen-containing compound, and wherein the deposition inhibitor modifies a surface of the semiconductor substrate to make the modified surface more resistant to metal deposition than the surface was before the modification; and (ii) causing contact of the semiconductor substrate with a metal precursor, and causing a reduction of the metal precursor to form a metal layer at least within the recessed feature on the semiconductor substrate, wherein the halogen-containing compound and the metal precursor are different.

In another aspect, a system is provided, wherein the system includes an apparatus provided herein and a stepper.

In another aspect, a non-transitory tangible computer machine-readable medium is provided, that includes program code for causing performance of any of the methods provided herein. For example it may include code configured for: (i) causing contact of a semiconductor substrate having a recessed feature with a deposition inhibitor, wherein the deposition inhibitor is a halogen-containing compound, and wherein the deposition inhibitor modifies a surface of the semiconductor substrate to make the modified surface more resistant to metal deposition than the surface was before the modification; and (ii) causing contact of the semiconductor substrate with a metal precursor, and causing a reduction of the metal precursor to form a metal layer at least within the recessed feature on the semiconductor substrate, wherein the halogen-containing compound and the metal precursor are different.

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.

methylpropene) that form after elimination of hydrogen halides from alkyl halides may also contribute to inhibition of metal nucleation on the surface.

Alkyl halide deposition inhibitors

The alkyl halide deposition inhibitors that can be used in any of the methods provided herein include alkyl fluorides, alkyl chlorides, alkyl bromides, and alkyl iodides, which may include one or more halogen atoms. Primary alkyl halides, secondary alkyl halides, and tertiary alkylhalides can be used. Examples of primary alkyl halides include methyl fluoride, methyl chloride, methyl bromide, methyl iodide, ethyl fluoride, ethyl chloride, ethyl bromide, ethyl iodide, 1-fluoropropane, 1-chloropropane, 1-bromopropane, and 1-iodopropane, 1-fluorobutane, 1-chlorobutane, 1-bromobutane, and 1-iodobutane. Examples of secondary alkyl halides include 2-fluoropropane, 2-chloropropane, 2-bromopropane, 2-iodopropane, 2-fluorobutane, 2-chlorobutane, 2-bromobutane, and 2-iodobutane. In some embodiments tertiary alkyl halides are preferred. Examples of tertiary alkyl halides include t-butyl fluoride (also known as 2-fluoro-2-methylpropane), t-butyl chloride (also known as 2-chloro-2-methylpropane), t-butyl bromide (also known as 2-bromo-2-methylpropane), and t-butyl iodide (also known as 2-iodo-2-methylpropane).

In some embodiments, alkyl halides having formula:

$$Hal - C(R')_2 - CH(R'')_2$$

are used, where Hal is a halogen, each R' is independently selected from hydrogen and an alkyl, and each R'' is independently selected from hydrogen and an alkyl. In some embodiments both R'' groups are hydrogens. Examples of such alkyl halides include t-butyl chloride, 2-chloro-2-methylbutane, 2-chloro-2-methylpentane, and 2-chloro-2-methylhexane. These alkyl halides are particularly suitable in some embodiments, because they are amenable to hydrogen halide elimination and formation of products containing double bonds, and may lead to more efficient surface modification and inhibition of metal nucleation.

Metal Precursors

Provided methods can use a variety of metal precursors for deposition of metals in accordance with embodiments provided herein. The precursors are selected such that they can be delivered to a process chamber in a gaseous (e.g., vapor) form, either alone or with an inert carrier gas. For example, an inert gas flowing over a solid or liquid precursor can deliver the precursor to the process chamber. Examples of metals that can be deposited using gas phase deposition, e.g., ALD and CVD deposition include molybdenum, tungsten, cobalt and ruthenium.

Molybdenum precursors

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

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

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

In some embodiments, the at least one organic precursor is a sulfur containing ligand that is capable of forming a molybdenum-sulfur bond. In some embodiments the at least one organic ligand in the precursor is a thioether. The term "thioether" is used herein broadly to include to include both unidentate and multidentate (e.g. bidentate ot tridentate) thioethers, as well as ligands that contain both thioether and thiolate (or other) moieties. An example of a unidentate thioether is dialkylsulfide R_2S, where each R is an alkyl, such as dimethylsulfide, diethylsulfide, diisobutyl sulfide, and the like. An example of a multidentate thioether ligand that also includes thiolate moieties is $(SCH_2CH_2SCH_2CH_2S)^{2-}$ An example of a monodentate thioether is thioether 18, shown in Figure 5, where each R is independently selected from the group consisting of alkyl, and fluoroalkyl. In some embodiments each R is independently selected from the group consisting of methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, and *t*-butyl. In some embodiments, the at least one organic ligand is a thiolate, such as a monoanionic thiolate **19**, wherein R is an alkyl or fluoroalkyl. For example, R can be methyl, ethyl, *n*-propyl, isopropyl,

CLAIMS

1. A method of forming a metal layer, the method comprising:

(a) providing a semiconductor substrate having a recessed feature;

(b) exposing the semiconductor substrate to a deposition inhibitor, wherein the deposition inhibitor is a halogen-containing compound, and wherein the deposition inhibitor modifies a surface of the semiconductor substrate to make the surface more resistant to metal deposition than the surface was before modification; and

(c) exposing the semiconductor substrate to a metal precursor and a reducing agent to form a metal layer at least within the recessed feature on the semiconductor substrate, wherein the metal precursor and the halogen-containing compound are different.

2. The method of claim 1, wherein the semiconductor substrate is exposed to the deposition inhibitor prior to exposure to the metal precursor.

3. The method of claim 1, wherein the halogen-containing compound is an alkyl halide.

4. The method of claim 1, wherein the halogen-containing compound is an iodine-containing compound.

5. The method of claim 1, wherein the metal layer comprises a molybdenum layer, or a cobalt layer, or a ruthenium layer, or any combination thereof.

6. The method of claim 1, wherein the halogen-containing compound is selected from the group consisting of I_2 (diiodine), HI (hydrogen iodide), CH_3I (methyl iodide), C_2H_5I (ethyl iodide), 1-iodopropane, 2-iodopropane, 1-iodobutane, sec-butyl iodide, t-butyl iodide, iodocyclopentane, iodocyclohexane, diiodomethane, 1,2-diiodoethane, 1,1-diiodopropane, 1,2-diiodopropane, 1,3-diiodopropane, 2,2-diiodopropane, 1,1-diiodobutane, 1,2-diiodobutane, 1,3-diiodobutane, 2,2-diiodobutane, 2,3-diiodobutane, 1,2-diiodo-2-methylpropane, 2,3-diiodo-2,3-dimethylbutane, 1,1,2,2-tetraiodoethane, 2,2,3,3-tetraiodobutane, 1,1,1,2,2,2-hexaiodoethane, 1,2-diiodocyclopentane, 1,2-diiodocyclohexane, iodobenzene, diiodobenzene, 2-iodopyridine, 3-iodopyridine, 4-iodopyridine, 3-iodo-1-nitrobenzene, 3-iodo-1-trifluoromethylbenzene, 4-iodoaniline, 4-iodo-1-dimethylaminobenzene, 4-iodophenol, (trimethylsilyl)methyl iodide, (trimethylsilyl)methyl diiodide, (trimethylsilyl)methyl triiodide, bis(trimethylsilyl)methyl iodide,

bis(trimethylsilyl)methyl diiodide, tris(trimethylsilyl)methyl iodide, 1-(trimethylsilyl)-1-iodoethane, 1-(trimethylsilyl)-1,2-diiodoethane, 1,1-bis(trimethylsilyl)-1,2-diiodoethane, 1,2-bis(trimethylsilyl)-1,2-diiodoethane, CHI_3 (triiodomethane), CI_4 (carbon tetraiodide), 1-iodoethene, 1-iodopropene, 2-iodopropene, 1-iodo-1-butene, 1-iodo-2-butene, 2-iodo-1-butene, 2-iodo-2-butene, iodoacetylene, 3,3-dimethyl-1-iodo-but-1-yne, 1,1-diiodoethene, 1,2-diiodoethene, 1,2-diiodopropene, 1,2-diiodo-2-propene, 1,2-diiodobutene, 1,2-diiodo-2-butene, 1,2-diiodo-3-butene, 3,4-diiodocyclohexene, 4,5-diiodocyclohexadiene, 1,2-diiodoacetylene, 1,1,2,2-tetraiodoethene, SiI_4 (silicon tetraiodide), $SiHI_3$ (triiodosilane), SiH_2I_2 (dioiodosilane), SiH_3I (iodosilane), $Si(CH_3)I_3$ (methylsilyl triiodide), $Si(CH_3)_2I_2$ (dimethylsilyl dioiodide), $Si(CH_3)_3I$ (trimethylsilyl iodide), $Si(CH_3)HI_2$ (diiodomethylsilane), $Si(CH_3)_2HI$ (iododimethylsilane), $Si(CH_3)H_2I$ (methyliodosilane), Si_2I_6 (hexaiododisilane), GeI_4 (germanium tetraiodide), $GeHI_3$ (triiodogermane), GeH_2I_2 (diiodogermane), GeH_3I (iodogermane), AlI_3 (aluminum triiodide), BI_3 (boron triiodide), TiI_4 (titanium tetraiodide), SnI_4 (tin tetraiodide), N-iodosuccinimide, 1,3-diiodo-5,5-dimethylhydantoin, N-iodophthalimide, N-iodosaccharin, 1-chloro-2-iodoethane, iodinechloride (ICl), and combinations thereof.

7. The method of claim 1, wherein the metal layer is a molybdenum layer, and the metal precursor is a molybdenum precursor.

8. The method of claim 7, wherein the molybdenum precursor comprises $MoCl_5$, Mo_2Cl_{10}, MoO_2Cl_2, $MoOCl_4$, bis(ethylbenzene)molybdenum or any combination thereof.

9. The method of claim 1, wherein the deposition inhibitor modifies a surface on a field region and near an opening of the recessed feature to a greater degree than a surface of a bottom of the recessed feature.

10. The method of claim 1, wherein the deposition inhibitor modifies the surface of the semiconductor substrate by at least one of physisorption and chemisorption.

11. The method of claim 1, wherein the deposition inhibitor modifies the surface of the semiconductor substrate by halogenating the surface of the substrate.

12. The method of claim 1, wherein the metal layer is deposited at a temperature of between about 250 °C and about 600 °C and a pressure of less than about 300 torr.

13. The method of claim 1, wherein the surface of the semiconductor substrate modified by the deposition inhibitor comprises a metal, a metal nitride, a metal oxide, a metal carbide, metal silicide, amorphous silicon, polycrystalline silicon, hydrogen-terminated silicon, silicon germanium, a silicon-containing dielectric, and any combination thereof.

14. The method of claim 1, wherein the semiconductor substrate provided in (a) comprises exposed metal nitride, wherein the exposed metal nitride lines sidewalls of the recessed feature and a bottom of the recessed feature.

15. The method of claim 1, wherein the semiconductor substrate provided in (a) comprises exposed titanium nitride, wherein the exposed titanium nitride lines sidewalls of the recessed feature and a bottom of the recessed feature.

16. The method of claim 1, wherein the semconductor substrate provided in (a) comprises an exposed silicon-containing dielectric and an exposed metal, wherein the exposed silicon-containing dielectric is exposed at sidewalls of the recessed feature, and the exposed metal is exposed at a bottom of the recessed feature.

17. The method of claim 1, wherein (c) comprises sequentially exposing the semiconductor substrate to the metal precursor and a reducing agent, and repeating the sequential exposure to perform at least 10 inhibitor-free deposition cycles.

18. The method of claim 1, wherein the method comprises:

(i) exposing the semiconductor substrate to the deposition inhibitor;

(ii) after (i), exposing the semiconductor substrate to the metal precursor;

(iii) after (ii) exposing the semiconductor substrate to a reducing agent to reduce the metal precursor to metal; and

(iv) repeating steps (i) – (iii) to perform at least 10 inhibitor-assisted deposition cycles.

19. The method of claim 18, wherein each inhibitor-assisted deposition cycle comprises a purging step after each of the exposure of the semiconductor substrate to the deposition inhibitor, exposure of the semiconductor substrate to the metal precursor, and the exposure of the semiconductor substrate to the reducing agent.

20. The method of claim 1, wherein the metal layer is deposited conformally.

21. The method of claim 1, wherein the metal layer is deposited in a bottom-up deposition mode to fill the recessed feature.

22. The method of claim 1, wherein the method comprises delivering the deposition inhibitor and the metal precursor to a process chamber contemporaneously.

23. An apparatus for processing a substrate, the apparatus comprising:

(a) a process chamber, having a substrate holder for holding a semiconductor substrate, and one or more inlets for introduction of reactants to the process chamber; and

(b) a controller comprising program instructions for:

(i) causing contact of a semiconductor substrate having a recessed feature with a deposition inhibitor, wherein the deposition inhibitor is a halogen-containing compound, and wherein the deposition inhibitor modifies a surface of the semiconductor substrate to make the modified surface more resistant to metal deposition than the surface was before the modification; and

(ii) causing contact of the semiconductor substrate with a metal precursor, and causing a reduction of the metal precursor to form a metal layer at least within the recessed feature on the semiconductor substrate, wherein the metal precursor and the halogen-containing compound are different.