oxy group (-O-). In some embodiments, the aliphatic-oxy group is -O-R, in which R is an optionally substituted aliphatic group, as defined herein.

By "aliphatic-oxycarbonyl" is meant an aliphatic group that is or can be coupled to a compound disclosed herein, wherein the aliphatic group is or becomes coupled through an oxycarbonyl group (-C(O)O-). In some embodiments, the aliphatic-oxycarbonyl group is -C(O)O-R, in which R is an optionally substituted aliphatic group, as defined herein.

By "alkyl-aryl," "alkenyl-aryl," and "alkynyl-aryl" is meant an alkyl, alkenyl, or alkynyl group, respectively and as defined herein, that is or can be coupled (or attached) to the parent molecular group through an aryl group, as defined herein. The alkyl-aryl, alkenyl-aryl, and/or alkynyl-aryl group can be substituted or unsubstituted. For example, the alkyl-aryl, alkenyl-aryl, and/or alkynyl-aryl group can be substituted with one or more substitution groups, as described herein for alkyl and/or aryl. Exemplary unsubstituted alkyl-aryl groups are of from 7 to 16 carbons (C_{7-16} alkyl-aryl), as well as those having an alkyl group with 1 to 6 carbons and an aryl group with 4 to 18 carbons (i.e., C_{1-6} alkyl-C_{4-18} aryl). Exemplary unsubstituted alkenyl-aryl groups are of from 7 to 16 carbons (C_{7-16} alkenyl-aryl), as well as those having an alkenyl group with 2 to 6 carbons and an aryl group with 4 to 18 carbons (i.e., C_{2-6} alkenyl-C_{4-18} aryl). Exemplary unsubstituted alkynyl-aryl groups are of from 7 to 16 carbons (C_{7-16} alkynyl-aryl), as well as those having an alkynyl group with 2 to 6 carbons and an aryl group with 4 to 18 carbons (i.e., C_{2-6} alkynyl-C_{4-18} aryl). In some embodiments, the alkyl-aryl group is -L-R, in which L is an aryl group or an arylene group, as defined herein, and R is an alkyl group, as defined herein. In some embodiments, the alkenyl-aryl group is -L-R, in which L is an aryl group or an arylene group, as defined herein, and R is an alkenyl group, as defined herein. In some embodiments, the alkynyl-aryl group is -L-R, in which L is an aryl group or an arylene group, as defined herein, and R is an alkynyl group, as defined herein.

By "alkenyl" is meant an unsaturated monovalent hydrocarbon having at least two carbon atom to 50 carbon atoms (C_{2-50}), such as two to 25 carbon atoms (C_{2-25}), or two to ten carbon atoms (C_{2-10}), and at least one carbon-carbon double bond, wherein the unsaturated monovalent hydrocarbon can be derived from removing one hydrogen atom from one carbon atom of a parent alkene. An alkenyl group can be branched, straight-chain, cyclic (e.g., cycloalkenyl), cis, or trans (e.g., E or Z). An exemplary alkenyl includes an optionally substituted C_{2-24} alkyl group having one or more double bonds. The alkenyl group can be monovalent or multivalent (e.g., bivalent) by removing one or more hydrogens to form appropriate attachment to the parent molecular group or appropriate attachment between the

aromatic, optionally substituted heteroaromatic, optionally substituted silyl, or optionally substituted silyloxy, as defined herein, or any combination thereof; or where R^1 and R^2, taken together with the nitrogen atom to which each are attached, can form a heterocyclyl group, as defined herein.

By "carbamoyloxy" is meant a carbamoyl group, as defined herein, attached to the parent molecular group through n oxy group, as defined herein. In some embodiments, the carbamoyloxy is $-OC(O)NR^1R^2$ group, where each of R^1 and R^2 is, independently, selected from hydrogen, optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted aromatic, optionally substituted heteroaromatic, optionally substituted silyl, or optionally substituted silyloxy, as defined herein, or any combination thereof; or where R^1 and R^2, taken together with the nitrogen atom to which each are attached, can form a heterocyclyl group, as defined herein.

By "carbonimidoyl" is meant a -C(NR)- group. In some embodiments, R is selected from hydrogen, optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted aromatic, optionally substituted heteroaromatic, optionally substituted silyl, optionally substituted alkyl, optionally substituted aryl, optionally substituted alkyl-aryl, or optionally substituted aryl-alkyl, optionally substituted silyloxy, as defined herein, or any combination thereof.

By "carbonyl" is meant a -C(O)- group, which can also be represented as >C=O.

By "carboxyl" is meant a $-CO_2H$ group or an anion thereof.

By "catalyst" is meant a compound, usually present in small amounts relative to reactants, capable of catalyzing a synthetic reaction, as would be readily understood by a person of ordinary skill in the art. In some embodiments, catalysts may include transition metal coordination complex.

By "cyanato" is meant a -OCN group.

By "cyano" is meant a -CN group.

By "cycloaliphatic" is meant an aliphatic group, as defined herein, that is cyclic.

By "cycloalkoxy" is meant a cycloalkyl group, as defined herein, attached to the parent molecular group through an oxygen atom. In some embodiments, the cycloalkoxy group is -O-R, in which R is a cycloalkyl group, as defined herein.

By "cycloalkylalkoxy" is meant a -O-L-R group, in which L is an alkyl group or an alkylene group, as defined herein, and R is a cycloalkyl group, as defined herein.

By "cycloalkyl" is meant a monovalent saturated or unsaturated non-aromatic cyclic hydrocarbon group of from three to eight carbons, unless otherwise specified, and is

X is fluoro, bromo, chloro, or iodo; and each of R^1 and R^2 is, independently, H or alkyl, as defined herein.

By "haloheteroaliphatic" is meant a heteroaliphatic, as defined herein, in which one or more hydrogen atoms, such as one to 10 hydrogen atoms, independently is replaced with a halogen atom, such as fluoro, bromo, chloro, or iodo.

By "heteroaliphatic" is meant an aliphatic group, as defined herein, including at least one heteroatom to 20 heteroatoms, such as one to 15 heteroatoms, or one to 5 heteroatoms, which can be selected from, but not limited to oxygen, nitrogen, sulfur, silicon, boron, selenium, phosphorous, and oxidized forms thereof within the group. A heteroaliphatic group is unsubstituted or substituted, e.g., by a functional group described herein. For example, the heteroaliphatic group can be substituted with one or more substitution groups, as described herein for alkyl.

By "heteroaliphatic-carbonyl" is meant a heteroaliphatic group that is or can be coupled to a compound disclosed herein, wherein the heteroaliphatic group is or becomes coupled through a carbonyl group (-C(O)-). In some embodiments, the heteroaliphatic-carbonyl group is -C(O)-R, in which R is an optionally substituted heteroaliphatic group, as defined herein.

By "heteroaliphatic-carbonyloxy" is meant a heteroaliphatic group that is or can be coupled to a compound disclosed herein, wherein the heteroaliphatic group is or becomes coupled through a carbonyloxy group (-OC(O)-). In some embodiments, the heteroaliphatic-carbonyloxy group is -OC(O)-R, in which R is an optionally substituted heteroaliphatic group, as defined herein.

By "heteroaliphatic-oxy" is meant a heteroaliphatic group that is or can be coupled to a compound disclosed herein, wherein the heteroaliphatic group is or becomes coupled through an oxy group (-O-). In some embodiments, the heteroaliphatic-oxy group is -O-R, in which R is an optionally substituted heteroaliphatic group, as defined herein.

By "heteroaliphatic-oxycarbonyl" is meant a heteroaliphatic group that is or can be coupled to a compound disclosed herein, wherein the heteroaliphatic group is or becomes coupled through an oxycarbonyl group (-C(O)O-). In some embodiments, the heteroaliphatic-oxycarbonyl group is -C(O)O-R, in which R is an optionally substituted heteroaliphatic group, as defined herein.

By "heteroalkyl," "heteroalkenyl," and "heteroalkynyl" is meant an alkyl, alkenyl, or alkynyl group (which can be branched, straight-chain, or cyclic), respectively, as defined herein, including at least one heteroatom to 20 heteroatoms, such as one to 15 heteroatoms, or

precursor and in step 223 the semiconductor substrate is exposed to the reducing agent. Both of these steps are performed in an absence of a silicon-containing reactant and constitute one silicon-free molybdenum metal deposition cycle. In step 225, steps 221-223 are repeated to perform a plurality of deposition cycles while inserting exposure of the substrate to a silicon-containing reactant after a pre-determined number of silicon-free molubdenum metal deposition cycles. For example, the substrate may be exposed to the silicon-containing reactant as a single exposure after every 5, 10, 20, or 50 silicon-free deposition cycles. Alternatively, one or more silicon-assisted deposition cycles, such as any of illustrated in Figures 2A-2C, may be inserted after a predetermined number of silicon-free cycles.

In some embodiments, the molybdenum-containing layer deposition involves depositing molybdenum-containing material (e.g., molubdenum silicide and/or molybdenum metal) using silicon-assisted deposition as described herein, followed by deposition of molybdenum metal using silicon-free deposition. For example, 2 - 2,000 silicon-assisted deposition cycles may be followed by 2 – 2,000 silicon-free deposition cycles. In some embodiments this process flow is used to deposit a molybdenum-containing layer that includes a molybdenum silicide layer at an interface with a silicon-containing dielectric and then form a molybdenum metal layer over the molybdenum silicide layer. The molybdenum silicide layer of the molybdenum-containing layer may be deposited using silicon-assisted deposition, and the molybdenum metal layer of the molybdenum-containing layer may be deposited using silicon-free deposition.

In some embodiments different molybdenum-containing precursors are used for silicon-assisted and silicon-free deposition. In one implementation, molybdenum silicide and/or molybdenum metal is first deposited using molybdenum pentachloride ($MoCl_5$) as a molybdenum-containing precursor in a silicon-assisted deposition, according to any of the methods provided in Figures 2A-2D. This is followed by depositing molybdenum metal in a silicon free deposition using a different molybdenum-containing precursor (e.g., MoO_2Cl_2). This process flow is illustrated in the process flow diagram of Figure 3. In step 301 the substrate is exposed to a molybdenum-containing precursor, a reducing agent, and a silicon-containing reactant to deposit the molybdenum-containing layer. For example, 2-2,000 cycles of silicon-assisted deposition may be conducted. The process then follows in step 305 by exposing the substrate to a different molybdenum-containing precursor and a reducing agent in an absence of a silicon-containing reactant to deposit a layer of molybdenum metal in silicon-free deposition. For example, 2 – 2,000 silicon-free deposition cycles may be performed in step 305.

cyclopropylpropyl, cyclobutylmethyl, and cyclobutylethyl. In some embodiments each R is an independently selected alkyl. In some embodiments ligands with branched alkyl substituents, such as isopropyl, and isobutyl are preferred, because such ligands provide more volatile molybdenum precursors.

In some embodiments, at least one organic ligand in the precursor is an amine. Suitable amines include unidentate amines (e.g., monoalkylamines, dialkylamines), bidentate amines (e.g., unsubstituted or N-alkyl substituted ethylenediamines), and amines of higher denticities (e.g., substituted or unsubstituted diethylenetriamine). An example of a monodentate amine is amine 1, shown in Figure 1, where at least one R is an alkyl or fluoroalkyl, and each R is independently selected from the group consisting of H, alkyl, and fluoroalkyl. In some embodiments at least one R is an alkyl, and each R is independently selected from H, and an alkyl. In some embodiments, the at least one organic ligand is an amide, such as a monoanionic amide 16, wherein at least one R is an alkyl or fluoroalkyl, and each R is independently selected from H, alkyl, and a fluoroalkyl. In some embodiments, the at least one organic ligand is an imide, such as a dianionic imide 17, wherein R is an alkyl or fluoroalkyl. While in general imide-containing precursors can be used for deposition of a variety of molybdenum-containing films (including molybdenum metal), in some embodiments they are more preferred for deposition of molybdenum nitride and molybdenum carbonitride, as they form strong molybdenum-nitrogen bonds, and can serve as sources of nitrogen for the resulting film. In some embodiments, at least one organic ligand in the precursor is an amidinate. An example of an amidinate is an amidinate 2 shown in Figure 4, where each R is independently selected from H, alkyl, and fluoroalkyl. Amidinate 2 is a monoanionic ligand that can form two molybdenum-nitrogen bonds, serving as a bidentate ligand.

In some embodiments, at least one organic ligand in the precursor is an amidate. An example of an amidate is an amidate 3 shown in Figure 4, where each R is independently selected from H, alkyl, and fluoroalkyl. Amidate 3 is a monoanionic ligand that can form one molybdenum-nitrogen, and one molybdenum-oxygen bond, serving as a bidentate ligand.

In some embodiments, at least one organic ligand in the precursor is a diazadiene. Examples of diazadienes are 1,4-diazabuta-1,3-dienes (DAD) 5, 6, and 7, where each R is independently selected from H, alkyl, and fluoroalkyl. An interesting property of this ligand is that it can exist in neutral form 5, monoanionic radical form 6, and dianionic form 7. Due to redox activity of monoanionic (radical) form 6, it can be relatively easily removed during