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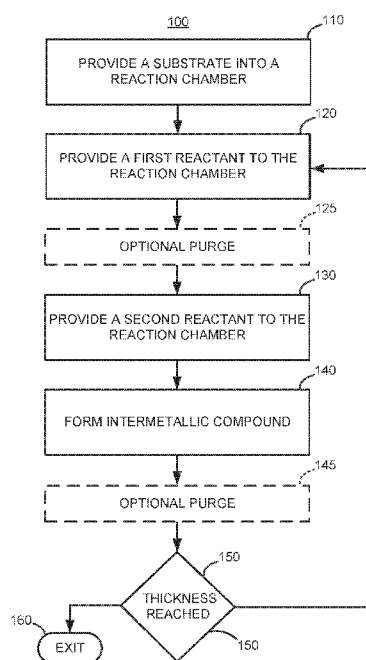


FIG. 1

(57) Abstract: A method of depositing a metal-containing material is disclosed. The method can include use of cyclic deposition techniques, such as cyclic chemical vapor deposition and atomic layer deposition. The metal-containing material can include intermetallic compounds. A structure including the metal-containing material and a system for forming the material are also disclosed.

CYCLIC DEPOSITION METHODS FOR FORMING METAL-CONTAINING
MATERIAL AND FILMS AND STRUCTURES INCLUDING THE METAL-
CONTAINING MATERIAL

5 PARTIES OF JOINT RESEARCH AGREEMENT

The invention claimed herein was made by, or on behalf of, and/or in connection with a joint research agreement between the University of Helsinki and ASM Microchemistry Oy. The agreement was in effect on and before the date the claimed invention was made, and the claimed invention was made as a result of activities undertaken within the scope of the agreement.

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FIELD OF INVENTION

The present disclosure relates generally to methods for depositing a metal-containing material on a surface of a substrate, films and structures including the metal-containing material, and reactors and systems for depositing the metal-containing material.

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BACKGROUND OF THE DISCLOSURE

Deposition of metal-containing material can be used in the manufacture of a variety of devices, such as semiconductor devices, flat panel display devices, photovoltaic devices, microelectromechanical systems (MEMS), magnetoresistance devices, superconductive devices, energy (e.g., hydrogen) storage devices, lithium or sodium ion batteries and the like and/or to form catalytic material. For many applications, it is often desirable to deposit the metal-containing material over a surface, which may include three-dimensional features, such as trenches and/or protrusions, which can have relatively high aspect ratios, in a uniform and/or conformal manner.

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Recently, because of their relatively unique physical and chemical properties, interest has grown in possibly using intermetallic compounds in the formation of various devices. Intermetallic compounds generally have a specific, ordered crystalline structure, which can be distinct from alloys formed of the same metals; the specific structure can lead to material properties that are superior to non-intermetallic compounds. Such properties include, for example, magnetoresistance, superconductivity, catalytic activity, and hydrogen storage capability. By way of examples, intermetallic compounds containing Co or Ni and Sn with varying stoichiometry have been studied as anode materials for Li- and Na-ion batteries, as ferromagnetic materials for magnetic devices, and for catalytic purposes.

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Metal-containing material, such as Co–Sn and Ni–Sn with varying stoichiometry, including the intermetallic Co_3Sn_2 and Ni_3Sn_2 phases of the material, have generally been prepared by, for example, ball milling, arc melting, different solution-based techniques, solvo- and hydrothermal routes, electrodeposition, sputtering, and electron beam evaporation.

5 Chemical vapor deposition (CVD) from two single-source reactants, $\text{Me}_3\text{SnCo}(\text{CO})_4$ and $\text{Ph}_3\text{SnCo}(\text{CO})_4$, has been employed to deposit an alloy of Co and Sn with 1:1 stoichiometry and only a minor constituent of Co_3Sn_2 . Ni_3Sn , Ni_3Sn_2 , and Ni_3Sn_4 have also been deposited by CVD using SnMe_4 and Ni substrates followed by hydrogen treatment at high temperatures. Although such techniques can be used to form intermetallic compounds, such techniques are generally not

10 well suited for forming uniform, conformal films of intermetallic material on a surface of a substrate.

Cyclic deposition techniques, such as atomic layer deposition, can be used to deposit material in a relatively uniform (e.g., uniform crystalline structure, uniform composition, and/or uniform thickness) and conformal manner over complex, three-dimensional structures on a

15 substrate surface in a controlled and reproducible manner. However, such techniques have generally not been employed to deposit several metal-containing materials, including intermetallic compounds. Rather, the intermetallic compounds in particular are typically formed using other techniques and/or require additional, often high-temperature processes.

Accordingly, improved methods for forming metal-containing material, such as

20 intermetallic compounds, are desired. Additionally, improved techniques for forming uniform and/or conformal films of metal-containing material are desired.

Any discussion of problems provided in this section has been included in this disclosure solely for the purpose of providing a context for the present invention, and should not be taken as an admission that any or all of the discussion was known at the time the invention was made.

SUMMARY OF THE DISCLOSURE

This summary is provided to introduce a selection of concepts in a simplified form. These concepts are described in further detail in the detailed description of example embodiments of the disclosure below. This summary is not intended to necessarily identify key

30 features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

In accordance with at least one embodiment of the disclosure, a method for depositing an intermetallic compound is disclosed. In accordance with various aspects, the method is a cyclic deposition process that includes providing a first gas-phase reactant (also referred to herein

as a precursor) comprising a first metal to a reaction chamber to react with a surface of a substrate to form a first metal species; and providing a second gas-phase reactant comprising a second metal to a reaction chamber to react with the first metal species to thereby form the intermetallic compound. Additional reactants can similarly be used to form intermetallic compounds including more than two metals. As set forth in more detail below, a film of the intermetallic compound can be formed on a substrate surface without additional high temperature and/or reducing steps. The cyclic deposition process can include, for example, atomic layer deposition.

In accordance with at least one other embodiment of the disclosure, a method for forming a metal-containing material is disclosed. The metal-containing material can include one, two, or three or more metals as described herein. The method can be a cyclic deposition process, such as an atomic layer deposition or cyclic chemical vapor deposition process. The cyclic deposition process can include providing a first gas-phase reactant comprising a first metal to a reaction chamber to form a first metal species and providing a second gas-phase reactant comprising a compound having a general formula of $R-M-H$ (e.g., $R_{(X-n)}-M^X-H_n$), wherein R is an organic group and M is a metal to react with the first metal species to thereby form the metal-containing material. In accordance with various examples, X is the formal oxidation state of M and n can range from 1 to 5. In accordance with various aspects, the metal-containing material comprises one or more of metal mixture, an alloy, and an intermetallic compound. A film comprising the metal-containing material can be metallic, conductive, non-conductive, or semiconductive. Exemplary films can be superconductive, magnetoresistive, ferromagnetic, or a catalyst.

In accordance with at least one additional embodiment of the disclosure, a method for supplying a first gas-phase reactant comprising a first metal and a second gas-phase reactant comprising a second metal (e.g., comprising a compound having a general formula of $R-M-H$ (e.g., $R_{(X-n)}-M^X-H_n$, wherein R is an organic group, X is the formal oxidation state of the metal, n is 1 to 5 and M is a metal) is provided. The method may comprise: providing a second gas-phase reactant source vessel configured for containing the second gas-phase reactant (e.g., any of the second gas-phase reactants described herein), fluidly connecting the second gas-phase reactant source vessel to the reaction chamber; heating second gas-phase reactant contained in the second gas-phase reactant source vessel to a temperature of about 0 °C to about 400 °C, about 20 °C to about 200 °C, or about 20 °C to about 100 °C; generating a vapor pressure of the second gas-phase reactant of at least 0.001 mbar; and supplying the second gas-phase reactant to the reaction chamber.

In some embodiments of the disclosure, a reactor system utilizing reactive volatile chemicals is provided. The reactor system can include a reaction chamber, a first gas-phase reactant source vessel in fluid communication with the reaction chamber, and a second gas-phase reactant source vessel in fluid communication with the reaction chamber. The second gas-phase reactant can include, for example, a compound having a general formula of $R-M-H$ —e.g., $R_{(X-n)}-M^X-H_n$, wherein R is an organic group, X is the formal oxidation state of the metal, n is 1 to 5, and M is a metal.

For purposes of summarizing the disclosure and the advantages achieved over the prior art, certain objects and advantages may have been described herein above. Of course, it is to be understood that not necessarily all such objects or advantages may be achieved in accordance with any particular embodiment of the disclosure. Thus, for example, those skilled in the art will recognize that the embodiments of the disclosure may be carried out in a manner that achieves or optimizes one advantage or group of advantages as taught or suggested herein without necessarily achieving other objects or advantages as may be taught or suggested herein.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

The subject matter of the present disclosure is particularly pointed out and distinctly claimed in the concluding portion of the specification. A more complete understanding of the present disclosure, however, may best be obtained by referring to the detailed description and claims when considered in connection with the drawing figures, wherein like numerals denote like elements and wherein:

FIG. 1 illustrates a process flow of an exemplary cyclical deposition method according to at least one embodiment of the disclosure;

FIG. 2 illustrates another process flow of an exemplary cyclical deposition method according to at least one embodiment of the disclosure;

FIG. 3 illustrates a schematic diagram of an exemplary device structure including a metal-containing film deposited according to at least one embodiment of the disclosure;

FIG. 4 illustrates an example of a metal halide compound utilized in a cyclical deposition process according to at least one embodiment of the disclosure;

FIG. 5 illustrates a schematic diagram of an exemplary reactor system according to at least one embodiment of the disclosure; and

FIG. 6 illustrates an exemplary second gas-phase reactant according to at least one embodiment of the disclosure.

It will be appreciated that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures may be exaggerated relative to other elements to help to improve understanding of illustrated embodiments of the present invention.

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DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

The description of exemplary embodiments of the present disclosure provided below is merely exemplary and is intended for purposes of illustration only; the following description is not intended to limit the scope of the invention. Moreover, recitation of multiple embodiments
10 having stated features is not intended to exclude other embodiments having additional features or other embodiments incorporating different combinations of the stated features.

As set forth in more detail below, exemplary embodiments of the disclosure relate to methods and apparatus for depositing metal-containing material, such as intermetallic compounds, and to films and structures that include the metal-containing material. While the
15 ways in which the present disclosure addresses various drawbacks of prior systems and methods are described in more detail below, in general, various systems and methods described herein employ improved reactants (sometimes generally referred to as precursors) and/or improved deposition techniques to deposit metal-containing material with desired properties.

As used herein, the terms “precursor” and/or “reactant” may refer to one or more
20 gases/vapors that take part in a chemical reaction or from which a gas-phase substance that takes part in a reaction is derived. The chemical reaction can take place in the gas phase and/or between a gas phase and a surface of a substrate and/or a species on a surface of a substrate.

As used herein, the term “cyclic deposition” may refer to the sequential introduction of reactants into a reaction chamber to deposit a film over a substrate and includes deposition
25 techniques such as atomic layer deposition and cyclical chemical vapor deposition.

As used herein, the term “cyclical chemical vapor deposition” may refer to any process wherein a substrate is sequentially exposed to two or more volatile reactants, which react and/or decompose on a substrate to produce a desired material.

As used herein, the term “atomic layer deposition” (ALD) may refer to a vapor
30 deposition process in which deposition cycles, e.g., a plurality of consecutive deposition cycles, are conducted in a reaction chamber. Typically, during each cycle, a first reactant is chemisorbed to a surface of a substrate, forming a monolayer or sub-monolayer that does not readily react with additional first reactant (i.e., a self-limiting reaction). Thereafter, another, second reactant or a reaction gas may subsequently be introduced into the process chamber for use in converting

the chemisorbed substance to the desired material. Further, purging steps may also be utilized during each deposition cycle to remove excess first reactant from the reaction chamber and/or remove excess second reactant, reaction gas, and/or reaction byproducts from the reaction chamber after conversion of the chemisorbed first and/or second reactant. Further, the term “atomic layer deposition,” as used herein, is also meant to include processes designated by related terms, such as chemical vapor atomic layer deposition, atomic layer epitaxy (ALE), molecular beam epitaxy (MBE), gas source MBE, organometallic MBE, and chemical beam epitaxy, when performed with alternating pulses of reactants, reactive gas, and/or purge (e.g., inert carrier) gas.

As used herein, the term “substrate” may refer to any material having a surface onto which a material can be deposited. A substrate can include a bulk material such as silicon (e.g., single crystal silicon), and may include one or more layers overlying the bulk material, including, for example, a chemisorbed species. Further, the substrate can include various features, such as trenches, vias, lines, and the like formed within or on at least a portion of the substrate. The features can have an aspect ratio, defined as a feature’s height divided by the feature’s width, of, for example, greater than or equal to 5, greater than or equal to 10, greater than or equal to 15, or greater than or equal to 20.

As used herein, the term “film,” “thin film,” “layer,” and “thin layer” may refer to any continuous or non-continuous material deposited—e.g., by methods disclosed herein. For example, “film,” “thin film,” “layer,” and “thin layer” can include 2D materials, nanorods, nanotubes, or nanoparticles or even partial or full molecular layers or partial or full atomic layers or clusters of atoms and/or molecules. “Film,” “thin film,” “layer,” and “thin layer” may comprise material or a layer with pinholes, but still be at least partially continuous.

As used herein, the term “metal-containing film” and “metal-containing material” may refer to a film or material that contains at least one metal species.

As used herein, the term “metal” can include a semimetal or metalloid.

As used herein, an “intermetallic” or an “intermetallic compound” may refer to a compound that includes two or more metal elements with a defined stoichiometry and an ordered crystal structure. Intermetallic compounds differ from metal alloys by their crystal structure; the crystalline structures of intermetallic compounds are arranged in a specific structure, whereas alloys typically exhibit the crystal structure of one of the participating metal components. An intermetallic compound is formed when the bonds between the unlike atoms are stronger than the bonds between the atoms of the same element.

A number of example materials are given throughout the current disclosure; it should be noted that the chemical formulas given for each of the example materials should not be construed as limiting, and that the non-limiting example materials given should not be limited by a given example stoichiometry.

5 The present disclosure includes methods for depositing metal-containing material—e.g., films of the metal-containing material—onto a substrate. The methods can be carried out using a cyclical deposition process to deposit the metal-containing material to, for example, form a metal-containing film on the substrate. Exemplary methods can deposit metal-containing films, such as films comprised, consisting essentially of, or consisting of an intermetallic compound at
10 relatively low temperatures. Additionally or alternatively, the methods can deposit metal-containing material with large-area thickness, crystallinity, and/or composition uniformity of film comprising, consisting essentially of, or consisting of the metal-containing material.

Turning now to the figures, FIG. 1 illustrates a cyclic deposition method 100 in accordance with at least one embodiment of the disclosure. Method 100 can be used to form an
15 intermetallic compound, such as a film of the intermetallic compound on a substrate surface.

Method 100 begins with a step 110 which comprises providing at least one substrate into a reaction chamber and heating the substrate to a deposition temperature. The deposition temperature may depend on, for example, one or more reactants used to form the intermetallic compound. By way of examples, the reaction chamber can be heated to greater than 0 °C and
20 less than 600 °C, less than 500 °C, less than 400 °C, less than 300 °C or less than 250 °C, or between about 20 °C to about 700 °C, about 50 °C to about 500 °C, or about 50 °C to about 400 °C, about 75 °C to about 300 °C or about 100 °C to about 250 °C. By way of particular examples, the intermetallic compound can include Co_3Sn_2 , and, in this case, the temperature can range from about 170 °C to about 200 °C; similarly, when the intermetallic compound includes
25 Ni_3Sn_2 , the temperature can range from about 125 °C to about 175 °C, or about 140 °C to about 160 °C. A pressure within the reaction chamber may be controlled to provide a desired pressure in the reaction chamber for a deposition process. For example, the pressure within the reaction chamber during the cyclical deposition process may be less than 1000 mbar, or less than 100 mbar, or less than 10 mbar, or less than 5 mbar, or even, in some instances, less than 1 mbar, or
30 from about 10^{-8} mbar to about 1000 mbar, from about 10^{-3} mbar to about 100 mbar, from about 10^{-2} mbar to about 50 mbar, or from about 0.1 mbar to about 10 mbar.

Method 100 may continue with a step 120, which includes providing a first gas-phase reactant comprising a first metal to the reaction chamber to react with a surface of a substrate to form a first metal species. This step may be at the same pressure and temperature noted above

in connection with step 110. A pulse time or a time that the first gas-phase reactant is provided to the reaction chamber can range from, for example, between about 0.01 seconds and about 60 seconds, or between about 0.05 seconds and about 10 seconds, or between about 0.1 seconds and about 5 seconds. During step 120, a flowrate of the first gas-phase reactant may be less than
5 2000 sccm, or less than 1000 sccm, or less than 500 sccm, or less than 200 sccm, or even less than 100 sccm, or may range from about 1 to about 5000 sccm, from about 5 to about 2000 sccm, or from about 10 to about 1000 sccm.

After the step of providing a first gas-phase reactant, any excess first gas-phase reactant and any reaction byproducts may be removed from the reaction chamber by a purge/pump
10 process (step 125). A duration of step 125 can be, for example, between about 0.01 seconds and about 60 seconds, or between about 0.05 seconds and about 10 seconds, or between about 0.1 seconds and about 5 seconds. A flow of a purge gas during step 125 may be less than 2000 sccm, or less than 1000 sccm, or less than 500 sccm, or less than 200 sccm, or even less than 100 sccm, or may range from about 1 to about 5000 sccm, from about 5 to about 2000 sccm, or
15 from about 10 to about 1000 sccm. Although separately illustrated, step 125 can be considered part of step 120.

Method 100 may continue with step 130 of providing a second gas-phase reactant comprising a second metal to the reaction chamber to react with the first metal species to thereby form the intermetallic compound. This step may be at the same or different pressure
20 and/or temperature noted above in connection with step 110. A pulse time or a time that the second gas-phase reactant is provided to the reaction chamber can range from between about 0.01 seconds and about 60 seconds, or between about 0.05 seconds and about 10 seconds, or between about 0.1 seconds and about 5 seconds. During step 130, the flowrate of the second gas-phase reactant may be the same or similar as the flowrates noted above during step 120.

As illustrated in FIG. 1, as the second gas-phase reactant reacts with species on the substrate surface, an intermetallic compound—e.g., a film comprising, consisting essentially of, or consisting of an intermetallic compound is formed (step 140).
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After step 140, any excess second gas-phase reactant and any reaction byproducts may be removed from the reaction chamber by a purge/pump process (step 145). A flow and/or
30 duration of a purge gas in this step can be the same or similar to those noted above in step 125. Further, although separately illustrated, step 145 can be considered part of step 130.

Steps 120 and 130 (and optionally purge steps 125 and/or 145) may constitute one deposition cycle. In some embodiments of the disclosure, method 100 may comprise repeating the deposition cycle one or more times. For example, method 100 may continue with a decision

gate 150, which determines if the cyclical deposition method 100 continues or exits via step 160. Decision gate 150 can be determined based on the thickness of or an amount of the deposited intermetallic compound. For example, if the thickness of the intermetallic compound is insufficient for the desired device structure, then the method 100 may return to step 120, and steps 120-145 may be repeated. Once the intermetallic compound has been deposited to a desired thickness or amount, the method may end at step 160, and the substrate may be subjected to additional processes to form one or more devices or device structures.

In accordance with various aspects of method 100, the intermetallic compound forms upon reacting the second gas-phase reactant with a first metal species that forms on a surface during step 120. Thus, the intermetallic compound or layer or film comprising, consisting essentially of, or consisting of the intermetallic compound can be formed without an additional reduction step and/or heating step. Further, as set forth above, the intermetallic compound can be formed at relatively low temperatures.

The first gas-phase reactant can include any first metal that is different from the second metal. By way of examples, the first metal can be or include a transition metal (e.g., a group 3-12 metal), a group 3-6 metal, a group 7-12 metal, a lanthanide metal, a group 8-11 metal, and/or a group 9-10 metal.

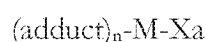
In accordance with alternative embodiments, such as those described below in connection with FIG. 2, the first gas-phase reactant can include a first metal that is the same as the second metal. When the first metal and the second metal are the same, an elemental metallic film can be formed. As noted above, such elemental metallic films can include semimetals or metalloids.

The first gas-phase reactant can be or include a metal halide compound, wherein the metal is or includes the first metal. The metal halide compound may comprise a metal chloride, a metal iodide, a metal fluoride, or a metal bromide. In some embodiments of the disclosure, the metal halide compound may comprise a metal species, including, but not limited to, at least one of cobalt, nickel, or copper. In some embodiments of the disclosure, the metal halide compound may comprise at least one of a cobalt chloride, a nickel chloride, and a copper chloride. In some embodiments, the metal halide compound may comprise a bidentate nitrogen containing adduct forming ligand. In some embodiments, the metal halide compound may comprise an adduct forming ligand including two nitrogen atoms, wherein each of the nitrogen atoms are bonded to at least one carbon atom. In some embodiments of the disclosure, the metal halide compound comprises one or more nitrogen atoms bonded to a central metal atom thereby forming a metal

complex. An example of such a compound is illustrated in FIG. 4. Additional first gas-phase reactants can include adduct forming ligands that include phosphorous, oxygen, and/or sulfur.

In some embodiments, the first gas-phase reactant may comprise a transition metal compound with an adduct forming ligand. In some embodiments, the first gas-phase phase reactant may comprise a transition metal compound. In some embodiments, the first gas-phase reactant may comprise a transition metal halide compound. In some embodiments, the first gas-phase reactant may comprise a transition metal compound with an adduct forming ligand, such as monodentate, bidentate, or multidentate adduct forming ligand. In some embodiments, the first gas-phase reactant may comprise a transition metal halide compound with adduct forming ligand, such as monodentate, bidentate, or multidentate adduct forming ligand. In some embodiments, the first gas-phase reactant may comprise a transition metal compound with adduct forming ligand comprising nitrogen, such as monodentate, bidentate, or multidentate adduct forming ligand comprising nitrogen. In some embodiments, the first gas-phase reactant may comprise a transition metal compound with adduct forming ligand comprising phosphorous, oxygen, or sulfur, such as monodentate, bidentate, or multidentate adduct forming ligand comprising phosphorous, oxygen or sulfur. For example, in some embodiments, the transition metal halide compound may comprise a transition metal chloride, a transition metal iodide, a transition metal fluoride, or a transition metal bromide. In some embodiments of the disclosure, the transition metal halide compound may comprise a transition metal species, including, but not limited to, at least one of cobalt, nickel, or copper. In some embodiments of the disclosure, the transition metal halide compound may comprise at least one of a cobalt chloride, a nickel chloride, or a copper chloride. In some embodiments, the transition metal halide compound may comprise a bidentate nitrogen containing adduct forming ligand. In some embodiment, the transition metal halide compound may comprise an adduct forming ligand including two nitrogen atoms, wherein each of the nitrogen atoms are bonded to at least one carbon atom. In some embodiments of the disclosure, the transition metal halide compound comprises one or more nitrogen atoms bonded to a central transition metal atom thereby forming a metal complex.

In some embodiments of the disclosure, the first gas-phase reactant may comprise a transition metal compound having the formula:



wherein each of the “adducts” is an adduct forming ligand and can be independently selected to be a mono-, a bi-, or a multidentate adduct forming ligand or mixtures thereof: n is from 1 to 4 in case of monodentate forming ligand, n is from 1 to 2 in case of bi- or multidentate

adduct forming ligand; M is a transition metal, such as, for example, cobalt (Co), copper (Cu), or nickel (Ni); wherein each of Xa is another ligand, and can be independently selected to be a halide or other ligand; wherein a is from 1 to 4, and some instances a is 2.

In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound, such as a transition metal halide compound, may comprise a monodentate, bidentate, or multidentate adduct forming ligand which coordinates to the transition metal atom, of the transition metal compound, through at least one of a nitrogen atom, a phosphorous atom, an oxygen atom, or a sulfur atom. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise a cyclic adduct ligand. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise mono-, di-, or polyamines. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise mono-, di-, or polyethers. In some embodiments, the adduct forming ligand in the transition metal compound may comprise mono-, di-, or polyphosphines. In some embodiments, the adduct forming ligand in the transition metal compound may comprise carbon and/or in addition to the nitrogen, oxygen, phosphorous, or sulfur in the adduct forming ligand.

In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise one monodentate adduct forming ligand. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise two monodentate adduct forming ligands. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise three monodentate adduct forming ligands. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise four monodentate adduct forming ligands. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise one bidentate adduct forming ligand. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise two bidentate adduct forming ligands. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise one multidentate adduct forming ligand. In some embodiments of the disclosure, the adduct forming ligand in the transition metal compound may comprise two multidentate adduct forming ligands.

In some embodiments of the disclosure, the adduct forming ligand comprises nitrogen, such as an amine, a diamine, or a polyamine adduct forming ligand. In such embodiments, the transition metal compound may comprise at least one of, triethylamine (TEA), N,N,N',N'-tetramethyl-1,2-ethylenediamine (CAS: 110-18-9) (TMEDA), N,N,N',N'-

tetraethylethylenediamine (CAS: 150-77-6) (TEEDA), N,N'-diethyl-1,2-ethylenediamine (CAS: 111-74-0) (DEEDA), N,N'-diisopropylethylenediamine (CAS: 4013-94-9), N,N,N',N'-tetramethyl-1,3-propanediamine (CAS: 110-95-2) (TMPDA), N,N,N',N'-tetramethylmethanediamine (CAS: 51-80-9) (TMMDA), N,N,N',N'',N''-pentamethyldiethylenetriamine (CAS: 3030-47-5) (PMDETA), diethylenetriamine (CAS: 111-40-0) (DIEN), triethylenetetraamine (CAS: 112-24-3) (TRIEN), tris(2-aminoethyl)amine (CAS: 4097-89-6) (TREN, TAEA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (CAS: 3083-10-1) (HMTETA), 1,4,8,11-tetraazacyclotetradecane (CAS: 295-37-4) (Cyclam), 1,4,7-trimethyl-1,4,7-triazacyclononane (CAS: 96556-05-7), or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (CAS: 41203-22-9).

In some embodiments of the disclosure, the adduct forming ligand comprises phosphorous, such as a phosphine, a diphosphine, or a polyphosphine adduct forming ligand. For example, the transition metal compound may comprise at least one of, triethylphosphine (CAS: 554-70-1), trimethyl phosphite (CAS: 121-45-), 1,2-bis(diethylphosphino)ethane (CAS: 6411-21-8) (BDEPE), or 1,3-bis(diethylphosphino)propane (CAS: 29149-93-7).

In some embodiments of the disclosure, the adduct forming ligand comprises oxygen, such as an ether, a diether, or a polyether adduct forming ligand. For example, the transition metal compound may comprise at least one of, 1,4-dioxane (CAS: 123-91-1), 1,2-dimethoxyethane (CAS: 110-71-4) (DME, monoglyme), diethylene glycol dimethyl ether (CAS: 111-96-6) (diglyme), triethylene glycol dimethyl ether (CAS: 112-49-2) (triglyme), or 1,4,7,10-tetraoxacyclododecane (CAS: 294-93-9) (12-Crown-4).

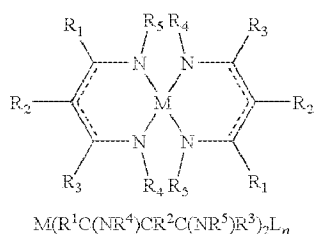
In some embodiments of the disclosure, the adduct forming ligand may comprise a thioether, or mixed ether amine, such as, for example, at least one of 1,7-diaza-12-crown-4: 1,7-dioxa-4,10-diazacyclododecane (CAS: 294-92-8), or 1,2-bis(methylthio)ethane (CAS: 6628-18-8).

In some embodiments, the transition metal halide compound may comprise cobalt chloride N,N,N',N'-tetramethyl-1,2-ethylenediamine (CoCl₂(TMEDA)). In some embodiments, the transition metal halide compound may comprise cobalt bromide tetramethylethylenediamine (CoBr₂(TMEDA)). In some embodiments, the transition metal halide compound may comprise cobalt iodide tetramethylethylenediamine (CoI₂(TMEDA)). In some embodiments, the transition metal halide compound may comprise cobalt chloride N,N,N',N'-tetramethyl-1,3-propanediamine (CoCl₂(TMPDA)). In some embodiments of the disclosure, the transition metal halide compound may comprise at least one of cobalt chloride N,N,N',N'-tetramethyl-1,2-ethylenediamine (CoCl₂(TMEDA)), nickel chloride tetramethyl-1,3-propanediamine (NiCl₂(TMPDA)), or nickel iodide tetramethyl-1,3-propanediamine (NiI₂(TMPDA)).

Other suitable first gas-phase reactants may be substantially free of halogen species. First gas-phase reactants that are substantially free of halogen species (non-halogen containing metal precursors) include $M(\text{dmap})_x$ (dmap = dimethylamino-2-propoxide), wherein M is a metal, β -diketonate, amidinate, and other typical ALD metal precursors. In some embodiments, the non-halogen containing metal precursor may comprise at least one of copper, cobalt and nickel. The non-halogen containing metal precursor may therefore comprise at least one of $\text{Cu}(\text{dmap})_2$, $\text{Ni}(\text{dmap})_2$ or $\text{Co}(\text{dmap})_2$.

In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand in which the metal center atom is bonded through at least one oxygen and at least one nitrogen atom in the bidentate ligand. In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand in which the metal center atom is bonded through at least one nitrogen atom in the bidentate ligand. In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand and at least one other ligand, such as monodentate ligand. In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand and at least two other ligands, such as monodentate ligands. In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand and at least one other ligand, such as monodentate ligand, which is bonded through N or O to the metal center atom. In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand in which the metal center atom is bonded through at least one nitrogen atom and bonded through at least one other atom than nitrogen in the bidentate ligand. In some embodiments the non-halogen containing metal precursor may therefore comprise at least one bidentate ligand in which the metal center atom is bonded through at least two nitrogen atoms in the bidentate ligand. In some embodiments the non-halogen containing metal precursor comprises at least two bidentate ligands. In some embodiments the non-halogen containing metal precursor includes two bidentate ligands.

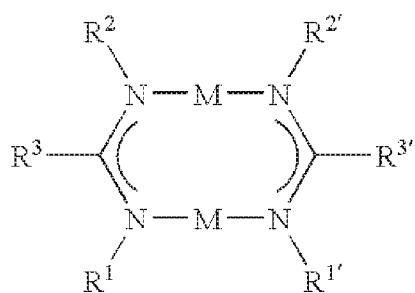
Some examples of suitable non-halide containing betadiketiminato (e.g., $\text{Ni}(\text{pda})_2$, (pda = pentane-2,4,-diketiminato) compounds include at least one β -diketiminato ligand, and have the general formula:



wherein M is a metal selected from nickel, cobalt, ruthenium, iridium, palladium, platinum, silver and gold. Each of R¹⁻⁵ is an organic ligand independently selected from H; and a C₁-C₄ linear or branched, alkyl group, alkylsilyl group, alkylamide group, alkoxide group, or alkylsilylamide group. Each L is independently selected from: a hydrocarbon; an oxygen-containing hydrocarbon; an amine; a polyamine; a bipyridine; an oxygen containing heterocycle; a nitrogen containing heterocycle; and combinations thereof; and n is an integer ranging from 0 to 4, inclusive. A particular example includes Ni(pda)₂.

Some examples of suitable non-halide containing amidinate compounds (e.g., Ni(iPr-AMD)₂) include compounds having a formula selected from the group consisting of M(I)AMD, M(II)AMD₂ and M(III)AMD₃ and oligomers thereof, where M is a metal and AMD is an amidinate moiety, such as copper(I) amidinates, cobalt(II) amidinates, or amidinates of nickel, iron, ruthenium, manganese, chromium, vanadium, niobium, tantalum, titanium and/or lanthanum.

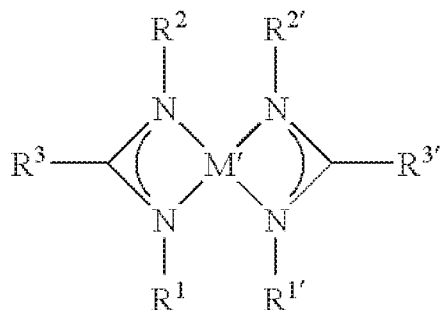
In one or more embodiments, precursors for monovalent metals include volatile metal(I) amidinates, [M(I)(AMD)]_x, where x=2, 3. Some of these compounds have a dimeric structure 1,



in which R¹, R², R³, R^{1'}, R^{2'} and R^{3'} are groups made from one or more non-metal atoms. In some embodiments, R¹, R², R³, R^{1'}, R^{2'} and R^{3'} may be chosen independently from hydrogen, alkyl, aryl, alkenyl, alkynyl, trialkylsilyl or fluoroalkyl groups or other non-metal atoms or groups. In some embodiments, R¹, R², R³, R^{1'}, R^{2'} and R^{3'} are each independently alkyl or fluoroalkyl or silylalkyl groups containing 1 to 4 carbon atoms. Suitable monovalent metals include copper(I), silver(I), gold(I), and iridium(I). In one or more embodiments, the metal amidinate is a copper amidinate, and the copper amidinate comprises copper(I) N,N'-diisopropylacetamidinate, corresponding to taking R¹, R², R^{1'} and R^{2'} as isopropyl groups, and R³ and R^{3'} as methyl groups in the general formula 1. In one or more embodiments, the metal(I) amidinate is a trimer having the general formula [M(I)(AMD)]₃.

In one or more embodiments, divalent metal precursors include volatile metal(II) bis-amidinates, [M(II)(AMD)₂]_x, where x=1, 2. These compounds may have a monomeric structure 2,

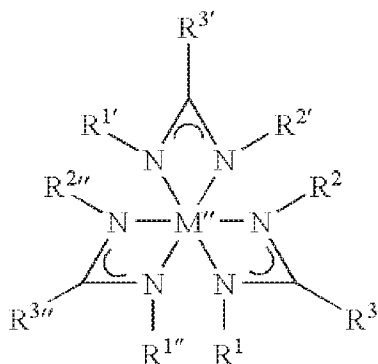
2



in which R^1 , R^2 , R^3 , $R^{1'}$, $R^{2'}$ and $R^{3'}$ are groups made from one or more non-metal atoms. In one or more embodiments, dimers of this structure, e.g., $[M(II)(AMD)_2]_2$, may also be used. In some embodiments, R^1 , R^2 , R^3 , $R^{1'}$, $R^{2'}$ and $R^{3'}$ may be chosen independently from hydrogen, alkyl, aryl, alkenyl, alkynyl, trialkylsilyl, or fluoroalkyl groups or other non-metal atoms or groups. In some embodiments, R^1 , R^2 , R^3 , $R^{1'}$, $R^{2'}$ and $R^{3'}$ are each independently alkyl or fluoroalkyl or silylalkyl groups containing 1 to 4 carbon atoms. Suitable divalent metals include cobalt, iron, nickel, manganese, ruthenium, zinc, titanium, vanadium, chromium, europium, magnesium and calcium. In one or more embodiments, the metal(II) amidinate is a cobalt amidinate, and the cobalt amidinate comprises cobalt(II) bis(N,N' -diisopropylacetamidinate), corresponding to taking R^1 , R^2 , $R^{1'}$ and $R^{2'}$ as isopropyl groups, and R^3 and $R^{3'}$ as methyl groups in the general formula 2.

In one or more embodiments, precursors for trivalent metals include volatile metal(III) tris-amidinates, $M(III)(AMD)_3$. Typically, these compounds have a monomeric structure 3,

3



in which R^1 , R^2 , R^3 , $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{1''}$, $R^{2''}$ and $R^{3''}$ are groups made from one or more non-metal atoms. In some embodiments, R^1 , R^2 , R^3 , $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{1''}$, $R^{2''}$ and $R^{3''}$ may be chosen independently from hydrogen, alkyl, aryl, alkenyl, alkynyl, trialkylsilyl, halogen or partly fluorinated alkyl groups. In some embodiments, R^1 , R^2 , R^3 , $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{1''}$, $R^{2''}$ and $R^{3''}$ are each independently alkyl groups containing 1 to 4 carbon atoms. Suitable trivalent metals include lanthanum, praseodymium and the other lanthanide metals, yttrium, scandium, titanium, vanadium, niobium, tantalum, chromium, iron, ruthenium, cobalt, rhodium, iridium, aluminum, gallium, indium, and bismuth. In one or more embodiments, the metal(III) amidinate is a

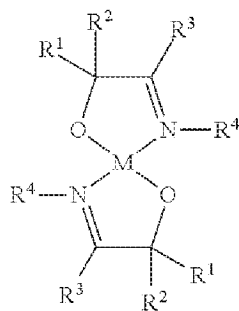
lanthanum amidinate, and the lanthanum amidinate comprises lanthanum(III) tris(N,N'-di-tert-butylacetamidinate), corresponding to taking R¹, R², R^{1'}, R^{2'}, R^{1''} and R^{2''} as tert-butyl groups and R³, R^{3'} and R^{3''} as methyl groups in the general formula 3.

As used herein, metal amidinates having the same ratio of metal to amidinate as the monomer, but varying in the total number of metallamidinate units in the compound are referred to as “oligomers” of the monomer compound. Thus, oligomers of the monomer compound M(R)AMD₂ include [M(II)(AMD)₂]_x, where x is 2, 3, etc. Similarly, oligomers of the monomer compound M(I)AMD include [M(I)AMD]_x, where x is 2, 3, etc.

Particular examples include (N,N'-diisopropylacetamidinato)copper ([Cu(iPr-AMD)]₂), bis(N,N'-diisopropylacetamidinato)cobalt ([Co(iPr-AMD)₂]), cobalt bis(N,N'-di-tert-butylacetamidinate) ([Co(tBu-AMD)₂]), lanthanum tris(N,N'-diisopropylacetamidinate) ([La(iPr-AMD)₃]), lanthanum tris(N,N'-diisopropyl-2-tert-butylamidinate) ([La(iPr-tBuAMD)₃]. ½C₆H₁₂), bis(N,N'-diisopropylacetamidinato)iron ([Fe(iPr-AMD)₂]₂), bis(N,N'-di-tert-butylacetamidinate) ([Fe(tBu-AMD)₂]), bis(N,N'-diisopropylacetamidinato)nickel ([Ni(iPr-AMD)₂]), bis(N,N'-diisopropylacetamidinato)manganese ([Mn(iPr-AMD)₂]₂), manganese bis(N,N'-di-tert-butylacetamidinate) ([Mn(tBu-AMD)₂]), tris(N,N'-diisopropylacetamidinato)titanium ([Ti(iPr-AMD)₃]), tris(N,N'-diisopropylacetamidinato)vanadium ([V(iPr-AMD)₃]), silver (N,N'-diisopropylacetamidinate) ([Ag(iPr-AMD)]_x(x=2 and x=3)), lithium N,N'-di-sec-butylacetamidinate, cobalt bis(N,N'-di-sec-butylacetamidinate) ([Co(sec-Bu-AMD)₂]), copper(I) N,N'-di-sec-butylacetamidinate dimer ([Cu(sec-Bu-AMD)]₂), bismuth tris(N,N'-di-tert-butylacetamidinate) dimer ([Bi(tBu-AMD)₃]₂), strontium bis(N,N'-di-tert-butylacetamidinate) ([Sr(tBu-AMD)₂]_n), bismuth oxide, Bi₂O₃, and tris(N,N'-diisopropylacetamidinato)ruthenium ([Ru(iPr-AMD)₃]).

Some examples of suitable non-halide containing iminoalkoxide compounds are described by the formula:

(I)



wherein M is a metal selected from Groups 2 to 12 of the Periodic Table; and R¹, R², R³, and R⁴ are each independently H or C₁-C₈ alkyl. In a refinement, R¹, R², R³, and R⁴ are each independently methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, or t-butyl. In another refinement, M is Cu, Cr, Mn, Fe, Co, or Ni. Specific examples of compounds having this

formula include, but are not limited to, bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)nickel(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)cobalt(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)iron(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)manganese(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)chromium(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)copper(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)nickel(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)cobalt(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)iron(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)copper(II), bis(3-((tert-butylimino)methyl)-2,2,4,4-tetramethylpentan-3-olate)manganese(II), bis(3-((tert-butylimino)methyl)-2,2,4,4-tetramethylpentan-3-olate)copper(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)nickel(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)cobalt(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)iron(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)manganese(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)chromium(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)copper(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)nickel(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)cobalt(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)iron(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)manganese(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)chromium(II), and bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)copper(II). Particular examples include bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)nickel(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)cobalt(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)iron(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)manganese(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)chromium(II), bis(1-(tert-butylimino)-2,3,3-trimethylbutan-2-olate)copper(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)nickel(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)cobalt(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)iron(II), bis(1-(tert-butylimino)-2,3-dimethylbutan-2-olate)copper(II), bis(3-((tert-butylimino)methyl)-2,2,4,4-tetramethylpentan-3-olate)manganese(II), bis(3-((tert-butylimino)methyl)-2,2,4,4-tetramethylpentan-3-olate)copper(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)cobalt(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)iron(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)manganese(II), bis(3-(isopropylimino)-2-methylbutan-2-olate)chromium(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)nickel(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)cobalt(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)iron(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)manganese(II), bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)chromium(II), and bis(3-(2,2-dimethylhydrazono)-2-methylbutan-2-olate)copper(II).

In some embodiments the non-halogen containing metal precursor does not comprise other metal atoms than the desired metal (e.g., Co, Ni, Cu). In some embodiments the metal in the non-halogen containing metal precursor has oxidation state of 0. In some embodiments the metal in the non-halogen containing metal precursor has oxidation state of +I. In some
 5 embodiments the metal in the non-halogen containing metal precursor has oxidation state of +III. In some embodiments the metal in the non-halogen containing metal precursor has oxidation state of +II. In some embodiments the oxidation state is the oxidation state of the metal in the precursor at room temperature. The oxidation state may change in different conditions, such as in different pressures, temperatures and/or atmospheres as well as when
 10 contacted with different surface materials at the said different conditions. In some embodiments the non-halogen containing metal precursor does not comprise halides, such as F, Cl, Br or I. In some embodiments the non-halogen containing metal precursor comprises carbon, hydrogen and nitrogen and optionally oxygen.

In some embodiments the non-halide containing copper precursor may comprise, for
 15 example, Cu(dmap)₂ or copper(I) N,N'-diisopropylacetamidinate. In some embodiments, copper precursors can be selected from the group consisting of copper betadiketonate compounds, copper betadiketiminato compounds, copper aminoalkoxide compounds, such as Cu(dmae)₂, Cu(deap)₂ or Cu(dmamb)₂, copper amidinate compounds, such as Cu(sBu-amd)₂, copper cyclopentadienyl compounds, copper carbonyl compounds and combinations thereof. In some
 20 embodiments, X(acac)_y or X(thd)_y compounds are used, where X is copper, y is generally, but not necessarily 2 or 3 and thd is 2,2,6,6-tetramethyl-3,5-heptanedionato. In some embodiments the non-halide containing copper precursor is copper(II)acetate, [Cu(HMDS)]₄ or Cu(nhc)HMDS (1,3-di-isopropyl-imidazolin-2-ylidene copper hexamethyl disilazide) or Cu-betadiketiminates, such as Cu(dki)VTMS (dki = diketiminato).

In some embodiments the non-halide containing nickel precursor may be, for example,
 25 bis(4-N-ethylamino-3-penten-2-N-ethyliminato)nickel (II). In some embodiments, nickel precursors can be selected from the group consisting of nickel betadiketonate compounds, nickel betadiketiminato compounds, nickel aminoalkoxide compounds, nickel amidinate compounds, nickel cyclopentadienyl compounds, nickel carbonyl compounds and combinations thereof. In
 30 some embodiments, X(acac)_y or X(thd)_y compounds are used, where X is nickel, y is generally, but not necessarily 2 or 3 and thd is 2,2,6,6-tetramethyl-3,5-heptanedionato.

In some embodiments the Co precursor is a Co beta-diketoiminato compound. In some embodiments the Co precursor is a Co ketoiminate compound. In some embodiments the Co precursor is a Co amidinate compound. In some embodiments the Co precursor is a Co beta-

diketonate compound. In some embodiments the Co precursor contains at least one ketoimine ligand or a derivative thereof. In some embodiments the Co precursor contains at least one amidine ligand or a derivative thereof. In some embodiments the Co precursor contains at least one ketonate ligand or a derivative thereof. In some embodiments the Co precursor is $\text{Co}_2(\text{CO})_8$, CCTBA, CoCp_2 , $\text{Co}(\text{Cp-amd})$, $\text{Co}(\text{Cp}(\text{CO})_2)$, $\text{tBu-AllylCo}(\text{CO})_3$ or $\text{Co}(\text{HMDS})_2$. Alternatively, metal hydrides and/or alanes may be used as a first gas-phase reactant (e.g., for hydride-hydride type reactions).

The second gas-phase reactant used in method 100 can include a metal-containing organic compound. For example, second gas-phase reactant can include a compound selected from the group consisting of compounds having formula of R-M-H (e.g., $\text{R}_{(\text{X-n})}\text{-M}^{\text{X}}\text{-H}_n$), wherein R is an organic group and M is a metal to react with the first metal species to thereby form the metal-containing material. In accordance with various examples, X is the formal oxidation state of M and n can range from 1 to 5. By way of particular examples, M can be or include Sn, In, Ga, Ge, As, Sb, Pb and Bi. Or, M could include Al. For example, M can include Sn, In, or Ga. R can be or include an alkyl group or cyclopentadienyl, amido, alkoxy, amidinato, guanidinato, imido, carboxylato, β -diketonato, β -ketoiminato, malonato, β -diketiminato group with or without additional donor functionalities. Exemplary alkyl groups can be independently selected from the group of C1-C5 alkyl groups. In some cases, the second gas-phase reactant (e.g., the R-M-H compound) can be a metal reducing agent. FIG. 6 illustrates the particular second gas-phase reactant example of tributyltin hydride (TBTH).

Intermetallic films comprised, consisting essentially of, or consisting of the intermetallic compound, such as Co_3Sn_2 or Ni_3Sn_2 , as described herein can exhibit magnetic hysteresis with high coercivity values exceeding 500 Oe. The resistivity values of such films (as well as film formed according to method 200) can range from about 10 to about $10^6 \mu\Omega\text{cm}$, from 20 to $10^4 \mu\Omega\text{cm}$, or from 50 to $1000 \mu\Omega\text{cm}$, for example, 80 to $180 \mu\Omega\text{cm}$, depending on film thickness and/or stoichiometry. Also, Ni_3Sn_2 thin films formed according to method 100 exhibit an intermetallic crystal structure and high purity. Exemplary intermetallic compounds and films can be used in a variety of applications, including, for example, magnetoresistive devices, superconductive devices, as catalysts, as energy (e.g., hydrogen) storage, and the like.

FIG. 2 illustrates another cyclic deposition method 200 in accordance with at least one embodiment of the disclosure. Method 200 can be used to deposit metal-containing material to, for example, form a film or layer comprising, consisting essentially of, or consisting of the metal-containing material. The metal-containing material can include any of the intermetallic compounds described above, as well as other metal-containing compounds described herein.

When films (e.g., formed via either method 100 or 200) consist essentially of or consist of an intermetallic compound, the film may exhibit superior properties as described herein.

Method 200 begins with step 210, which can be the same or similar to step 110. For example, the temperature and pressures within the reaction chamber can be the same or similar to those set forth in step 110.

Method 200 may continue with step 220, which includes providing a first gas-phase, such as any of the first gas-phase reactants described above. This step may be at the same pressure and temperature noted above in connection with step 210. A pulse time or a time that the first gas-phase reactant is provided to the reaction chamber can range from between about 0.01 seconds and about 60 seconds, or between about 0.05 seconds and about 10 seconds, or between about 0.1 seconds and about 5 seconds. During step 220, a flowrate of the first gas-phase reactant may be less than 2000 sccm, or less than 1000 sccm, or less than 500 sccm, or less than 200 sccm, or even less than 100 sccm, or may range from about 1 to about 5000 sccm, from about 5 to about 2000 sccm, or from about 10 to about 1000 sccm.

After step 220 of providing a first gas-phase reactant, any excess first gas-phase reactant and any reaction byproducts may be removed from the reaction chamber by a purge/pump process (step 225). A flow of a purge gas during step 225 may be less than 2000 sccm, or less than 1000 sccm, or less than 500 sccm, or less than 200 sccm, or even less than 100 sccm, or may range from about 1 to about 5000 sccm, from about 5 to about 2000 sccm, or from about 10 to about 1000 sccm. Although separately illustrated, step 125 can be considered part of step 120.

Method 200 may continue with step 230, which includes providing a second gas-phase reactant comprising a compound having a general formula of R-M-H, wherein R is an organic group and M is a metal to react with the first metal species (e.g., on the substrate surface) to thereby form the metal-containing material. The compound having a general formula of R-M-H can be the same as described above. A pulse time or a time that the second gas-phase reactant is provided to the reaction chamber can range from between about 0.01 seconds and about 60 seconds, or between about 0.05 seconds and about 10 seconds, or between about 0.1 seconds and about 5 seconds. During step 230, a flowrate of the second gas-phase reactant may be less than 2000 sccm, or less than 1000 sccm, or less than 500 sccm, or less than 200 sccm, or even less than 100 sccm, or may range from about 1 to about 5000 sccm, from about 5 to about 2000 sccm, or from about 10 to about 1000 sccm. Although separately illustrated, step 225 can be considered part of step 220.

As illustrated in FIG. 2, as the second gas-phase reactant reacts with species on the substrate surface, a metal-containing material—e.g., a film comprising, consisting essentially of, or consisting of the metal-containing material is formed.

After step 230, any excess second gas-phase reactant and any reaction byproducts may be removed from the reaction chamber by a purge/pump process (step 245). A flowrate of a purge gas can be the same as noted above in step 225. Further, although separately illustrated, step 245 can be considered part of step 230.

Steps 220-245 can be repeated as desired in the same or similar manner as steps 120-145 described above in connection with FIG. 1. For example, the steps can be repeated until a desired film thickness or amount of metal-containing material is deposited onto the substrate.

First gas-phase reactant used in step 220 can be or include any of the first gas-phase reactants described herein. As noted above, the first gas-phase reactant and the second gas-phase reactant can include the same or different metals. For example, by combining a first gas-phase reactants, such as GeCl_3 (dioxane) or some other Ge precursor with R_3GeH , an elemental Ge film can be formed. Other elemental films (or multi-metal films) can similarly be formed.

Second gas-phase reactant comprising a compound having a general formula of R-M-H , wherein R is an organic group and M is a metal can be or include any of the R-M-H compounds described herein, such as those described above in connection with method 100.

In accordance with some embodiments of the disclosure, method 100 and/or method 200 can include atomic layer deposition (ALD). ALD is based on typically self-limiting reactions, whereby sequential and alternating pulses of reactants are used to deposit about one atomic (or molecular) monolayer of material per deposition cycle. The deposition conditions and reactants are typically selected to provide self-saturating reactions, such that an adsorbed layer of one reactant leaves a surface termination that is non-reactive with the gas phase reactants of the same reactant. The substrate is subsequently contacted with a different reactant that reacts with the previous termination to enable continued deposition. Thus, each cycle of alternated pulses typically leaves no more than about one monolayer of the desired material. However, as mentioned above, in one or more ALD cycles, more than one monolayer of material may be deposited, for example, if some gas phase reactions occur despite the alternating nature of the process.

In some embodiments, the cyclical deposition processes are used to form metal-containing films on a substrate and the cyclical deposition process may be an ALD-type process. In some embodiments, the cyclical deposition may be a hybrid ALD/CVD or cyclical CVD process. For example, in some embodiments, the growth rate of the ALD process may be low

compared with a CVD process. One approach to increase the growth rate may be that of operating at a higher substrate temperature than that typically employed in an ALD process, resulting in a chemical vapor deposition process, but still taking advantage of the sequential introduction of reactants. Such a process may be referred to as cyclical CVD.

5 The cyclical deposition processes described herein may be performed in an ALD or CVD deposition system with a heated substrate. For example, in some embodiments, methods may comprise heating the substrate to a temperature of between approximately 80 °C and approximately 150 °C, or even heating the substrate to a temperature of between approximately 80 °C and approximately 120 °C. Of course, the appropriate temperature window for any given
10 cyclical deposition process, such as for an ALD reaction, will depend upon the surface termination and reactant species involved. Here, the temperature varies depending on the reactants being used and is generally at or below about 700 °C. In some embodiments, the deposition temperature is generally at or above about 100 °C for vapor deposition processes, in some embodiments, the deposition temperature is between about 100 °C and about 300 °C, and
15 in some embodiments, the deposition temperature is between about 120 °C and about 200 °C. In some embodiments, the deposition temperature is less than about 500 °C, or less than below about 400 °C, or less than about 350 °C, or below about 300 °C. In some instances, the deposition temperature can be below about 300 °C, below about 200 °C or below about 100 °C. In some instances, the deposition temperature can be above about 20 °C, above about 50 °C and
20 above about 75 °C. In some embodiments of the disclosure, the deposition temperature, i.e., the temperature of the substrate during deposition, is the same or similar to the temperatures noted above in connection with methods 100 and 200.

As illustrated in FIGS. 1 and 2, cyclic processes, including ALD processes, may include purge steps, such as purge steps 125, 145, 225, and 245 described above. Purge gases used
25 during such steps can include one or more inert gases, such as argon (Ar) or nitrogen (N₂), to prevent or mitigate gas-phase reactions between reactants, between process steps and to enable self-saturating surface reactions. In some embodiments, however, the substrate may additionally or alternatively be moved (e.g., to another reaction chamber) to separately contact a first gas-phase reactant and a second gas-phase reactant. Thus, steps 120/130 and/or steps 220/230
30 need not be performed in the same reaction chamber. Additionally or alternatively, a vacuum pump may be used to assist in the purging.

It should be appreciated that in some embodiments of the disclosure, the order of providing a first gas-phase reactant and providing a second gas-phase reactant may be such that the substrate is first contacted with the second gas-phase reactant followed by the first gas-phase

reactant. In other words, steps 120, 130 and 220, 230 can be reversed. In addition, in some embodiments, the cyclical deposition process may comprise contacting the substrate with first gas-phase reactant one or more times prior to contacting the substrate with second gas-phase reactant one or more times and similarly may alternatively comprise contacting the substrate with the second gas-phase reactant one or more times prior to contacting the substrate with the first gas-phase reactant one or more times.

At least some embodiments of the disclosure (e.g., method 100 and/or method 200) may comprise non-plasma reactants, e.g., the first and second gas-phase reactants are substantially free of ionized reactive species. In some embodiments, the first and second gas-phase reactants are substantially free of ionized reactive species, excited species or radical species. For example, both the first gas-phase reactant and the second gas-phase reactant may comprise non-plasma reactants to prevent ionization damage to the underlying substrate and the associated defects thereby created. The use of non-plasma reactants may be especially useful when the underlying substrate contains fragile fabricated, or least partially fabricated, semiconductor device structures, as the high energy plasma species may damage and/or deteriorate device performance characteristics.

Although not illustrated in FIG. 2, in some embodiments of the disclosure, exemplary methods of the disclosure may comprise an additional process step comprising contacting the substrate with a third vapor phase reactant comprising a reducing agent. In some embodiments, the reducing agent may comprise at least one of hydrogen (H_2), a hydrogen (H_2) plasma, ammonia (NH_3), an ammonia (NH_3) plasma, hydrazine (N_2H_4), silane (SiH_4), disilane (Si_2H_6), trisilane (Si_3H_8), germane (GeH_4), digermane (Ge_2H_6), borane (BH_3), diborane (B_2H_6), tertiary butyl hydrazine ($C_4H_{12}N_2$), a selenium reactant, a boron reactant, a phosphorous reactant, a sulfur reactant, an organic reactant (e.g., alcohols, aldehydes, or carboxylic acids) or a hydrogen reactant. In some embodiments of the disclosure, exemplary cyclical deposition methods of the disclosure may comprise contacting the substrate with a second vapor phase reactant which is a reducing agent (without any additional precursor/reactant contacting steps). However, as noted above, in accordance with at least some examples, no reducing agent or reduction reaction is required to form the desired material, such as intermetallic material.

If used, the third vapor phase reactant comprising a reducing agent may be introduced into the reaction chamber and contact the substrate at a number of process stages in an exemplary cyclical deposition method. In some embodiments of the disclosure, the reducing agent may be introduced into the reaction chamber and contact the substrate separately from the first gas-phase reactant and/or separately from the second gas-phase reactant. For example, the

reducing agent may be introduced into the reaction chamber and contact the substrate prior to contacting the substrate with the first gas-phase reactant, after contacting the substrate with the first gas-phase reactant and prior to contacting the substrate with the second gas-phase reactant, and/or after contacting the substrate with the second gas-phase reactant. In some embodiments of the disclosure, the reducing agent may be introduced into the reaction chamber and contact the substrate simultaneously with the first gas-phase reactant and/or simultaneously with the second gas-phase reactant. For example, the reducing agent and the first gas-phase reactant may be co-flowed into the reaction chamber and simultaneously contact the substrate, and/or the reducing agent and the second gas-phase reactant may be co-flowed into the reaction chamber and simultaneously contact the substrate.

In some embodiments, the growth rate of the metal-containing material and/or intermetallic compound is from about 0.005 Å/cycle to about 5 Å/cycle, from about 0.01 Å/cycle to about 2.0 Å/cycle. In some embodiments, the growth rate of metal-containing material and/or intermetallic compound is more than about 0.05 Å/cycle, more than about 0.1 Å/cycle, more than about 0.15 Å/cycle, more than about 0.20 Å/cycle, more than about 0.25 Å/cycle, or more than about 0.3 Å/cycle. In some embodiments, the growth rate of the metal-containing material and/or intermetallic compound is less than about 2.0 Å/cycle, less than about 1.0 Å/cycle, less than about 0.75 Å/cycle, less than about 0.5 Å/cycle, or less than about 0.2 Å/cycle. In some embodiments of the disclosure, the growth rate of the metal-containing material and/or intermetallic compound may be approximately 0.4 Å/cycle. By way of particular examples, in the case of Co_3Sn_2 , the growth ranged from about 0.7 and 1.3 Å/cycle at deposition temperatures of about 170-200 °C, and in the case of Ni_3Sn_2 , a growth rate of about 1.3 Å/cycle at 160 °C was observed when $\text{NiCl}_2(\text{TMPDA})$ was used as a first gas-phase reactant.

FIG. 3 illustrates a structure 300 that includes a substrate 302 and a layer or film 304. Structure 300 can be or include a partially-fabricated device structure. As noted above, substrate 302 can include bulk material, such as bulk semiconductor material, and layers formed thereon and/or therein. Film 302 can include an intermetallic compound or a metal-containing material, such as intermetallic compound or metal-containing material deposited according to the embodiments described herein. In some embodiments, film 304 may be continuous at a thickness below approximately 100 nanometers, or below approximately 60 nanometers, or below approximately 50 nanometers, or below approximately 40 nanometers, or below approximately 30 nanometers, or below approximately 25 nanometers, or below approximately 20 nanometers, or below approximately 15 nanometers, or below approximately 10 nanometers, or below approximately 5 nanometers, or lower. The continuity referred to herein can be

physical continuity or electrical continuity. In some embodiments, the thickness at which film 304 may be physically continuous may not be the same as the thickness at which a film is electrically continuous, and the thickness at which a film 304 may be electrically continuous may not be the same as the thickness at which a film is physically continuous.

5 In some embodiments, the intermetallic and/or metal-containing film (e.g., film 304) deposited according to some of the embodiments described herein may have a thickness from about 20 nanometers to about 100 nanometers. In some embodiments, the intermetallic and/or metal-containing film deposited according to some of the embodiments described herein may have a thickness from about 20 nanometers to about 60 nanometers. In some embodiments, the
10 intermetallic and/or metal-containing film deposited according to some of the embodiments described herein may have a thickness greater than about 20 nanometers, or greater than about 30 nanometers, or greater than about 40 nanometers, or greater than about 50 nanometers, or greater than about 60 nanometers, or greater than about 100 nanometers, or greater than about 250 nanometers, or greater than about 500 nanometers. In some embodiments, the intermetallic
15 and/or metal-containing film deposited according to some of the embodiments described herein may have a thickness of less than about 50 nanometers, less than about 30 nanometers, less than about 20 nanometers, less than about 15 nanometers, less than about 10 nanometers, less than about 5 nanometers, less than about 3 nanometers, less than about 2 nanometers, or even less than about 1 nanometer.

20 In some embodiments of the disclosure, the intermetallic and/or metal-containing film may be deposited on a three-dimensional structure, e.g., a non-planar substrate comprising high aspect ratio features. In some embodiments, the step coverage of the intermetallic and/or metal-containing film may be equal to or greater than about 50%, or greater than about 80%, or greater than about 90%, or greater than about 95%, or greater than about 98%, or greater than about
25 99%, or greater in structures having aspect ratios (height/width) of more than about 2, more than about 5, more than about 10, more than about 25, more than about 50, or even more than about 100.

The intermetallic compound and/or metal-containing material or corresponding films thereof comprises the first metal and the second metal as described herein. By way of particular
30 examples, the first metal can include Co, Ni, Pt, or any of the other first metals noted herein and the second metal can include Sn, In, Ga, Ge, As, Sb, Pb and Bi (e.g., Sn, In, or Fe) or any of the other second metals noted herein, including Al. Exemplary intermetallic and/or metal-containing compounds include (hexagonal) Co_3Sn_2 or Ni_3Sn_2 . Intermetallic and/or metal-containing compounds could also have other stoichiometry or other crystal structure, which can

be obtained by, for example, heat treatment or by tuning the deposition conditions. Other exemplary intermetallic compounds and/or metal-containing materials comprise compounds of In-Sb, Pt-In, Pt-Sn, Pt-Ir, Pd-Pt, Ru-Pt, Ru, Co, Co-W, Ru-Mn, Cu-Mn, and Co-Pt. Other particular examples of intermetallic compounds and/or metal-containing materials include Co, Ni, Cu, and/or Pt and one or more of Sn, In, Ga, Ge, As, Sb, Pb, Al, and Bi. In some cases, a film including the intermetallic compound and/or metal-containing material does not include Al, Ga, and/or In and a transition metal.

In some embodiments of the disclosure, intermetallic compound and/or metal-containing material and/or films including same, as described herein, may comprise less than about 5 atomic % oxygen, less than about 2 atomic % oxygen, less than about 1 atomic % oxygen, or less than about 0.5 atomic % oxygen. In further embodiments, the compounds, materials, or films may comprise less than about 5 atomic % hydrogen, or less than about 2 atomic % hydrogen, or less than about 1 atomic % hydrogen, or even less than about 0.5 atomic % hydrogen. In yet further embodiments, the compounds, materials, or films may comprise less than about 5 atomic % carbon, or less than about 2 atomic % carbon, or less than about 1 atomic % carbon, or even less than about 0.5 atomic % carbon. In yet further embodiments, the compounds, materials, and films may comprise less than about 5 atomic % halide species, or less than about 2 atomic % halide species, or less than about 1 atomic % halide species, or even less than about 0.5 atomic % halide species. In some embodiments, the atomic % composition of the intermetallic compounds, metal-containing materials, and films including same may be determined utilizing time of flight elastic recoil detection analysis (ToF-ERDA).

Reactors capable of being used to deposit metal-containing films can be used to form the intermetallic compounds, metal-containing materials, and films described herein. Such reactors include ALD reactors, as well as CVD reactors equipped with appropriate equipment and means for providing the reactants. According to some embodiments, a hot-walled, cross-flow reactor can be used. According to some embodiments, other cross-flow, batch, minibatch, or spatial ALD reactors may be used.

Examples of suitable reactors that may be used include commercially available single substrate (or single wafer) deposition equipment such as Pulsar® reactors (such as the Pulsar® 2000 and the Pulsar® 3000 and Pulsar® XP ALD), and EmerALD® XP and the EmerALD® reactors, available from ASM America, Inc. of Phoenix, Arizona and ASM Europe B.V., Almere, Netherlands. Other commercially available reactors include those from ASM Japan K.K. (Tokyo, Japan) under the tradename Eagle® XP and XP8. In some embodiments, the reactor is a spatial ALD reactor, in which the substrate moves or rotates during processing.

In some embodiments of the disclosure, a batch reactor may be used. Suitable batch reactors include, but are not limited to, Advance® 400 Series reactors commercially available from ASM Europe B.V. (Almere, Netherlands) under the trade names A400 and A412 PLUS. In some embodiments, the wafers rotate during processing. In other embodiments, the batch reactor comprises a minibatch reactor configured to accommodate 10 or fewer substrates (e.g., semiconductor wafers), 8 or fewer substrates, 6 or fewer substrates, 4 or fewer substrates, or 2 or fewer substrates. In some embodiments in which a batch reactor is used, wafer-to-wafer non-uniformity is less than 3% (1sigma), less than 2%, less than 1% or even less than 0.5%.

The deposition processes described herein can optionally be carried out in a reactor or a reaction chamber connected to a cluster tool. In a cluster tool, because each reaction chamber is dedicated to one type of process, the temperature of the reaction chamber in each module can be kept constant, which improves the throughput compared to a reactor in which the substrate is heated up to the process temperature before each run. Additionally, in a cluster tool it is possible to reduce the time to pump the reaction chamber to the desired process pressure levels between substrates. In some embodiments of the disclosure, the deposition process may be performed in a cluster tool comprising multiple reaction chambers, wherein each individual reaction chamber may be utilized to expose the substrate to an individual reactant gas and the substrate may be transferred between the different reaction chambers for exposure to multiple reactant gases, the transfer of the substrate being performed under a controlled environment to prevent oxidation/contamination of the substrate. In some embodiments of the disclosure, the deposition process may be performed in a cluster tool comprising multiple reaction chambers, wherein each individual reaction chamber may be configured to heat the substrate to a different deposition temperature.

A stand-alone reactor can be equipped with a load-lock. In that case, it is not necessary to cool down the reaction space between each run.

FIG. 5 schematically illustrates a reactor system 500 in accordance with at least one embodiment of the disclosure. Reactor system 500 can be used to, for example, perform the cyclic deposition (e.g., ALD) methods as described herein and/or to form the structures, films, compounds and/or materials as described herein.

In the illustrated example, reactor system 500 includes an optional substrate handling system 502, a reaction chamber 504, a gas distribution system 506, and optionally a wall 508 disposed between reaction chamber 504 and substrate handling system 502. System 500 can also include a first gas-phase reactant source 512, a second gas-phase reactant source 514, and an exhaust source 510. Although illustrated with two gas sources 512, 514, reactor system 500 can

include any suitable number of reactant gas sources. By way of examples, exemplary reactor systems can include at least two reactant gas sources (e.g., sources that include compounds that become the first or second gas-phase reactant) and optionally one or more carrier and/or purge gas sources 516. Reactor system 500 also includes a susceptor 518 to hold one or more substrates 520 during processing.

Reactor system 500 can include any suitable number of reaction chambers 104 and substrate handling systems 502. By way of example, reaction chamber 504 of reactor system 500 includes a cross-flow, hot-wall epitaxial reaction chamber. An exemplary reactor system including a horizontal flow reactor is available as a system from ASM.

It should be noted that FIG. 5 is a simplified schematic version of reactor system 500 and does not contain each and every element, such as, but not limited to, valves, electrical connections, mass flow controllers, seals, and gas conduits, that may be utilized in the reactor system 500.

In some embodiments of the disclosure, one or more reactant source vessels 522, 524 are in fluid communication, via conduits or other appropriate means 526, 528, to the reaction chamber 504 and may further be coupled to gas distribution system 506 disposed between reactant source vessels 522, 524 and reaction chamber 504. Gas distribution system 506 can include, for example, a manifold, valve control systems, mass flow control systems, and/or other mechanism to control a gaseous reactant originating reactant source vessels 522 or 524. Reactant source vessels 522, 524 may be configured for storing a metal-containing compound (e.g., an organometallic or metal organic compound) that is or that upon heating becomes the first gas-phase reactant and the second gas-phase reactant, respectively. In some embodiments, the reactant source vessels 522, 524 may comprise a quartz material, which may be substantially chemically inert to the respective first and second reactants stored within source vessels 522, 524. In alternative embodiments of the disclosure, reactant source vessels 522, 524 may be fabricated from a corrosion resistant metal or metal alloy, such as, for example, Hastelloy, Monel, or a combination thereof.

In some embodiments of the disclosure, reactant source vessels 522, 524 may further comprise one or more heating units 526, 528 configured for heating the compound stored in reactant source vessels 522, 524 to a desired temperature. In some embodiments, the one or more heating units may be utilized to heat the compound to a temperature of approximately greater than 0 °C, or approximately greater than 20 °C, or approximately greater than 100 °C, or approximately greater than 150 °C, or approximately greater than 200 °C, or approximately greater than 200 °C, or approximately greater than 300 °C, or even approximately greater than

400 °C. In some embodiments, the one or more heating units 526, 528 may be configured to heat the compound stored in the reactant source vessels 522, 524 to a temperature of approximately about 25 °C to about 200 °C, about 25 °C to about 300 °C, or about 25 °C to about 400 °C. By way of particular examples, when a gas-phase reactant includes Bu_3SnH , the temperature could range from about 20 °C to about 40 °C, or be about 30 °C; when a reactant includes $\text{CoCl}_2(\text{TMEDA})$, the temperature could range from about 150 °C to about 190 °C, or be about 170 °C; when the reactant includes $\text{NiCl}_2(\text{TMPDA})$, the temperature could range from about 140 °C to about 180 °C, or be about 157 °C; and when the reactant included $\text{Ni}(\text{dmap})_2$, the temperature could range from about 50 °C to about 70 °C, or be about 62 °C.

In some embodiments, one or more heating units 526, 528 associated with reactant source vessels 522, 524 are configured for converting a compound from a solid to either a liquid or a gas to form the first gas-phase reactant or the second gas-phase reactant. In some embodiments, the one or more heating units 526, 528 associated with reactant source vessels 522, 524, respectively, may be utilized to control the viscosity of the reactant compound stored in reactant source vessels 522, 524. In some embodiments, the one or more heating units 526, 528 associated with the respective reactant source vessels 522, 524 may be configured for controlling the vapor pressure generated by the compound stored within reactant source vessels 522, 524. In some embodiments of the disclosure, the compound may have a vapor pressure greater than 0.01 mbar at a temperature greater than 25 °C, or greater than 50 °C, or even greater than 100 °C. In some embodiments of the disclosure, the compound may have a vapor pressure greater than 0.01 mbar at a temperature of less than 350 °C, or less than 250 °C, or less than 200 °C, or even less than 150 °C. In some embodiments of the disclosure, the compound may have a vapor pressure greater than 0.1 mbar at a temperature greater than 25 °C, or even greater than 100 °C. In some embodiments of the disclosure, the compound may have a vapor pressure greater than 0.1 mbar at a temperature of less than 400 °C, or less than 200 °C, or even less than 100 °C. In some embodiments of the disclosure, the compound may have a vapor pressure greater than 1 mbar at a temperature of greater than 25 °C, or even greater than 100 °C. For example, the compound may be heated to a temperature greater than 150 °C, generating a vapor pressure of greater than 0.001 mbar.

In some embodiments of the disclosure, a vapor passageway 530 may be connected to the reactant source vessel 522 (and/or reactant source vessel 524), such that one or more carrier gases (e.g., from source 516 or another source) may be transported from a carrier gas storage vessel into reactant source vessel 522 via the vapor passageway 530. In some embodiments, a mass flow controller (not shown) may be placed on vapor passageway 530 and disposed

proximate to reactant source vessel 522. For example, a mass flow controller may be calibrated to control the mass flux of the carrier gas entering reactant source vessel 522, thereby allowing greater control over the subsequent flow of the reactant vapor from out of the reactant source vessel 522 to the reaction chamber 504.

5 In some embodiments, the carrier gas (e.g., hydrogen, nitrogen, helium, argon, or any mixtures thereof) may be flowed over an exposed surface of the compound, thereby picking up a portion of the vapor from the compound and transporting the compound (now a first or second gas-phase reactant), along with the carrier gas, to reaction chamber 504. In alternative
10 embodiments of the disclosure, the carrier gas may be “bubbled” through the compound, e.g., by optional vapor passageway (not illustrated), thereby agitating and picking up a portion of metal-containing compound and transporting metal-containing compound vapor (now the first or second gas-phase reactant) to reaction chamber 504 via gas conduit 526.

In some embodiments of the disclosure, reactor system 500 may further comprise a system operation and control mechanism 532 that provides electronic circuitry and mechanical
15 components to selectively operate valves, manifold, pumps, and other equipment associated with reactor system 500. Such circuitry and components operate to introduce reactants, purge gas, and/or carrier gases from the respective reactant source vessels, 522, 524 and purge gas vessel 534. The system operation and control mechanism 532 may also control the timing of gas pulse sequences, the temperature of the substrate and/or reaction chamber, and the pressure of the
20 reaction chamber and various other operations necessary to provide proper operation to reactor system 500. Operation and control mechanism 532 may include control software and electrically or pneumatically controlled valves to control the flow of reactants, carrier gases, and/or purge gases into and out of reaction chamber 504. System operation and control mechanism 532 can include modules, such as software and/or hardware components, e.g., a FPGA or ASIC, which
25 perform certain tasks. A module can adversely be configured to reside on the addressable storage medium of system operation and control mechanism 532 and be configured to execute one or more processes.

Various other configurations of reactor systems are possible, including different number and kind of reactant sources and purge gas sources. Further, there are many arrangements of
30 valves, conduits, reactant sources, purge gas sources that may be used to accomplish the goal of selectively feeding gases into reaction chamber 504.

Examples

The examples provide below illustrate particular processes, films, and structures in accordance with exemplary embodiments of the disclosure. These examples are illustrative and are not meant to limit the scope of the disclosure.

- 5 1. A cyclic deposition process for depositing an intermetallic compound, the cyclic deposition method comprising the steps of:
providing a first gas-phase reactant comprising a first metal to a reaction chamber to react with a surface of a substrate to form a first metal species; and
providing a second gas-phase reactant comprising a second metal to the reaction
10 chamber to react with the first metal species to thereby form the intermetallic compound.
2. The cyclic deposition process of example 1, further comprising repeating the steps of providing the first gas-phase reactant and providing the second gas-phase reactant until a desired
15 film thickness is achieved.
3. The cyclic deposition process of example 1, further comprising one or more purging steps, wherein at least one of the purging steps occurs after the step of providing the first gas-phase reactant and before the step of providing the second gas-phase reactant.
- 20 4. The cyclic deposition process of example 1, wherein the cyclic deposition process comprises atomic layer deposition.
5. The cyclic deposition process of example 1, wherein the cyclic deposition process comprises cyclic chemical vapor deposition.
- 25 6. The cyclic deposition process of example 1, wherein a temperature within a reaction chamber during the steps of providing the first gas-phase reactant and providing the second gas-phase reactant is greater than 0 °C and less than 600 °C, less than 500 °C, less than 400 °C, less than 300 °C or less than 250 °C, or between about 20 °C to about 700 °C, about 50 °C to about
30 500 °C, or about 50 °C to about 400 °C, about 75 °C to about 300 °C or about 100 °C to about 250 °C.
7. The cyclic deposition process of example 1, wherein the second gas-phase reactant comprises a metal-containing organic compound.

8. The cyclic deposition process of example 1, wherein the second gas-phase reactant is selected from the group consisting of compounds having formula of R-M-H wherein R is an organic group and M is a metal.
- 5 9. The cyclic deposition process of example 1, wherein the second metal is selected from the group consisting of Sn, In, Al, Ga, Ge, As, Sb, Pb and Bi.
10. The cyclic deposition process of example 1, wherein the second metal is selected from the group consisting of Sn, , Ge, As, Sb, Pb and Bi.
- 10 11. The cyclic deposition process of example 1, wherein the second metal comprises Sn.
12. The cyclic deposition process of example 1, wherein the second metal comprises In.
- 15 13. The cyclic deposition process of example 1, wherein the second metal comprises Ga.
14. The cyclic deposition process of example 8, wherein the group consisting of compounds having formula of R-M-H have formula of $R_{(X-n)}-M^X-H_n$, wherein X is the formal oxidation state of the metal and n is 1 to 5.
- 20 15. The cyclic deposition process of any of examples 8 and 14, wherein R comprises an alkyl group or other organic group.
16. The cyclic deposition process of any of examples 8 and 14, wherein R is independently
25 selected from the group consisting of C1-C5 alkyl groups.
17. The cyclic deposition process of any of examples 8 and 14, wherein R is
cyclopentadienyl, amido, alkoxy, amidinato, guanidinato, imido, carboxylato, β -diketonato, β -
ketoiminato, malonato, β -diketiminato group with or without additional donor functionalities.
- 30 18. The cyclic deposition process of example 1, wherein the second gas-phase reactant comprises a metallic reducing agent.

19. The cyclic deposition process of example 1, wherein the first metal is selected from the group consisting of transition metals.
20. The cyclic deposition process of example 1, wherein the first metal is selected from the group consisting of group 3-6 metals.
21. The cyclic deposition process of example 1, wherein the first metal is selected from the group consisting of group 7-12 metals.
22. The cyclic deposition process of example 1, wherein the first metal is selected from the group consisting of lanthanides.
23. The cyclic deposition process of example 1, wherein the first metal is selected from the group consisting of group 8-11 metals.
24. The cyclic deposition process of example 1, wherein the first metal is selected from the group consisting of group 9-10 metals.
25. The cyclic deposition process of example 1, wherein the first gas-phase reactant is selected from the group consisting of metal halides.
26. The cyclic deposition process of example 1, wherein the first gas-phase reactant comprises $M(\text{dmap})_x$ (dmap = dimethylamino-2-propoxide), wherein M is a metal.
27. The cyclic deposition process of example 1, wherein the first gas-phase reactant is selected from the group consisting of metal hydrides and alanes.
28. The cyclic deposition process of example 1, wherein the first gas-phase reactant comprises a diamine adduct of a corresponding metal chloride.
29. The cyclic deposition process of example 1, wherein the first gas-phase reactant comprises a metal halide compound comprising a bidentate nitrogen containing adduct ligand.

30. The cyclic deposition process of example 29, wherein the adduct ligand comprises two nitrogen atoms, and wherein each of nitrogen atoms bonded to at least one carbon atom.
31. The cyclic deposition process of example 1, wherein the first gas-phase reactant
5 comprises at least one of cobalt chloride (TMEDA) and nickel chloride (TMPDA).
32. The cyclic deposition process of example 1, wherein the second gas-phase reactant comprises TBTH.
- 10 33. The cyclic deposition process of example 1, wherein the intermetallic compound does not include Al, Ga, and/or In and a transition metal.
34. A cyclic deposition process for forming a metal-containing material, the cyclic deposition process comprising:
15 providing a first gas-phase precursor comprising a first metal to a reaction chamber to form a first metal species; and
providing a second gas-phase reactant comprising a compound having a general formula of R-M-H, wherein R is an organic group and M is a metal to react with the first metal species to thereby form the metal-containing material.
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35. The cyclic deposition process of example 34, wherein the first metal and the second metal are the same.
36. The cyclic deposition process of example 34, wherein the metal-containing material
25 comprises elemental metal.
37. The cyclic deposition process of example 1 or 34, wherein the metal-containing material comprises a mixture of, for example, In and Ge or other first and/or second metals.
- 30 38. The cyclic deposition process of example 34, further comprising repeating the steps of providing the first gas-phase reactant and providing the second gas-phase reactant until a desired film thickness is achieved.

39. The cyclic deposition process of example 34, further comprising one or more purging steps, wherein at least one of the purging steps occurs after the step of providing the first gas-phase reactant and before the step of providing the second gas-phase reactant.

5 40. The cyclic deposition process of example 34, wherein the cyclic deposition process comprises atomic layer deposition.

41. The cyclic deposition process of example 34, wherein the cyclic deposition process comprises cyclic chemical vapor deposition.

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42. The cyclic deposition process of example 34, wherein a temperature within a reaction chamber during the steps of providing the first gas-phase reactant and providing the second gas-phase reactant is greater than 0 °C and less than 600 °C, less than 500 °C, less than 400 °C, less than 300 °C or less than 250 °C, or between about 20 °C to about 700 °C, about 50 °C to about 500 °C, or about 50 °C to about 400 °C, about 75 °C to about 300 °C or about 100 °C to about 250 °C.

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43. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of Sn, In, Ga, Al, Ge, As, Sb, Pb and Bi.

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44. The cyclic deposition process of example 34, wherein the second metal is selected from the group consisting of Sn, , Ge, As, Sb, Pb and Bi.

45. The cyclic deposition process of example 34, wherein the second metal comprises Sn.

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46. The cyclic deposition process of example 34, wherein the second metal comprises In.

47. The cyclic deposition process of example 34, wherein the second metal comprises Ga.

30 48. The cyclic deposition process of example 34, wherein the metal-containing material comprises one or more of a metal mixture, an alloy, and an intermetallic compound.

49. The cyclic deposition process of example 34, wherein the metal-containing material is one or more of metallic, conductive, non-conductive, semiconductive, superconductive, catalytic, ferromagnetic and magnetoresistive.
- 5 50. The cyclic deposition process of example 34, wherein the compound having a general formula of R-M-H has formula of $R_{(X-n)}-M^X-H_n$, wherein X is the formal oxidation state of the metal and n is 1 to 5.
- 10 51. The cyclic deposition process of example 34, wherein R comprises an alkyl group or other organic group.
52. The cyclic deposition process of example 34, wherein R is independently selected from the group consisting of C1-C5 alkyl groups.
- 15 53. The cyclic deposition process of any of examples 34-52, wherein R is cyclopentadienyl, amido, alkoxy, amidinato, guanidinato, imido, carboxylato, β -diketonato, β -ketoiminato, malonato, β -diketiminato group with or without additional donor functionalities.
- 20 54. The cyclic deposition process of example 34, wherein the second gas-phase reactant comprises a metallic reducing agent.
55. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of transition metals.
- 25 56. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of group 3-6 metals.
57. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of group 7-12 metals.
- 30 58. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of lanthanides.

59. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of group 8-11 metals.
60. The cyclic deposition process of example 34, wherein the first metal is selected from the group consisting of group 9-10 metals.
61. The cyclic deposition process of example 34, wherein the first gas-phase reactant is selected from the group consisting of metal halides.
62. The cyclic deposition process of example 34, wherein the first gas-phase reactant comprises $M(\text{dmap})_x$ (dmap = dimethylamino-2-propoxide), wherein M is a metal.
63. The cyclic deposition process of example 34, wherein the first gas-phase reactant is selected from the group consisting of metal hydrides and alanes.
64. The cyclic deposition process of example 34, wherein the first gas-phase reactant comprises a diamine adduct of a corresponding metal chloride.
65. The cyclic deposition process of example 34, wherein the first gas-phase reactant comprises a metal halide compound comprising a bidentate nitrogen containing adduct ligand.
66. The cyclic deposition process of example 65, wherein the adduct ligand comprises two nitrogen atoms, and wherein each of nitrogen atoms bonded to at least one carbon atom.
67. The cyclic deposition process of example 34, wherein the first gas-phase reactant comprises at least one of cobalt chloride (TMEDA) and nickel chloride (TMPDA).
68. The cyclic deposition process of example 34, wherein the second gas-phase reactant comprises TBTH.
69. A film formed according to a process of any of examples 1-33.
70. The film of example 69, wherein the film is metallic, conductive, semiconductive, or non-conductive.

71. The film of example 69, wherein the film is superconductive.

72. The film of example 69, wherein the film is magnetoresistive.

5 73. The film of example 69, wherein the film is ferromagnetic.

74. The film of example 69, wherein the film is a catalyst.

75. A film formed according to a process of any of examples 34-68.

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76. The film of example 75, wherein the film comprises one or more of a metal mixture, an alloy, and an intermetallic compound.

77. A device structure including the film according to one or more of examples 69 and 76.

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The example embodiments of the disclosure described above do not limit the scope of the invention, since these embodiments are merely examples of the embodiments of the invention, which is defined by the appended claims and their legal equivalents. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various
20 modifications of the disclosure, in addition to those shown and described herein, such as alternative useful combinations of the elements described, may become apparent from the description. Such modifications and embodiments are also intended to fall within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A cyclic deposition process for depositing an intermetallic compound, the cyclic deposition method comprising the steps of:
providing a first gas-phase reactant comprising a first metal to a reaction chamber to react with a surface of a substrate to form a first metal species; and
providing a second gas-phase reactant comprising a second metal to the reaction chamber to react with the first metal species to thereby form the intermetallic compound.
2. The cyclic deposition process of claim 1, wherein the second gas-phase reactant comprises a metal-containing organic compound.
3. The cyclic deposition process of claim 1, wherein the second gas-phase reactant is selected from the group consisting of compounds having formula of R-M-H wherein R is an organic group and M is a metal.
4. The cyclic deposition process of claim 1, wherein the second metal is selected from the group consisting of Sn, In, Al, Ga, Ge, As, Sb, Pb and Bi.
5. The cyclic deposition process of claim 3, wherein the group consisting of compounds having formula of R-M-H have formula of $R_{(X-n)}-M^X-H_n$, wherein X is the formal oxidation state of the metal and n is 1 to 5.
6. The cyclic deposition process of any of claims 3 and 5, wherein R is independently selected from the group consisting of C1-C5 alkyl groups.
7. The cyclic deposition process of any of claims 3 and 5, wherein R is cyclopentadienyl, amido, alkoxy, amidinato, guanidinato, imido, carboxylato, β -diketonato, β -ketoiminato, malonato, β -diketiminato group with or without additional donor functionalities.
8. The cyclic deposition process of claim 1, wherein the second gas-phase reactant comprises a metallic reducing agent.

9. The cyclic deposition process of claim 1, wherein the first gas-phase reactant comprises a diamine adduct of a corresponding metal chloride.
10. The cyclic deposition process of claim 1, wherein the first gas-phase reactant comprises a metal halide compound comprising a bidentate nitrogen containing adduct ligand.
11. The cyclic deposition process of claim 1, wherein the first gas-phase reactant comprises at least one of cobalt chloride (TMEDA) and nickel chloride (TMPDA).
12. The cyclic deposition process of claim 1, wherein the second gas-phase reactant comprises TBTH.
13. A cyclic deposition process for forming a metal-containing material, the cyclic deposition process comprising:
 - providing a first gas-phase precursor comprising a first metal to a reaction chamber to form a first metal species; and
 - providing a second gas-phase reactant comprising a compound having a general formula of $R-M-H$, wherein R is an organic group and M is a metal to react with the first metal species to thereby form the metal-containing material,
 - wherein a temperature within the reaction chamber is greater than 0 °C and less than 600 °C.
14. The cyclic deposition process of claim 13, wherein the metal-containing material comprises elemental metal.
15. The cyclic deposition process of claim 13, wherein the first metal is selected from the group consisting of Sn, In, Ga, Al, Ge, As, Sb, Pb and Bi.
16. The cyclic deposition process of claim 13, wherein the compound having a general formula of $R-M-H$ has formula of $R_{(X-n)}-M^X-H_n$, wherein X is the formal oxidation state of the metal and n is 1 to 5.
17. The cyclic deposition process of claim 13, wherein the first gas-phase reactant comprises a diamine adduct of a corresponding metal chloride.

18. The cyclic deposition process of claim 13, wherein the first gas-phase reactant comprises at least one of cobalt chloride (TMEDA) and nickel chloride (TMPDA).
19. The cyclic deposition process of claim 13, wherein the second gas-phase reactant comprises TBTH.
20. A device structure including the film according to one or more of claims 1-19.

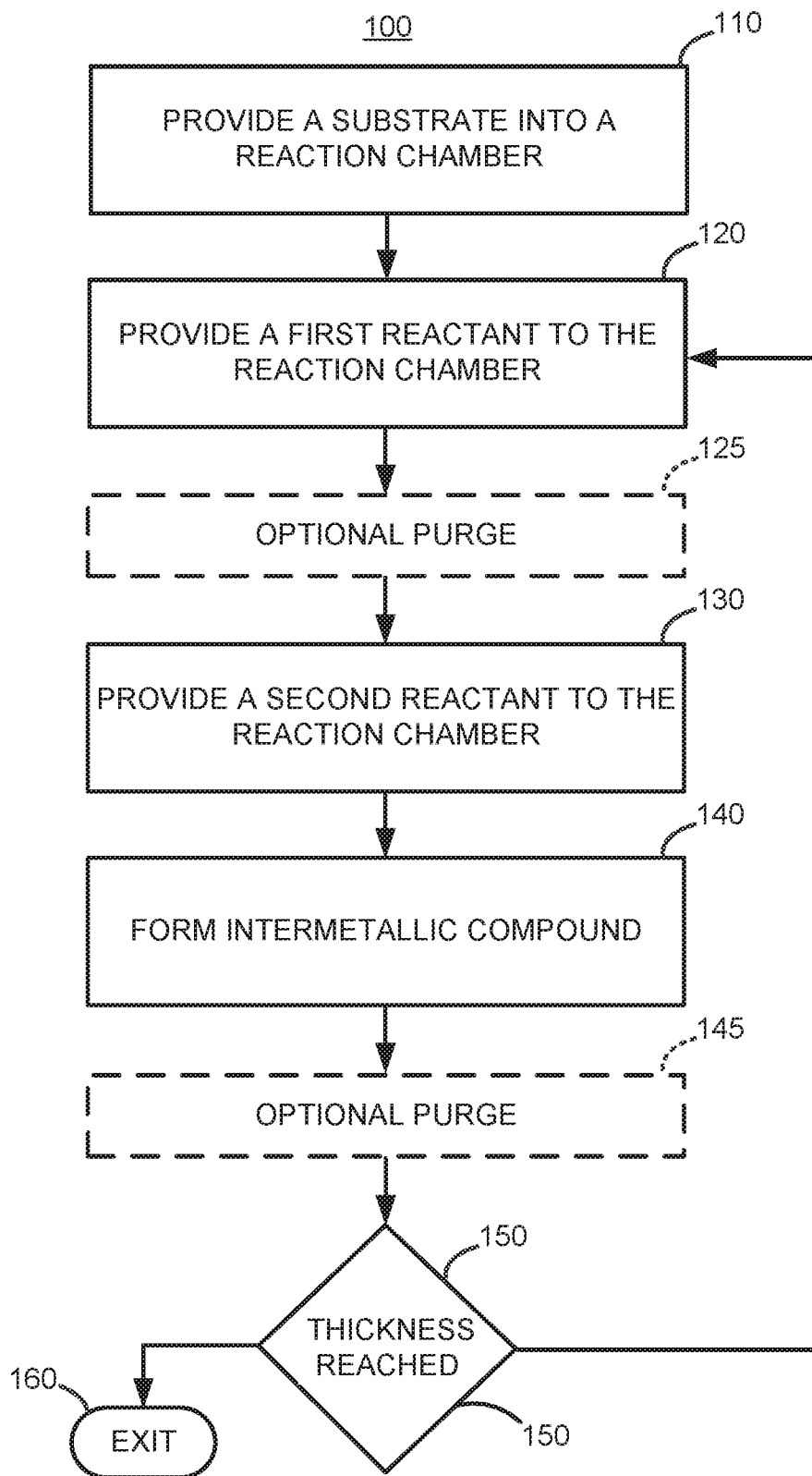


FIG. 1

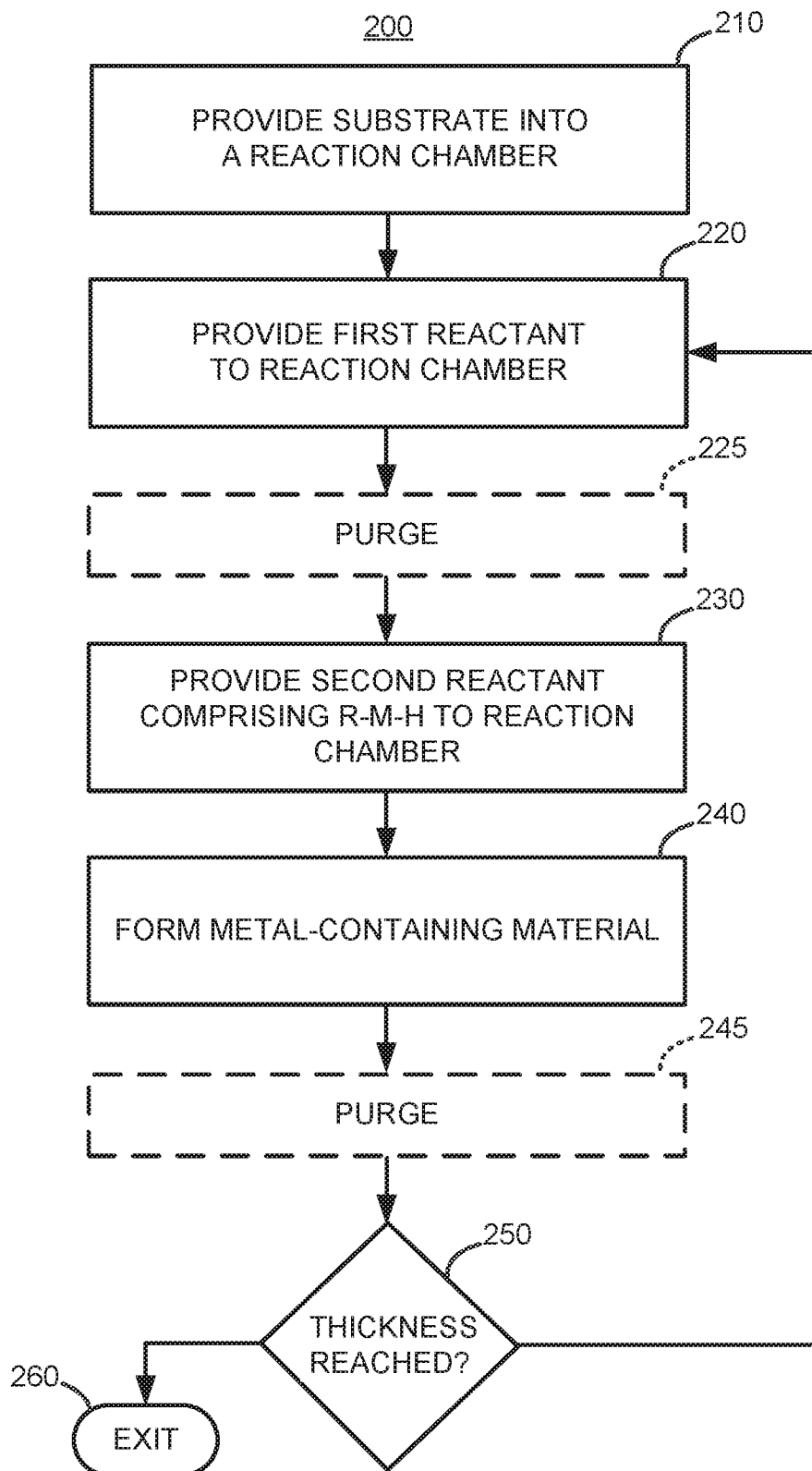


FIG. 2

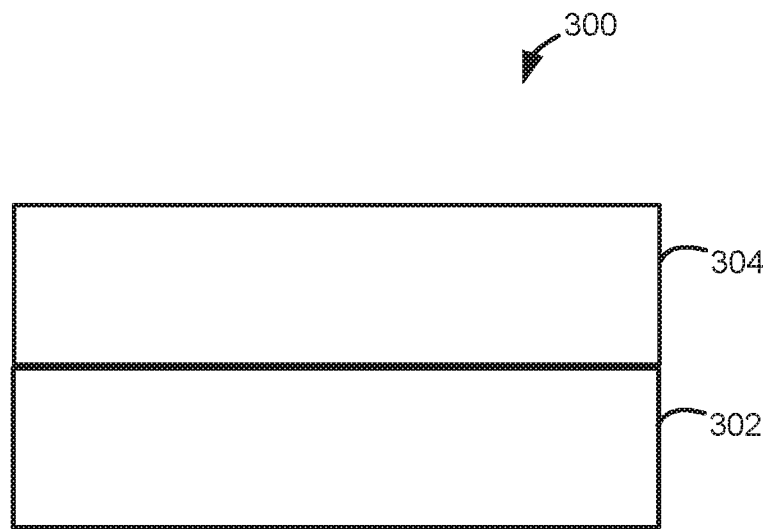


FIG. 3

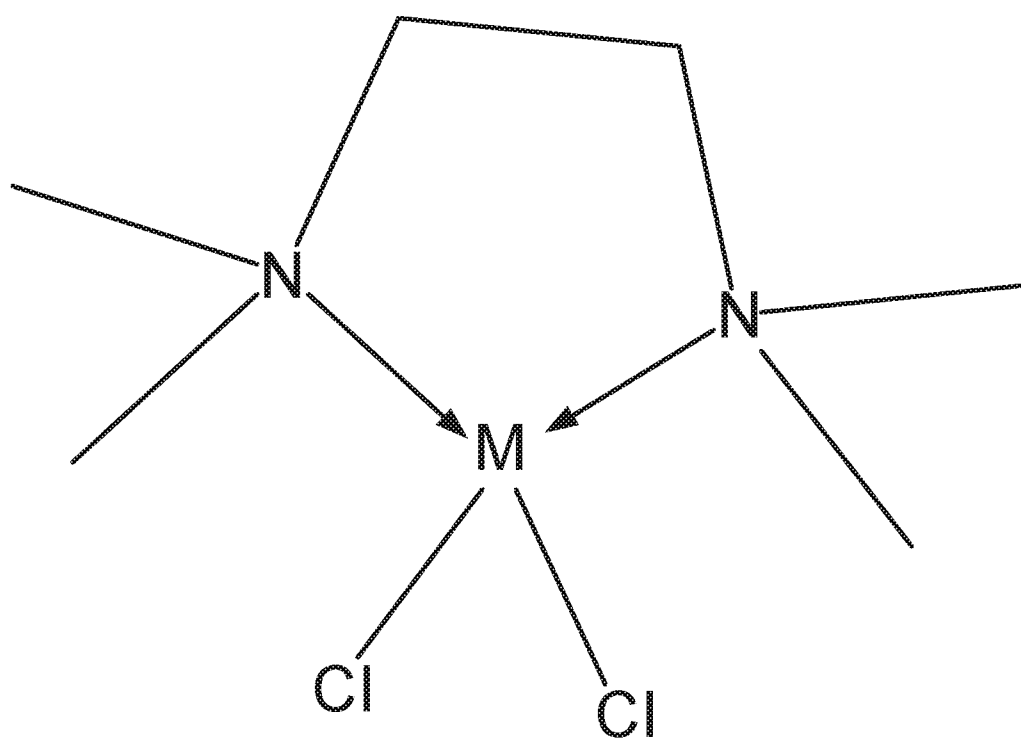
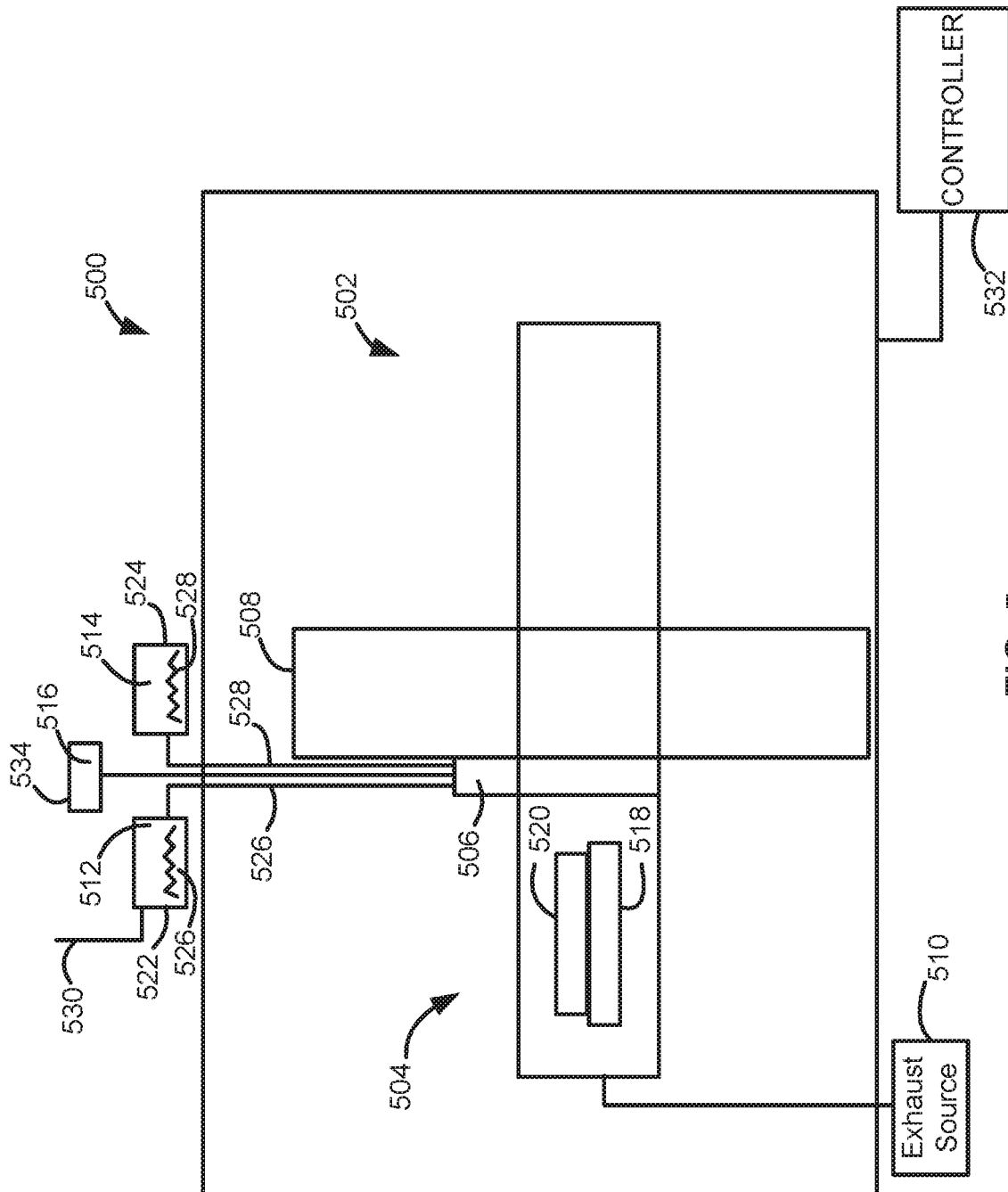


FIG. 4



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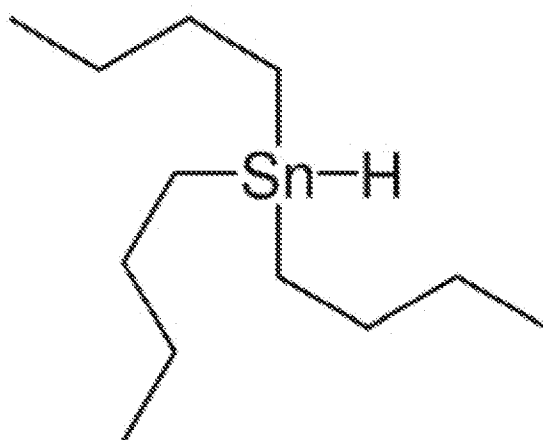


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/000817

A. CLASSIFICATION OF SUBJECT MATTER INV. C23C16/06 C23C16/08 C23C16/18 C23C16/455 G11B5/62 ADD.																				
According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C23C G11B																				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 2015/004316 A1 (THOMPSON DAVID [US] ET AL) 1 January 2015 (2015-01-01) claims 1-20</td> <td>1-6,8,20</td> </tr> <tr> <td>X</td> <td>US 2014/017408 A1 (GANDIKOTA SRINIVAS [US] ET AL) 16 January 2014 (2014-01-16) claims 1-20</td> <td>1-3,5,6,20</td> </tr> <tr> <td>X</td> <td>US 2012/302055 A1 (PORE VILJAMI J [FI] ET AL) 29 November 2012 (2012-11-29) claims 21,26-30</td> <td>1,2,20</td> </tr> <tr> <td>X</td> <td>US 2007/148350 A1 (RAHTU ANTTI [FI] ET AL) 28 June 2007 (2007-06-28) claims 1-17</td> <td>1,2,20</td> </tr> <tr> <td></td> <td>- / - -</td> <td></td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2015/004316 A1 (THOMPSON DAVID [US] ET AL) 1 January 2015 (2015-01-01) claims 1-20	1-6,8,20	X	US 2014/017408 A1 (GANDIKOTA SRINIVAS [US] ET AL) 16 January 2014 (2014-01-16) claims 1-20	1-3,5,6,20	X	US 2012/302055 A1 (PORE VILJAMI J [FI] ET AL) 29 November 2012 (2012-11-29) claims 21,26-30	1,2,20	X	US 2007/148350 A1 (RAHTU ANTTI [FI] ET AL) 28 June 2007 (2007-06-28) claims 1-17	1,2,20		- / - -	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	US 2015/004316 A1 (THOMPSON DAVID [US] ET AL) 1 January 2015 (2015-01-01) claims 1-20	1-6,8,20																		
X	US 2014/017408 A1 (GANDIKOTA SRINIVAS [US] ET AL) 16 January 2014 (2014-01-16) claims 1-20	1-3,5,6,20																		
X	US 2012/302055 A1 (PORE VILJAMI J [FI] ET AL) 29 November 2012 (2012-11-29) claims 21,26-30	1,2,20																		
X	US 2007/148350 A1 (RAHTU ANTTI [FI] ET AL) 28 June 2007 (2007-06-28) claims 1-17	1,2,20																		
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.																				
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Date of the actual completion of the international search		Date of mailing of the international search report																		
12 December 2019		20/12/2019																		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Battistig, Marcello																		

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/000817

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/155832 A1 (HAMALAINEN JANI [FI] ET AL) 7 June 2018 (2018-06-07) paragraph [0135]; claims 1-29 -----	1,20
E	WO 2019/158960 A1 (ASM IP HOLDING BV [NL]; GHENT UNIV) 22 August 2019 (2019-08-22) claims 1-27 -----	1,2,20
A	US 2014/242806 A1 (KNAPP DAVID [US] ET AL) 28 August 2014 (2014-08-28) claims 1-20; example 5 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2019/000817

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015004316 A1	01-01-2015	CN 105164791 A EP 3014651 A1 KR 20160024846 A TW 201504468 A US 2015004316 A1 WO 2014210328 A1	16-12-2015 04-05-2016 07-03-2016 01-02-2015 01-01-2015 31-12-2014
US 2014017408 A1	16-01-2014	US 2014017408 A1 WO 2014008365 A1	16-01-2014 09-01-2014
US 2012302055 A1	29-11-2012	KR 20120120902 A KR 20180018598 A KR 20180114536 A TW 201303062 A TW 201638373 A TW 201710542 A US 2012270393 A1 US 2012302055 A1 US 2016035852 A1 US 2017352737 A1 US 2019081149 A1	02-11-2012 21-02-2018 18-10-2018 16-01-2013 01-11-2016 16-03-2017 25-10-2012 29-11-2012 04-02-2016 07-12-2017 14-03-2019
US 2007148350 A1	28-06-2007	US 2007148350 A1 US 2013183445 A1 US 2016118262 A1 US 2018130666 A1 US 2019267231 A1	28-06-2007 18-07-2013 28-04-2016 10-05-2018 29-08-2019
US 2018155832 A1	07-06-2018	JP 2018095961 A KR 20180063852 A US 2018155832 A1	21-06-2018 12-06-2018 07-06-2018
WO 2019158960 A1	22-08-2019	TW 201936969 A WO 2019158960 A1	16-09-2019 22-08-2019
US 2014242806 A1	28-08-2014	CN 105026613 A JP 6411385 B2 JP 2016513185 A KR 20150122659 A TW 201435135 A US 2014242806 A1 WO 2014134481 A1	04-11-2015 24-10-2018 12-05-2016 02-11-2015 16-09-2014 28-08-2014 04-09-2014