US 20110206863A1

(19) **United States**
(12) **Patent Application Publication**
Meiere
(10) **Pub. No.: US 2011/0206863 A1**
(43) **Pub. Date: Aug. 25, 2011**

(54) **ORGANOMETALLIC COMPOUNDS HAVING STERICALLY HINDERED AMIDES**

(76) Inventor: **Scott Houston Meiere**, Williamsville, NY (US)

(21) Appl. No.: **13/100,769**

(22) Filed: **May 4, 2011**

Related U.S. Application Data

(62) Division of application No. 11/807,142, filed on May 25, 2007, now Pat. No. 7,956,168.

(60) Provisional application No. 60/818,506, filed on Jul. 6, 2006.

Publication Classification

(51) **Int. Cl.**

C07F 5/00	(2006.01)
C23C 16/448	(2006.01)
C23C 16/50	(2006.01)
C23C 16/48	(2006.01)

(52) **U.S. Cl.** **427/569**; 534/15; 427/248.1; 427/595

(57) **ABSTRACT**

This invention relates to organometallic compounds represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition; a process for producing the organometallic compounds, and a method for producing a film or coating from organometallic precursor compounds.

ORGANOMETALLIC COMPOUNDS HAVING STERICALLY HINDERED AMIDES

RELATED APPLICATION

[0001] This application is a divisional application of prior U.S. application Ser. No. 11/807,142, filed May 25, 2007, now allowed, which claims priority to U.S. Provisional Application Ser. No. 60/818,506, filed on Jul. 6, 2006, the entire contents of which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] This invention relates to organometallic compounds containing sterically hindered amides, a process for producing the organometallic compounds containing sterically hindered amides, and a method for producing a film or coating from organometallic precursor compounds containing sterically hindered amides.

BACKGROUND OF THE INVENTION

[0003] Chemical vapor deposition methods are employed to form films of material on substrates such as wafers or other surfaces during the manufacture or processing of semiconductors. In chemical vapor deposition, a chemical vapor deposition precursor, also known as a chemical vapor deposition chemical compound, is decomposed thermally, chemically, photochemically or by plasma activation, to form a thin film having a desired composition. For instance, a vapor phase chemical vapor deposition precursor can be contacted with a substrate that is heated to a temperature higher than the decomposition temperature of the precursor, to form a metal or metal oxide film on the substrate. Preferably, chemical vapor deposition precursors are volatile, heat decomposable and capable of producing uniform films under chemical vapor deposition conditions.

[0004] The semiconductor industry is currently considering the use of thin films of various metals for a variety of applications. Many organometallic complexes have been evaluated as potential precursors for the formation of these thin films. A need exists in the industry for developing new compounds and for exploring their potential as chemical vapor deposition precursors for film depositions.

[0005] Lanthanide-based materials such as oxides, silicates, aluminates, and silicon/aluminum oxynitrides are candidates for high-K dielectrics in next-generation semiconductor devices. However, due to the inherent properties of the lanthanides, such as larger atomic radii (compared to transition metals), participation of the f-orbitals, and propensity for the +3 oxidation state (Cotton, F. A.; Wilkenson, G. W. *Advanced Inorganic Chemistry*; Schumann et al., *Chem. Rev.* 2002, 102, 1851) lanthanide systems often have high-coordination numbers and form dimers, higher oligomers, and/or adducts with other molecules. This scenario is the case for many amide-based systems, and severely limits the availability of stable compounds with sufficient volatility for chemical vapor deposition and atomic layer deposition applications.

[0006] U.S. Patent Application Publication Nos. US 2002/0187644 A1 and US 2002/0175393 A1 disclose metalloamide precursor compositions having stated utility for forming dielectric thin films such as gate dielectric, high dielectric constant metal oxides, and ferroelectric metal oxides and to a low temperature chemical vapor deposition process for deposition of such dielectric thin films utilizing the compositions.

[0007] In developing methods for forming thin films by chemical vapor deposition or atomic layer deposition methods, a need continues to exist for precursors that preferably are liquid at room temperature, have adequate vapor pressure, have appropriate thermal stability (i.e., for chemical vapor deposition will decompose on the heated substrate but not during delivery, and for atomic layer deposition will not decompose thermally but will react when exposed to co-reactant), can form uniform films, and will leave behind very little, if any, undesired impurities (e.g., halides, carbon, etc.). Therefore, a need continues to exist for developing new compounds and for exploring their potential as chemical vapor or atomic layer deposition precursors for film depositions. It would therefore be desirable in the art to provide a precursor that possesses some, or preferably all, of the above characteristics.

SUMMARY OF THE INVENTION

[0008] This invention relates in part to organometallic compounds represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition.

[0009] This invention also relates in part to a process for the production of an organometallic compound comprising (i) reacting in a first pot a nitrogen-containing compound with an alkali metal, or an alkali metal-containing compound, or an alkaline earth metal, or an alkaline earth metal-containing compound, in the presence of a solvent and under reaction conditions sufficient to produce a first reaction mixture comprising a base material, (ii) adding said base material to a second pot containing a metal source compound and optionally an amine compound, (iii) reacting in said second pot said base material with said metal source compound and optionally said amine compound under reaction conditions sufficient to produce a second reaction mixture comprising said organometallic compound, and (iv) separating said organometallic compound from said second reaction mixture; wherein said organometallic compound is represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition. The

organometallic compound yield resulting from the process of this invention can be 60% or greater, preferably 75% or greater, and more preferably 90% or greater.

[0010] This invention further relates in part to a method for producing a film, coating or powder by decomposing an organometallic precursor compound represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition; thereby producing the film, coating or powder. Typically, the decomposing of said organometallic precursor compound is thermal, chemical, photochemical or plasma-activated.

[0011] This invention yet further relates in part to organometallic precursor compound mixtures comprising (a) an organometallic precursor compound represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition; and (b) one or more different organometallic precursor compounds (e.g., a hafnium-containing, aluminum-containing, strontium-containing, barium-containing, titanium-containing organometallic precursor compound).

[0012] This invention relates in particular to 'next generation' depositions involving amide-based lanthanide precursors. These precursors can have advantages over the other known precursors. These lanthanum-containing materials can be used for a variety of purposes such as dielectrics, barriers, and electrodes, and in many cases show improved properties (thermal stability, desired morphology, less diffusion, lower leakage, less charge trapping, and the like) than other metal containing films.

[0013] The invention has several advantages. For example, the processes of the invention are useful in generating organometallic compounds that have varied chemical structures and physical properties. Films generated from the organometallic compound precursors can be deposited with a short incubation time, and the films deposited from the organometallic compound precursors exhibit good smoothness.

[0014] This invention relates in particular to chemical vapor deposition and atomic layer deposition precursors for next generation devices, specifically organometallic precursors are preferred that are liquid at room temperature, i.e., 20° C.

[0015] The organometallic precursor compounds of this invention can provide desired properties of an atomic layer deposition precursor for applications involving nanolaminate structures in tandem with other materials, for example, a material such as Al_2O_3.

DETAILED DESCRIPTION OF THE INVENTION

[0016] As indicated above, this invention relates to organometallic compounds represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition. The organometallic compounds of this invention are preferably a liquid at 20° C.

[0017] Maintaining the monomeric nature of the organometallic molecules is important to achieve sufficient volatility. The formation of dimers, oligomers, or other species containing two or more metal centers may render the compound too large, and thus the additional molecular weight can limit utilization as a precursor.

[0018] The steric bulk of the organometallic molecule, as imparted by the bulky amide ligands, is important to prevent the formation of dimers, oligomers, or other species containing two or more metal centers, which can limit volatility. Furthermore, the steric bulk inhibits coordination numbers higher than the oxidation state of the central element, which aids in the prevention of the formation of less volatile and more polar species (e.g., the so called 'ate' compounds, which can incorporate alkali metals (e.g., Li) and halogens (e.g., Cl) if present during the reaction). It should be noted that in some cases coordination of a small neutral molecule (e.g., diethyl ether, trimethylamine), although technically increasing the coordination number above the oxidation state of the central element, may yield a precursor with acceptable properties, and is within the scope of this invention.

[0019] The organometallic compounds of this invention preferably have a steric bulk greater than the steric bulk of tris(diethylamino)lanthanum or tris(diisopropylamino)lanthanum.

[0020] The molecular weight of the organometallic molecules is limited by the requirement for sufficient volatility. Although a molecule may be monomeric with a coordination number equivalent to the oxidation state of the central element, if the ligands are too large (e.g., high molecular weight), the compound may not be useful as a precursor due to lack of vapor pressure. The organometallic molecules of this invention are preferably neutral molecules that are not dimers, oligomers, or other species containing two or more metal centers.

[0021] Typically, the organometallic compounds of this invention have a molecular weight of less than about 1000, preferably less than about 750, and more preferably less than about 500.

[0022] The organometallic compounds of this invention have a melting point sufficient for vapor deposition. Typically, the organometallic compounds have a melting point less than about 200° C., preferably less than about 100° C., and more preferably less than about 50° C.

[0023] The organometallic compounds of this invention have a volatility suitable for vapor deposition. Typically, the organometallic compounds of this invention have a volatility of at least 0.1 Torr at 200° C., preferably a volatility of at least 0.1 Torr at 150° C., and more preferably a volatility of at least 0.1 Torr at 100° C.

[0024] The organometallic compounds of this invention exhibit thermal stability sufficient for vapor deposition. Typically, the organometallic compounds have a thermal stability in which less than about 1 weight percent of said organometallic compound decomposes at a temperature of 100° C. over a period of 1 day, preferably a thermal stability in which less than about 1 weight percent of said organometallic compound decomposes at a temperature of 100° C. over a period of 1 month, and more preferably a thermal stability in which less than about 1 weight percent of said organometallic compound decomposes at a temperature of 100° C. over a period of 1 year.

[0025] Typically, R_1 and R_2 are the same or different and are independently hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, tert-amyl, cyclohexadienyl, adamantyl, phenyl, benzyl, silyl, dimethylsilyl, diethylsilyl, trimethylsilyl, triethylsilyl, dimethylethylsilyl, diethylmethylsilyl, and the like.

[0026] In general, R_1 and R_2 are the same or different and are independently hydrogen, alkyl; a substituted or unsubstituted, saturated or unsaturated, hydrocarbon, aromatic hydrocarbon, cycloaliphatic hydrocarbon, aromatic heterocycle, cycloaliphatic heterocycle, alkyl halide, silylated hydrocarbon, ether, polyether, thioether, ester, lactone, amide, amine, polyamine, nitrile; or mixtures thereof. R_1 and R_2 can also include substituted or unsubstituted, saturated or unsaturated, cyclic amido or amino groups, for example, aziridinyl, azetidinyl, pyrrolidinyl, thiazolidinyl, piperidinyl, pyrrolyl, pyridinyl, pyrimidinyl, pyrrolinyl, pyrazolyl, thiazolyl, oxazolyl, imidazolyl, imidazolidinonyl, imidazolidinethionyl, quinolinyl, isoquinolinyl, carbazolyl, triazolyl, indolyl and purinyl. Preferably, each of R_1 and R_2 is the same or different and is independently hydrogen, alkyl, or mixtures thereof.

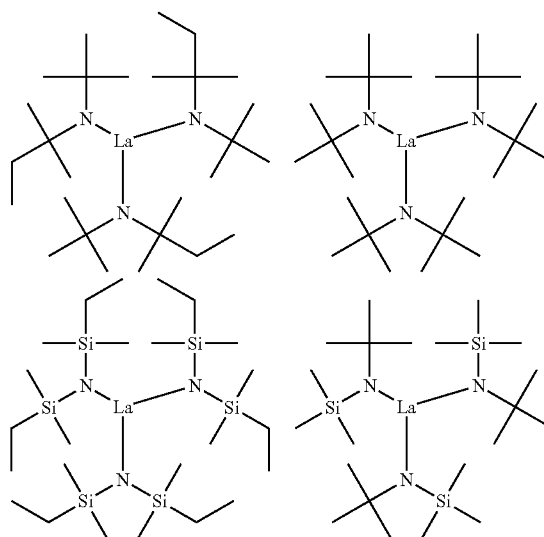
[0027] Typically, M is a Group 2 (e.g., Sr, Ba) Group 3 (e.g., Sc, Y), Group 13 (Al, Ga) or a lanthanide series element (e.g., La, Ce, Pr, Nd, Dy, Er, and Yb). M can also be a Group 1, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 16, 17, 18 or an actinide series element. M is preferably selected from a Group 2 element, a Group 13 element, a Group 14 element, a transition metal, or a lanthanide series element. More preferably, M is selected from Sr, Ba, Sc, Y, Al, Ga, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.

[0028] Illustrative organometallic compounds of this invention include, for example, tris(bis(cyclohexyl)amino) lanthanum, tris(tert-butylisopropyl)amino)lanthanum, tris (bis(dimethylsilyl)amino)lanthanum, tris((trimethylsilyl) (dimethylethylsilyl)amino)lanthanum, tris(bis(tert-butyl) amino)lanthanum, tris(bis(tert-amyl)amino)lanthanum, tris (tert-amyl-tert-butylamino)lanthanum, tris(tert-butyltrimethylsilylamino)lanthanum, tris(bis (dimethylethylsilyl)amino)lanthanum, and the like. Preferred organometallic compounds include, for example, lanthanum amides.

[0029] In an embodiment of this invention, the organometallic compounds include, for example, tris(bis(dimethylsilyl)amino)lanthanum, tris((trimethylsilyl)(dimethylethylsilyl) amino)lanthanum, and tris(bis(dimethylethylsilyl)amino) lanthanum.

[0030] In another embodiment of this invention, the organometallic compounds include, for example, tris(bis(cyclohexyl)amino)lanthanum, tris(tert-butylisopropyl)amino)lanthanum, tris(bis(tert-butyl)amino)lanthanum, tris(bis(tert-amyl)amino)lanthanum, tris(tert-amyl-tert-butylamino) lanthanum, and tris(tert-butyltrimethylsilylamino) lanthanum.

[0031] Illustrative organometallic compounds of this invention can be represented by the formulae:



[0032] The organometallic precursor compounds of this invention may be homoleptic, i.e., all R radicals are the same such as tris(bis(tert-amyl)amino)lanthanum or heteroleptic, i.e., one or more of the R radicals are different from each other such as tris(tert-butyltrimethylsilylamino)lanthanum.

[0033] As indicated above, this invention also relates to a process for the production of an organometallic compound comprising (i) reacting in a first pot a nitrogen-containing compound with an alkali metal, or an alkali metal-containing compound, or an alkaline earth metal, or an alkaline earth metal-containing compound, in the presence of a solvent and under reaction conditions sufficient to produce a first reaction mixture comprising a base material, (ii) adding said base material to a second pot containing a metal source compound and optionally an amine compound, (iii) reacting in said second pot said base material with said metal source compound and optionally said amine compound under reaction conditions sufficient to produce a second reaction mixture comprising said organometallic compound, and (iv) separating said organometallic compound from said second reaction mixture; wherein said organometallic compound is represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or

metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition. The organometallic compound yield resulting from the process of this invention can be 60% or greater, preferably 75% or greater, and more preferably 90% or greater.

[0034] In the processes described herein, the metal source compound, e.g., a pure metal, a metal halide, a metal pseudohalide, and the like, starting material may be selected from a wide variety of compounds known in the art. The invention herein most prefers metals selected from Sr, Ba, Sc, Y, Al, lanthanides, and the like. Illustrative metal source compounds include, for example, $La(CF_3SO_3)_3$, $LaCl_3$, $LaBr_3$, LaI_3, $SrCl_2$, and the like. Other illustrative metal source compounds include, for example, $La(OiPr)_3$, and the like. Preferred metal source compounds include, for example, lanthanide halides and lanthanide trifluoromethanesulfonate. The metal source compound starting material can typically be any compound or pure metal containing the central metal atom.

[0035] The processes of this invention for synthesizing organometallic compounds with bulky amide ligands can also utilize triflate-based metal source compounds. While most metalloamide compounds are reportedly synthesized from the metal halides (e.g., $LaCl_3$), reaction rates with bulky amide compounds can be slow or non-detectable due to the larger steric profile of the ligands. Therefore, the triflate compounds, which possess better leaving groups, are more suited for this application. Furthermore, the resulting triflate ions are less likely to remain in the coordination sphere (e.g., bridging) compared to halides (e.g., Cl), and therefore are better suited for producing neutral monomeric species. In addition, the increased solubility of the bulky amides, as well as the triflates, may allow for the utilization of hydrocarbon solvents (e.g., toluene), which may be desirable in cases where coordination of a heteroatom containing solvent (e.g., tetrahydrofuran or ether) to the desired compound is problematic.

[0036] The concentration of the metal source compound starting material can vary over a wide range, and need only be that minimum amount necessary to react with the base material and optionally the amine compound and to provide the given metal concentration desired to be employed and which will furnish the basis for at least the amount of metal necessary for the organometallic compounds of this invention. In general, depending on the size of the reaction mixture, metal source compound starting material concentrations in the range of from about 1 millimole or less to about 10,000 millimoles or greater, should be sufficient for most processes.

[0037] In the processes described herein, the amine compounds may be selected from a wide variety of compounds known in the art. Illustrative amine compounds include, for example, diisopropylamine, di-tert-amylamine, tert-butylisopropylamine, di-tert-butylamine, dicyclohexylamine, tert-butyltrimethylsilylamine, diethyltetramethyldisilazane, and the like. Preferred amine compound starting materials can be represented by the formula $NR_3R_4R_5$ wherein each of R_3, R_4 and R_5 is the same or different and is independently hydrogen, alkyl; a substituted or unsubstituted, saturated or unsaturated, hydrocarbon, aromatic hydrocarbon, cycloaliphatic hydrocarbon, aromatic heterocycle, alkyl halide, silylated hydrocarbon, ether, polyether, thioether, ester, lactone, amide, amine, polyamine, nitrile; or mixtures thereof. The amine compounds can include cyclic and chelating systems. The amine compounds can also include the HCl salt of amines such as ammonium chloride, dimethylammonium chloride, and the like. Preferably, each of R_3, R_4 and R_5 is the same or different and is independently hydrogen, alkyl, or mixtures thereof. Preferred amine compounds include, for example, di-tert-amylamine, tert-butylisopropylamine, di-tert-butylamine, tert-butyltrimethylsilylamine, and diethyltetramethyldisilazane.

[0038] The concentration of the amine compound starting material can vary over a wide range, and need only be that minimum amount necessary to react with the base starting material and metal source compound. In general, depending on the size of the reaction mixture, amine compound starting material concentrations in the range of from about 1 millimole or less to about 10,000 millimoles or greater, should be sufficient for most processes.

[0039] In the processes described herein, the base starting material may be selected from a wide variety of compounds known in the art. Illustrative bases include any base with a pKa greater than about 10, preferably greater than about 20, and more preferably greater than about 25. The base material is preferably lithium diisopropylamide, lithium di-tert-amylamide, lithium tert-butylisopropylamide, lithium di-tert-butylamide, sodium di-tert-butylamide, lithium dicyclohexylamide, lithium tert-butyltrimethylsilylamide, lithium bis(ethyldimethylsilyl)amide, and the like. Lithium amides are preferred base starting materials.

[0040] The concentration of the base starting material can vary over a wide range, and need only be that minimum amount necessary to react with the amine compound starting material and metal source compound. In general, depending on the size of the first reaction mixture, base starting material concentrations in the range of from about 1 millimole or less to about 10,000 millimoles or greater, should be sufficient for most processes.

[0041] In one embodiment, the base starting material may be generated in situ, for example, lithiated amides, and the like. Generating the base starting material in situ in the reaction vessel immediately prior to reaction with the metal source compound is beneficial from a purity standpoint by eliminating the need to isolate and handle any reactive solids. It is also less expensive.

[0042] With the in situ generated base starting material in place, addition of the metal source compound, e.g., $La(CF_3SO_3)_3$, can be performed through liquid or solid addition, or in some cases more conveniently as a solvent solution or slurry. Although certain metal source compounds are moisture sensitive and are used under an inert atmosphere such as nitrogen, it is generally to a much lower degree than the amine compounds, for example, lithiated amides, amines and the like. Furthermore, many metal source compounds are denser and easier to transfer.

[0043] The base starting material can be prepared from the reaction of a nitrogen-containing compound and an alkali

metal, or an alkali metal-containing compound, or an alkaline earth metal, or an alkaline earth metal-containing compound. The base starting material can be prepared by conventional processes known in the art.

[0044] The solvent employed in the processes of this invention may be any saturated and unsaturated hydrocarbons, aromatic hydrocarbons, aromatic heterocycles, alkyl halides, silylated hydrocarbons, ethers, polyethers, thioethers, esters, thioesters, lactones, amides, amines, polyamines, nitriles, silicone oils, other aprotic solvents, or mixtures of one or more of the above; more preferably, pentanes, heptanes, octanes, nonanes, decanes, xylene, tetramethylbenzene, dimethoxyethanes, diglyme, fluorinated hydrocarbons, and mixtures of one or more of the above; and most preferably hexanes, ethers, THF, benzene, toluene, and mixtures of one of more of the above. Any suitable solvent which does not unduly adversely interfere with the intended reaction can be employed. Mixtures of one or more different solvents may be employed if desired. The amount of solvent employed is not critical to the subject invention and need only be that amount sufficient to solubilize the reaction components in the reaction mixture. In general, the amount of solvent may range from about 5 percent by weight up to about 99 percent by weight or more based on the total weight of the reaction mixture starting materials.

[0045] Reaction conditions for the processes for the reaction of the base material, the metal source compound, and optionally the amine compound, such as temperature, pressure and contact time, may also vary greatly and any suitable combination of such conditions may be employed herein. The reaction temperature may be the reflux temperature of any of the aforementioned solvents, and more preferably between about −80° C. to about 150° C., and most preferably between about 20° C. to about 80° C. Normally the reaction is carried out under ambient pressure and the contact time may vary from a matter of seconds or minutes to a few hours or greater. The reactants can be added to the reaction mixture or combined in any order. The stir time employed can range from about 0.1 to about 400 hours, preferably from about 1 to 75 hours, and more preferably from about 4 to 16 hours, for all steps. In the embodiment of this invention which is carried out in a single pot, the base material is not separated from the first reaction mixture prior to reacting with the metal source compound and optionally the amine compound. In a preferred embodiment, the metal source compound is added to the first reaction mixture at ambient temperature or at a temperature greater than ambient temperature.

[0046] The organometallic compounds prepared from the reaction of the base material, the metal source compound and optionally the amine compound may be selected from a wide variety of compounds. For purposes of this invention, organometallic compounds include compounds having a metal-nitrogen bond. Illustrative organometallic compounds include, for example, metal amides, metal amines and the like.

[0047] The organometallic compounds of this invention can also be prepared by a one pot process. The one pot process is particularly well-suited for large scale production since it can be conducted using the same equipment, some of the same reagents and process parameters that can easily be adapted to manufacture a wide range of products. The process provides for the synthesis of organometallic compounds using a process where all manipulations can be carried out in a single vessel, and which route to the organometallic compounds does not require the isolation of an intermediate complex. A one pot process is described in U.S. patent application Ser. No. 10/678,074, filed Oct. 6, 2003, which is incorporated herein by reference.

[0048] For organometallic compounds prepared by the processes of this invention, purification can occur through recrystallization, more preferably through extraction of reaction residue (e.g., hexane) and chromatography, and most preferably through sublimation and distillation.

[0049] Those skilled in the art will recognize that numerous changes may be made to the processes described in detail herein, without departing in scope or spirit from the present invention as more particularly defined in the claims below.

[0050] Examples of techniques that can be employed to characterize the organometallic compounds formed by the synthetic methods described above include, but are not limited to, analytical gas chromatography, nuclear magnetic resonance, thermogravimetric analysis, inductively coupled plasma mass spectrometry, differential scanning calorimetry, vapor pressure and viscosity measurements.

[0051] Relative vapor pressures, or relative volatility, of organometallic compound precursors described above can be measured by thermogravimetric analysis techniques known in the art. Equilibrium vapor pressures also can be measured, for example by evacuating all gases from a sealed vessel, after which vapors of the compounds are introduced to the vessel and the pressure is measured as known in the art.

[0052] The organometallic compound precursors described herein are preferably liquid at room temperature, i.e., 20° C., and are well suited for preparing in-situ powders and coatings. For instance, a liquid organometallic compound precursor can be applied to a substrate and then heated to a temperature sufficient to decompose the precursor, thereby forming a metal or metal oxide coating on the substrate. Applying a liquid precursor to the substrate can be by painting, spraying, dipping or by other techniques known in the art. Heating can be conducted in an oven, with a heat gun, by electrically heating the substrate, or by other means, as known in the art. A layered coating can be obtained by applying an organometallic compound precursor, and heating and decomposing it, thereby forming a first layer, followed by at least one other coating with the same or different precursors, and heating.

[0053] Liquid organometallic compound precursors such as described above also can be atomized and sprayed onto a substrate. Atomization and spraying means, such as nozzles, nebulizers and others, that can be employed are known in the art.

[0054] In preferred embodiments of the invention, an organometallic compound, such as described above, is employed in gas phase deposition techniques for forming powders, films or coatings. The compound can be employed as a single source precursor or can be used together with one or more other precursors, for instance, with vapor generated by heating at least one other organometallic compound or metal complex. More than one organometallic compound precursor, such as described above, also can be employed in a given process.

[0055] As indicated above, this invention relates to organometallic precursor mixtures comprising (a) an organometallic precursor compound represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group

or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition; and (b) one or more different organometallic precursor compounds (e.g., a hafnium-containing, aluminum-containing, strontium-containing, barium-containing, titanium-containing organometallic precursor compound).

[0056] Deposition can be conducted in the presence of other gas phase components. In an embodiment of the invention, film deposition is conducted in the presence of at least one non-reactive carrier gas. Examples of non-reactive gases include inert gases, e.g., nitrogen, argon, helium, as well as other gases that do not react with the organometallic compound precursor under process conditions. In other embodiments, film deposition is conducted in the presence of at least one reactive gas. Some of the reactive gases that can be employed include but are not limited to hydrazine, oxygen, hydrogen, air, oxygen-enriched air, ozone (O_3), nitrous oxide (N_2O), water vapor, organic vapors, ammonia and others. As known in the art, the presence of an oxidizing gas, such as, for example, air, oxygen, oxygen-enriched air, O_3, N_2O or a vapor of an oxidizing organic compound, favors the formation of a metal oxide film.

[0057] As indicated above, this invention also relates in part to a method for producing a film, coating or powder. The method includes the step of decomposing at least one organometallic compound precursor, thereby producing the film, coating or powder, as further described below. More particularly, this invention relates in part to a method for producing a film, coating or powder by decomposing an organometallic precursor compound represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition; thereby producing the film, coating or powder. Typically, the decomposing of said organometallic precursor compound is thermal, chemical, photochemical or plasma-activated.

[0058] Deposition methods described herein can be conducted to form a film, powder or coating that includes a single metal or a film, powder or coating that includes a single metal oxide. Mixed films, powders or coatings also can be deposited, for instance mixed metal oxide films. A mixed metal oxide film can be formed, for example, by employing several organometallic precursors, at least one of which being selected from the organometallic compounds described above.

[0059] Gas phase film deposition can be conducted to form film layers of a desired thickness, for example, in the range of from about 1 nm to over 1 mm. The precursors described herein are particularly useful for producing thin films, e.g., films having a thickness in the range of from about 10 nm to about 100 nm. Films of this invention, for instance, can be considered for fabricating metal electrodes, in particular as n-channel metal electrodes in logic, as capacitor electrodes for DRAM applications, and as dielectric materials.

[0060] The method also is suited for preparing layered films, wherein at least two of the layers differ in phase or composition. Examples of layered film include metal-insulator-semiconductor, and metal-insulator-metal.

[0061] In an embodiment, the invention is directed to a method that includes the step of decomposing vapor of an organometallic compound precursor described above, thermally, chemically, photochemically or by plasma activation, thereby forming a film on a substrate. For instance, vapor generated by the compound is contacted with a substrate having a temperature sufficient to cause the organometallic compound to decompose and form a film on the substrate.

[0062] The organometallic compound precursors can be employed in chemical vapor deposition or, more specifically, in metalorganic chemical vapor deposition processes known in the art. For instance, the organometallic compound precursors described above can be used in atmospheric, as well as in low pressure, chemical vapor deposition processes. The compounds can be employed in hot wall chemical vapor deposition, a method in which the entire reaction chamber is heated, as well as in cold or warm wall type chemical vapor deposition, a technique in which only the substrate is being heated.

[0063] The organometallic compound precursors described above also can be used in plasma or photo-assisted chemical vapor deposition processes, in which the energy from a plasma or electromagnetic energy, respectively, is used to activate the chemical vapor deposition precursor. The compounds also can be employed in ion-beam, electron-beam assisted chemical vapor deposition processes in which, respectively, an ion beam or electron beam is directed to the substrate to supply energy for decomposing a chemical vapor deposition precursor. Laser-assisted chemical vapor deposition processes, in which laser light is directed to the substrate to affect photolytic reactions of the chemical vapor deposition precursor, also can be used.

[0064] The method of the invention can be conducted in various chemical vapor deposition reactors, such as, for instance, hot or cold-wall reactors, plasma-assisted, beam-assisted or laser-assisted reactors, as known in the art.

[0065] Examples of substrates that can be coated employing the method of the invention include solid substrates such as metal substrates, e.g., Al, Ni, Ti, Co, Pt, Ta; metal aluminates; metal silicides, e.g., $TiSi_2$, $CoSi_2$, $NiSi_2$; semiconductor materials, e.g., Si, SiGe, GaAs, InP, diamond, GaN, SiC; insulators, e.g., SiO_2, Si_3N_4, HfO_2, Ta_2O_5, Al_2O_3, barium strontium titanate (BST); barrier materials, e.g., TiN, TaN; or on substrates that include combinations of materials. In addition, films or coatings can be formed on glass, ceramics, plastics, thermoset polymeric materials, and on other coatings or film layers. In preferred embodiments, film deposition is on a substrate used in the manufacture or processing of electronic components. In other embodiments, a substrate is

employed to support a low resistivity conductor deposit that is stable in the presence of an oxidizer at high temperature or an optically transmitting film.

[0066] The method of this invention can be conducted to deposit a film on a substrate that has a smooth, flat surface. In an embodiment, the method is conducted to deposit a film on a substrate used in wafer manufacturing or processing. For instance, the method can be conducted to deposit a film on patterned substrates that include features such as trenches, holes or vias. Furthermore, the method of the invention also can be integrated with other steps in wafer manufacturing or processing, e.g., masking, etching and others.

[0067] Chemical vapor deposition films can be deposited to a desired thickness. For example, films formed can be less than 1 micron thick, preferably less than 500 nanometer and more preferably less than 200 nanometers thick. Films that are less than 50 nanometer thick, for instance, films that have a thickness between about 1 and about 20 nanometers, also can be produced.

[0068] Organometallic compound precursors described above also can be employed in the method of the invention to form films by atomic layer deposition (ALD) or atomic layer nucleation (ALN) techniques, during which a substrate is exposed to alternate pulses of precursor, oxidizer and inert gas streams. Sequential layer deposition techniques are described, for example, in U.S. Pat. No. 6,287,965 and in U.S. Pat. No. 6,342,277. The disclosures of both patents are incorporated herein by reference in their entirety.

[0069] For example, in one ALD cycle, a substrate is exposed, in step-wise manner, to: a) an inert gas; b) inert gas carrying precursor vapor; c) inert gas; and d) oxidizer, alone or together with inert gas. In general, each step can be as short as the equipment will permit (e.g. milliseconds) and as long as the process requires (e.g. several seconds or minutes). The duration of one cycle can be as short as milliseconds and as long as minutes. The cycle is repeated over a period that can range from a few minutes to hours. Film produced can be a few nanometers thin or thicker, e.g., 1 millimeter (mm).

[0070] The method of the invention also can be conducted using supercritical fluids. Examples of film deposition methods that use supercritical fluid that are currently known in the art include chemical fluid deposition; supercritical fluid transport-chemical deposition; supercritical fluid chemical deposition; and supercritical immersion deposition.

[0071] Chemical fluid deposition processes, for example, are well suited for producing high purity films and for covering complex surfaces and filling of high-aspect-ratio features. Chemical fluid deposition is described, for instance, in U.S. Pat. No. 5,789,027. The use of supercritical fluids to form films also is described in U.S. Pat. No. 6,541,278 B2. The disclosures of these two patents are incorporated herein by reference in their entirety.

[0072] In an embodiment of the invention, a heated patterned substrate is exposed to one or more organometallic compound precursors, in the presence of a solvent, such as a near critical or supercritical fluid, e.g., near critical or supercritical CO_2. In the case of CO_2, the solvent fluid is provided at a pressure above about 1000 psig and a temperature of at least about 30° C.

[0073] The precursor is decomposed to form a metal film on the substrate. The reaction also generates organic material from the precursor. The organic material is solubilized by the solvent fluid and easily removed away from the substrate. Metal oxide films also can be formed, for example by using an oxidizing gas.

[0074] In an example, the deposition process is conducted in a reaction chamber that houses one or more substrates. The substrates are heated to the desired temperature by heating the entire chamber, for instance, by means of a furnace. Vapor of the organometallic compound can be produced, for example, by applying a vacuum to the chamber. For low boiling compounds, the chamber can be hot enough to cause vaporization of the compound. As the vapor contacts the heated substrate surface, it decomposes and forms a metal or metal oxide film. As described above, an organometallic compound precursor can be used alone or in combination with one or more components, such as, for example, other organometallic precursors, inert carrier gases or reactive gases.

[0075] In a system that can be used in producing films by the method of the invention, raw materials can be directed to a gas-blending manifold to produce process gas that is supplied to a deposition reactor, where film growth is conducted. Raw materials include, but are not limited to, carrier gases, reactive gases, purge gases, precursor, etch/clean gases, and others. Precise control of the process gas composition is accomplished using mass-flow controllers, valves, pressure transducers, and other means, as known in the art. An exhaust manifold can convey gas exiting the deposition reactor, as well as a bypass stream, to a vacuum pump. An abatement system, downstream of the vacuum pump, can be used to remove any hazardous materials from the exhaust gas. The deposition system can be equipped with in-situ analysis system, including a residual gas analyzer, which permits measurement of the process gas composition. A control and data acquisition system can monitor the various process parameters (e.g., temperature, pressure, flow rate, etc.).

[0076] The organometallic compound precursors described above can be employed to produce films that include a single metal or a film that includes a single metal oxide. Mixed films also can be deposited, for instance mixed metal oxide films. Such films are produced, for example, by employing several organometallic precursors. Metal films also can be formed, for example, by using no carrier gas, vapor or other sources of oxygen.

[0077] Films formed by the methods described herein can be characterized by techniques known in the art, for instance, by X-ray diffraction, Auger spectroscopy, X-ray photoelectron emission spectroscopy, atomic force microscopy, scanning electron microscopy, and other techniques known in the art. Resistivity and thermal stability of the films also can be measured, by methods known in the art.

[0078] Atomic layer deposition and chemical vapor deposition of silicates and aluminates can be useful for many next generation materials (e.g., lanthanum aluminates for dielectrics).

[0079] Various modifications and variations of this invention will be obvious to a worker skilled in the art and it is to be understood that such modifications and variations are to be included within the purview of this application and the spirit and scope of the claims.

1. A process for the production of an organometallic compound comprising (i) reacting in a first pot a nitrogen-containing compound with an alkali metal, or an alkali metal-containing compound, or an alkaline earth metal, or an alkaline earth metal-containing compound, in the presence of a solvent and under reaction conditions sufficient to produce

a first reaction mixture comprising a base material, (ii) adding said base material to a second pot containing a metal source compound and optionally an amine compound, (iii) reacting in said second pot said base material with said metal source compound and optionally said amine compound under reaction conditions sufficient to produce a second reaction mixture comprising said organometallic compound, and (iv) separating said organometallic compound from said second reaction mixture; wherein said organometallic compound is represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition.

2. The process of claim **1** wherein the metal source compound comprises a pure metal, a metal halide, or a metal pseudohalide.

3. The process of claim **1** wherein the metal source compound comprises $La(CF_3SO_3)_3$, $LaCl_3$, $LaBr_3$, LaI_3, or $SrCl_2$.

4. The process of claim **1** wherein the metal source compound comprises a lanthanide halide or a lanthanide trifluoromethanesulfonate.

5. The process of claim **1** wherein the base material comprises lithium diisopropylamide, lithium di-tert-amylamide, lithium tert-butylisopropylamide, lithium di-tert-butylamide, sodium di-tert-butylamide, lithium dicyclohexylamide, lithium tert-butyltrimethylsilylamide, or lithium bis(ethyldimethylsilyl)amide.

6. The process of claim **1** wherein the base material has a pKa greater than about 10.

7. The process of claim **1** wherein the amine compound comprises diisopropylamine, di-tert-amylamine, tert-butylisopropylamine, di-tert-butylamine, dicyclohexylamine, tert-butyltrimethylsilylamine, or diethyltetramethyldisilazane.

8. The process of claim **1** wherein the organometallic compound yield is 60% or greater.

9. A method for producing a film, coating or powder by decomposing an organometallic precursor compound represented by the formula $M(NR_1R_2)_x$ wherein M is a metal or metalloid, R_1 is the same or different and is a hydrocarbon group or a heteroatom-containing group, R_2 is the same or different and is a hydrocarbon group or a heteroatom-containing group; R_1 and R_2 can be combined to form a substituted or unsubstituted, saturated or unsaturated cyclic group; R_1 or R_2 of one (NR_1R_2) group can be combined with R_1 or R_2 of another (NR_1R_2) group to form a substituted or unsubstituted, saturated or unsaturated cyclic group; x is equal to the oxidation state of M; and wherein said organometallic compound has (i) a steric bulk sufficient to maintain a monomeric structure and a coordination number equal to the oxidation state of M with respect to anionic ligands, and (ii) a molecular weight sufficient to possess a volatility suitable for vapor deposition; thereby producing the film, coating or powder.

10. The method of claim **9** wherein the decomposing of said organometallic precursor compound is thermal, chemical, photochemical or plasma-activated.

11. The method of claim **9** wherein said organometallic precursor compound is vaporized and the vapor is directed into a deposition reactor housing a substrate.

12. The method of claim **11** wherein said substrate is comprised of a material selected from the group consisting of a metal, a metal silicide, a metal aluminate, a semiconductor, an insulator and a barrier material.

13. The method of claim **11** wherein said substrate is a patterned wafer.

14. The method of claim **9** wherein said film, coating or powder is produced by a gas phase deposition.

15. The method of claim **9** wherein said film, coating or powder is produced by a chemical vapor deposition or atomic layer deposition.

* * * * *