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(21) International Application Number: PCT/US96/09434 (22) International Filing Date: 6 June 1996 (06.06.96) (30) Priority Data: 477,797 7 June 1995 (07.06.95) US (71) Applicant: ADVANCED TECHNOLOGY MATERIALS, INC. [US/US]; 7 Commerce Drive, Danbury, CT 06810-4169 (US). (72) Inventors: KIRLIN, Peter, S.; 11 Kingswood Drive #72, Bethel, CT 06801 (US). BROWN, Duncan, W.; 60 Teapot Hill Road, Wilton, CT 06897 (US). BAUM, Thomas, W.; 2 Handol Lane, New Fairfield, CT 06812 (US). VAARTSTRA, Brian, A.; 3417 Braden Lane, Nampa, ID 83653 (US). GARDINER, Robin, A.; 23 Knollwood Drive, Bethel, CT 06801 (US). (74) Agent: HULTQUIST, Steven, J.; P.O. Box 14329, Research Triangle Park, NC 27709 (US).		(81) Designated States: CA, JP, KR, <u>SC</u> , European patent (AT, BE, CH, DE, DK, ES, FI, FR, <u>GB</u> , GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: METAL COMPLEX SOURCE REAGENTS FOR CHEMICAL VAPOR DEPOSITION (57) Abstract A metalorganic complex of the formula MA_yX, wherein M is a y-valent metal; A is a monodentate or multidentate organic ligand coordinated to M which allows complexing of MA_y with X; y is an integer having a value of 2, 3 or 4; each of the A ligands may be the same or different; and X is a monodentate or multidentate ligand coordinated to M and containing one or more atoms independently selected from the group consisting of atoms of the elements C, N, H, S, O and F. The metal M may be selected from the group consisting of Cu, Ba, Sr, La, Nd, Ce, Pr, Sm, Eu, Th, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Bi, Ti, Y, Pb, Ni, Pd, Pt, Al, Ga, In, Ag, Au, Co, Rh, Ir, Fe, Ru, Sn, Li, Na, K, Rb, Cs, Ca, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. A may be selected from the group consisting of β-diketonates and their sulfur and nitrogen analogs, β-ketoesters and their sulfur and nitrogen analogs, cyclopentadienyls, alkyls, perfluoroalkyls, alkoxides, perfluoroalkoxides, and Schiff bases. X may for example comprise a ligand such as tetraglyme, tetrahydrofuran, bipyridine, crown ether, or thioether.		

METAL COMPLEX SOURCE REAGENTS FOR CHEMICAL VAPOR DEPOSITION

DESCRIPTION

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Field of the Invention

The present invention generally relates to thermally decomposable organometallic compounds and complexes which are useful in chemical vapor deposition (CVD) processes, for formation of metal films on substrates.

Description of the Related Art

15 CVD requires source reagents which are sufficiently volatile to permit their gas phase transport into the decomposition reactor. The source reagent must decompose in the CVD reactor to deposit only the desired element(s) at the desired growth temperature on the substrate. Premature gas phase reactions are desirably avoided, and it generally is
20 desired to controllably deliver source reagents into the CVD reactor to effect correspondingly close control of stoichiometry.

Many potentially useful metals do not form compounds which are well suited for CVD. Although some source reagents are solids
25 which are amenable to sublimation for gas-phase transport into the CVD reactor, the sublimation temperature may be very close to decomposition temperature. Accordingly, the reagent may begin to decompose in the lines leading to the CVD reactor, and it then becomes difficult to control the stoichiometry of the deposited films.

30

Accordingly, there is a continuing search in the art for improved source reagent compositions which are amenable to vaporization to form the source component vapor for CVD processes, for applications such as the formation of diffusion barriers, conductors, dielectrics,
35 protective coatings, phosphors, electroluminescent structures,

ferroelectrics, giant magnetoresistive films, corrosion-resistant films, and mixed metal films.

5 In the chemical vapor deposition of multicomponent material systems, multiple source reagents are delivered to the CVD reactor. A particularly advantageous way of delivering multiple source reagents is to accurately mix neat liquid source reagents or liquid solutions of source reagents and then flash vaporize the mixture and deliver the resulting vapor to the reactor. It is possible in this situation for the reagents to undergo reactions, either in the liquid phase before
10 vaporization or in the gas phase after vaporization. If these reactions convert a source reagent to an insoluble or non-volatile product, or to a material of different chemical or physical properties, then the elements contained in that product will not reach the substrate and the stoichiometry of the deposited film will be incorrect.
15

Examples of this problem (wherein Et is ethyl; tBu is tert-butyl; iPr is isopropyl; and thd is tetramethylheptanedionate) include the following:

20

(i) during deposition of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, using $(\text{Et})_4\text{Pb}$, $\text{Zr}(\text{OtBu})_4$, and $\text{Ti}(\text{OiPr})_4$ source reagents, ligand exchange between the Zr and Ti reagents resulted in formation of $\text{Zr}(\text{OiPr})_4$ (and perhaps other products of which $\text{Zr}(\text{OiPr})_4$ is a monomer), which had very low volatility and
25 which condensed in the gas manifold or vaporizer;

30

(ii) when solutions of $\text{Ba}(\text{thd})_2$ and $\text{Ti}(\text{OiPr})_4$ were mixed prior to vaporization, an insoluble precipitate was formed, presumably $\text{Ba}(\text{OiPr})_2$; and

35

(iii) when solutions of $\text{Pb}(\text{thd})_2$ and $\text{Ti}(\text{OiPr})_4$ were mixed in butyl acetate, the reagents reacted to form compounds of differing physical properties, such as $\text{Pb}(\text{OiPr})_2$ and $\text{Ti}(\text{OiPr})_2(\text{thd})_2$.

Another specific example illustrating this problem is the preparation of films of strontium bismuth tantalate and strontium

bismuth niobate ($\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$) by CVD for use in non-volatile ferroelectric random access memories. The most commonly used strontium source reagents are β -diketonate complexes such as $\text{Sr}(\text{thd})_2$. When a solution is heated containing the following source reagents for deposition of $\text{SrBi}_2\text{Ta}_2\text{O}_9$:

$\text{Sr}(\text{thd})_2$; $\text{Ta}(\text{OEt})_5$; and $\text{Bi}(\text{Ph})_3$ wherein Ph =phenyl,

the ethoxide ligands of the tantalum reagent exchange with the thd ligands of the strontium reagent, leading to the formation of undesirable strontium alkoxide species that have reduced volatility and that can decompose in the vaporization zone. Alternatively, when these reagents are provided separately in bubblers, similar ligand exchange reactions occur in the gas phase; the resulting solids constrict the gas lines or alter the film stoichiometry.

In certain instances, such problems can be avoided by using identical ligands on the metals to make ligand exchange a degenerate reaction (i.e., where the exchanging ligand is identical to the original ligand). Examples of this approach include the use of tetraethylorthosilicate, triethylborate and triethylphosphite for deposition of borophosphosilicate glasses (*J. Electrochem. Soc.*, 1987, 134(2), 430). In many instances, however, this method for avoiding the problem is not possible because the appropriate compound does not exist, is too unstable or involatile to be used for CVD, or otherwise has disadvantageous physicochemical material properties. For example, for deposition of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, a reagent system with identical ligands is problematic because while $\text{Pb}(\text{thd})_2$ and $\text{Zr}(\text{thd})_4$ are stable and volatile, $\text{Ti}(\text{thd})_4$ does not exist and $\text{Ti}(\text{thd})_3$ is extremely air sensitive. Similarly, while $\text{Ti}(\text{OtBu})_4$ and $\text{Zr}(\text{OtBu})_4$ are stable and volatile, $\text{Pb}(\text{OtBu})_2$ is thermally unstable at temperatures required for volatilization.

The foregoing problems are also encountered in the circumstance where the metal source reagent is provided in a liquid solution and the solvent contains moieties which react with ligands of the source reagent compound to produce undesirable ligand exchange reaction by-products

which display different physical properties and are involatile or insoluble.

Accordingly, it is an object of the present invention to provide improved metal source reagent compositions for the deposition of corresponding metals and metal oxides via CVD processes.

Other objects and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

SUMMARY OF THE INVENTION

The present invention generally relates to a metalorganic complex of the formula:



wherein:

M is a y-valent metal;

A is a monodentate or multidentate organic ligand coordinated to M which allows complexing of MA_y with X; y is an integer having a value of 2, 3 or 4;

each of the A ligands may be the same or different; and

X is a monodentate or multidentate ligand coordinated to M

and containing one or more atoms independently selected from the group consisting of atoms of the elements C, N, H, S, O and F.

In such complex, M may for example be selected from the group consisting of Cu, Ba, Sr, La, Nd, Ce, Pr, Sm, Eu, Th, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Bi, Tl, Y, Pb, Ni, Pd, Pt, Al, Ga, In, Ag, Au, Co, Rh, Ir, Fe, Ru, Sn, Li, Na, K, Rb, Cs, Ca, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W. The ligand A may be selected from the group consisting of β -diketonates and their sulfur and nitrogen analogs, β -ketoesters and their sulfur and nitrogen analogs, cyclopentadienyls, alkyls, perfluoroalkyls, alkoxides, perfluoroalkoxides, and Schiff bases. Specific examples of A include:

- 5
- (i) 2,2,6,6-tetramethyl-3,5-heptanedionate;
 - (ii) 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate;
 - (iii) 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate;
 - (iv) cyclopentadienyl;
 - (v) 4,4'-(ethane-1,2-diyl-diimino) bis (3-pentene-2-one);
 - (vi) pentamethylcyclopentadienyl and other substituted cyclopentadienyls;
 - (vii) 2,4-pentanedionate; and
 - (viii) 1,1,1-trifluoro-2,4-pentanedionate.

10

The ligand X in such complexes may, for example, be selected from the group consisting of:

- 15
- (i) oxyhydrocarbyl ligands;
 - (ii) nitrogenous oxyhydrocarbyl ligands;
 - (iii) fluoroxyhydrocarbyl ligands; and
 - (iv) thiooxyhydrocarbyl ligands.

Specific classes of X ligand species include:

20

- (a) amines and polyamines;
- (b) bipyridines;
- (c) ligands of the formula:

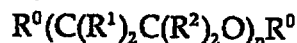
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wherein G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;

30

- (d) crown ethers;
- (e) thioethers; and
- (f) ligands of the formula:



wherein:

35

$R^0 =$ H, methyl, ethyl, n-propyl, cyanato,
perfluoroethyl,

perfluoro-n-propyl, or vinyl;

5

$R^1 =$ H, F, or a sterically acceptable hydrocarbyl
substituent;

$R^2 =$ H, F, or a sterically acceptable hydrocarbyl
substituent;

$n =$ 2, 3, 4, 5, or 6; and

10

each R^0 , R^1 , and R^2 may be the same as or different from
the other R^0 , R^1 , and R^2 , respectively.

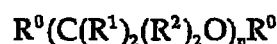
Examples of such ligand X include tetraglyme, tetrahydrofuran,
bipyridine, and 18-crown-6 ethers.

15

In the foregoing metalorganic complexes MA_yX , A is an organic
ligand which is coordinative to M, which allows complexing of MA_y
with the ligand X, and which forms the sub-complex MA_y with M
which is stable, e.g., under standard temperature and pressure (STP)
20 conditions (i.e., 25 degrees Centigrade, 1 atmosphere pressure), and thus
may be referred to as a "stable STP sub-complex MA_y ."

In a more specific aspect, the ligand X may have the formula:

25



wherein:

$R^0 =$ H, methyl, ethyl, n-propyl, cyanato,
perfluoroethyl,

perfluoro-n-propyl, or vinyl;

30

$R^1 =$ H, F, or a sterically acceptable hydrocarbyl
substituent;

$R^2 =$ H, F, or a sterically acceptable hydrocarbyl
substituent;

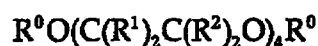
$n =$ 2, 3, 4, 5, or 6; and

35

each R^0 , R^1 , and R^2 may be the same as or different from the other R^0 , R^1 , and R^2 , respectively.

In a further specific aspect, the ligand X may have the formula:

5



wherein:

each R^0 , R^1 , and R^2 is selected independently, and

$R^0 = H, CH_3$, or C_2H_5 ;

10

R^1 and $R^2 = H$ or F .

In the metalorganic complexes described above, each of the ligands A may be a constituent moiety of a single group which is coordinately attached to M thereby. Alternatively, the ligand X and at least one of the ligands A may be a constituent moiety of a single group which is coordinately attached to M thereby.

In use, for the formation of metal or metal oxide films on a substrate, the metalorganic complexes of the invention may be employed in a solvent or suspending agent for the complex(es), to thereby form a metal source reagent solution comprising the metalorganic complex(es) and the solvent or suspending agent. Such metal source reagent liquid solution may then be volatilized to yield a metal source vapor, and the metal source vapor may be contacted with a substrate in a CVD reactor, to deposit the metal-containing film on the substrate.

TABLE I

30	<u>Metal Source Reagent(s)</u>	<u>Solvent Medium</u>
	Ba(thd) ₂ (tetraglyme)	85-98% butyl acetate and 1-15% tetraglyme
	Sr(thd) ₂ (tetraglyme)	
	Ti(OiPr) ₂ (thd) ₂	
35		

	Ca(thd) ₂ (tetraglyme) Sr(thd) ₂ (tetraglyme)	75-95% isopropanol with 5-25% tetraglyme
5	Ir(acac) ₃ or Ir(thd) ₃	butyl acetate
	La(thd) ₃ (MeO) ₃ P=O	tetrahydrofuran
10	Nb(OiPr) ₄ thd	45-88% tetrahydrofuran 10-35% isopropanol 2-20% tetraglyme
15	Pb(thd) ₂ La(thd) ₃ Ti(OiPr) ₂ (thd) ₂	80-98% tetrahydrofuran and 2-20% tetraglyme
20	Pb(thd) ₂ Zr(thd) ₄ Ti(OiPr) ₂ (thd) ₂	45-88% tetrahydrofuran 10-35% isopropanol 2-20 % tetraglyme
	Ru(acac) ₃ or Ru(thd) ₃	butyl acetate
25	Sr(thd) ₂ (tetraglyme) BiPh ₃ Ta(OiPr) ₄ (thd)	45-88% tetrahydrofuran 10-35% isopropanol 2-20 % tetraglyme
30	[O=Ti(thd) ₂] _n wherein n is 1 or 2	butyl acetate
	Zr(thd) ₄ Y(thd) ₃	80-98% tetrahydrofuran and 2-20% tetraglyme
35	[O=Zr(thd) ₂] _n wherein n is 1 or 2	butyl acetate or butyl acetate/tetraglyme

	Cu(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
5	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
10	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	
	Ga(sthd) ₃	
	Ce(sthd) ₄	
15	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Ga(sthd) ₃	
	Ce(sthd) ₄	
20	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Sr(sthd) ₂	
	Ga(sthd) ₃	
	Ce(sthd) ₄	
25	Cu(shfac) ₂	45-88% tetrahydrofuranacetate 10-35% isopropanol 2-20 % tetraglyme
	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetraglyme
30	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Ti(hfac) ₃	85-99% butyl acetate and 1-15% tetraglyme
	Ti(hfac) ₃	butyl acetate
35	Mo(hfac) ₃	butyl acetate

Mo(thd)₃

butyl acetate

5 wherein when the solvent medium contains multiple solvent components, the percentages specified are percentages by weight, based on the weight of the total solvent medium, and with the total percentage of all solvent components being 100%.

10 A further aspect of the invention relates to sulfur-based complexes having utility for forming a metal sulfide film on a substrate, comprising sulfur-containing metal source reagent compounds in a solvent medium, in which the sulfur-containing metal source reagent may complex with a suitable ligand deriving from the solvent medium.

15 Illustrative sulfur-containing metal source compounds and appertaining solvent media, are set out in Table II below.

TABLE II

	<u>Metal Source Compound</u>	<u>Solvent Medium</u>
20	Cu(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
25	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	
30	Ga(sthd) ₃	
	Ce(sthd) ₄	
	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Ga(sthd) ₃	
35	Ce(sthd) ₄	

- Ca(sthd)₂ 85-99% butyl acetate and 1-15% tetrathiocyclodecane
 Sr(sthd)₂
 Ga(sthd)₃
 Ce(sthd)₄
- 5 Cu(shfac)₂ 45-88% tetrahydrofuran
 10-35% isopropanol
 2-20 % tetraglyme
- 10 The volatilization of the above-identified sulfur-containing metal source compounds from the solution creates a metal source vapor which may be delivered (transported) to a CVD reactor, for deposition of the metal on the substrate in the form of a sulfide. Such deposition of the metal on the substrate may be carried out in the
- 15 presence of a sulfur-containing gas, e.g., a sulfur-containing gas selected from the group of sulfur compounds consisting of hydrogen sulfide, t-butyl thiol, and cyclohexyl thiol.

- Alternatively, a source compound not containing sulfur, such as
- 20 those identified in Table III below, may be contacted with a substrate under CVD conditions, and in the presence of a sulfur compound or component, to form a metal sulfide film on the substrate.

TABLE III

25	<u>Metal Source Compound</u>	<u>Solvent Medium</u>
	Cu(hfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
30	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Cu(hfac) ₂	45-88% tetrahydrofuran
35		10-35% isopropanol
		2-20 % tetraglyme

	Ti(hfac) ₃	85-99% butyl acetate and 1-15% tetraglyme
	Ti(hfac) ₃	butyl acetate
5	Mo(hfac) ₃	butyl acetate
	Mo(thd) ₃	butyl acetate.

- 10 The sulfur constituent in such formation of a metal sulfide film may for example comprise a sulfur-containing component in the solvent phase of the precursor source composition, such as hydrogen sulfide. Alternatively, the sulfur constituent required to form the metal sulfide film may be introduced in the vapor phase during the CVD
- 15 metal film deposition process, whereby the vapor phase sulfur combines with the metal film being formed on the substrate, yielding the desired metal sulfide film.

- 20 Such metal sulfide films may have utility in the fabrication of display phosphor screens or detector, and metal sulfide films because of their lubricious character, have potential utility in a wide variety of tribological applications, as wear inhibitor films.

- 25 Compositions according to the invention, comprising a metal source reagent solution including a metal β -thioketonate source reagent and a compatible solvent medium for the metal β -thioketonate source reagent, may be employed for directly forming a metal sulfide film on a substrate. The metal moiety of the metal β -thioketonate source reagent may be a metal such as Cu, Sr, Ca, Ga, Ce, Ti, and Mo. By volatilizing the
- 30 metal source reagent liquid solution to yield a metal source vapor, and contacting the metal source vapor with the substrate, a metal sulfide film may be advantageously deposited on the substrate. Such contacting of the metal source vapor with the substrate may advantageously be carried out in the presence of hydrogen sulfide or other sulfur source
- 35 gas or component, such as t-butylthiol, or cyclohexylthiol, to enhance the efficacy of the metal sulfide film formation.

Alternatively, a metal sulfide film may be formed on a substrate via CVD processing, wherein a metal source reagent whose metal moiety is reactive with sulfur to form a metal sulfide film, is deposited on a substrate in the presence of hydrogen sulfide vapor, or other sulfur-containing vapor, to form the metal sulfide film. As a still further alternative, a metal source reagent in accordance with the invention may be provided in a liquid solution containing a sulfur constituent, e.g., hydrogen sulfide, t-butylthiol and cyclohexyl thiol, whereby the volatilization of the reagent solution results in the formation of a metal sulfide film.

As an example of the use of metal reagent compositions in accordance with the invention, for forming a metal-containing film on a substrate, a listing is set out in Table IV below of illustrative compositions of metal-containing films, together with corresponding metal source reagent and solvent medium species, which may be employed in the formation of such metal and metal oxide films. It will be recognized that in some instances of the compositions set out in the Table, the solvent species, e.g., tetraglyme, may advantageously complex in situ with the metal source compound, to form a stabilized complex, which facilitates highly efficient deposition of the metal deposition species from the resulting complex.

TABLE IV

<u>Metal Containing Film</u>	<u>Metal Source Reagent</u>	<u>Solvent Medium</u>
Ir	Ir(acac) ₃ or Ir(thd) ₃	butyl acetate
LaPO ₄	La(thd) ₃ O=P(OMe) ₃	tetrahydrofuran
PbLa _x Ti _{1-x} O ₃	Pb(thd) ₂ La(thd) ₃ Ti(OiPr) ₂ (thd) ₂	tetrahydrofuran/tetraglyme

5	$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ $x = 0 \text{ to } 1$	$\text{Pb}(\text{thd})_2$ $[\text{O}=\text{Zr}(\text{thd})_2]_n$ $[\text{O}=\text{Ti}(\text{thd})_2]_n$ $n = 1 \text{ or } 2$	tetrahydrofuran/isopropanol/ tetraglyme, or butyl acetate/tetraglyme
	RuO_2	$\text{Ru}(\text{acac})_3$ or $\text{Ru}(\text{thd})_3$	butyl acetate
10	$\text{SrBi}_2\text{Ta}_2\text{O}_9$	$\text{Sr}(\text{thd})_2$ tetraglyme BiPh_3 $\text{Ta}(\text{OiPr})_4\text{thd}$	tetrahydrofuran/isopropanol/ tetraglyme
15	Ta_2O_5	$\text{Ta}(\text{OR})_4(\text{thd})$ $\text{R} = \text{ethyl, isopropyl}$	tetrahydrofuran/isopropanol/ tetraglyme
	TiO_2	$[\text{O}=\text{Ti}(\text{thd})_2]_n$ $n = 1 \text{ or } 2$	butyl acetate/tetraglyme
20	V_2O_5	$\text{O}=\text{V}(\text{thd})_3$	butyl acetate/tetraglyme.
	ZrO_2	$[\text{O}=\text{Zr}(\text{thd})_2]_n$ $n = 1 \text{ or } 2$	butyl acetate/tetraglyme
25	CuS	$\text{Cu}(\text{shfac})_2$	butyl acetate/tetraglyme
	SrS	$\text{Sr}(\text{shfac})_2$	butyl acetate/tetraglyme
30	SrS	$\text{Sr}(\text{sthd})_2$	butyl acetate/tetraglyme
	SrS	$\text{Sr}(\text{sthd})_2$	butyl acetate/tetrathiocyclodecane
35	$(\text{Ca, Sr})\text{Ga}_2\text{S}_4$, cerium-doped	$\text{Ca}(\text{sthd})_2$ $\text{Sr}(\text{sthd})_2$ $\text{Ga}(\text{sthd})_3$ $\text{Ce}(\text{sthd})_4$	butyl acetate/tetraglyme

5	(Ca, Sr)Ga ₂ S ₄ , cerium-doped	Ca(sthd) ₂ Sr(sthd) ₂ Ga(sthd) ₃ Ce(sthd) ₄	butyl acetate/ tetrathiocyclodecane
	CuS	Cu(shfac) ₂	tetrahydrofuranacetate isopropanol tetraglyme
	CuS	Cu(hfac) ₂	butyl acetate/tetraglyme
	SrS	Sr(thd) ₂	butyl acetate/tetraglyme
10	SrS	Sr(thd) ₂	butyl acetate/tetrathiocyclodecane
	CuS	Cu(hfac) ₂	tetrahydrofuranacetate isopropanol tetraglyme
20	TiS ₂	Ti(hfac) ₃	butyl acetate/tetraglyme
	TiS ₂	Ti(hfac) ₃	butyl acetate
25	MoS ₂	Mo(hfac) ₃	butyl acetate
	MoS ₂	Mo(thd) ₃	butyl acetate.

30 As an extension of the above-discussed method for forming a metal sulfide film on a substrate, the metal sulfide film may advantageously be reacted with a metal-coreactant to form a binary metal sulfide film on the substrate, e.g., CuInS, CuGaS, CuSeS, etc.

35 In a specific aspect of the present invention, metal-organic source reagent-containing liquid compositions employed to carry out the

chemical vapor deposition (CVD) process are advantageously stabilized in character, meaning that the metal-organic source reagent therein is resistant to degradation via ligand exchange reactions, e.g., non-degenerative ligand exchanges which adversely affect the chemical
5 identity and suitability of the reagent compositions for CVD applications.

Such metal source reagent liquid solutions may for example comprise:

10

(i) at least one metal coordination complex, each of such metal coordination complexes including a metal coordinatively binding at least one ligand in a stable complex, wherein such at least one ligand is selected from the group consisting of β -diketonates and β -ketoesters,
15 and their sulfur and nitrogen analogs (i.e., corresponding ligands containing S or N atoms in place of the O atom(s) in the β -diketonates and β -ketoesters); and

20

(ii) a solvent for such metal coordination complex(es).

A generalized formula for each of such metal coordination complexes is



25

wherein:

M is a metal selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, Lu, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm,
30 Fe, Ru, Eu, Co, Rh, Ir, Gd, Ni, Tb, Th, Cu, Dy, Ho, Al, Tl, Er, Sn, Pb, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, Tm, Bi, and Yb;

A is selected from the group consisting of β -diketonates and β -ketoesters, and their sulfur and nitrogen analogs;

35

R is selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and (fully or partially) fluorinated derivatives thereof (i.e., wherein hydrogen substituent(s) of the C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, or C₆-C₁₀ aryl ligand, is/are replaced by fluorine substituent(s));

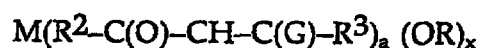
B is selected from the group consisting of polyethers, polyamines, polythiols, bipyridines, glymes, alcohols, crown ethers, crown thioethers, cyclic polyamines (cyclenes), thioglymes, arylthiols, and aliphatic thiols (mercaptans).

Q is hydrocarbyl or halohydrocarbyl, e.g., a ligand selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof;

a, x, y, and z are stoichiometric coefficients for the ligands A, OR, B, and Q, respectively, wherein a is ≥ 1 ; each of x, y, and z is independently ≥ 0 ; and A_a(OR)_xB_yQ_z is in stoichiometric relationship to metal M.

Thus, each of the metal complexes in such solutions comprises at least one ligand A coordinated to the central atom M of the complex, and M may optionally have additionally coordinated thereto one or more of the ligands OR, B, and Q, in which the resulting complex is appropriately stoichiometrically constituted to define a stable complex.

One class of source reagent complexes usefully employed in reagent solutions in the process of the invention comprise those of the formula:



wherein:

a, x, M and R are as defined hereinabove;

R² and R³ are independently selected from C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof; and

5

G is oxygen, sulfur, or nitrogen moiety of the formula =NR_b, in which R_b is selected from the group consisting of H, C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof.

10

The solvent utilized in the source reagent solutions in the process of the invention may comprise any suitable solvent species, or combination of solvent species, with which the metal complexes are compatible, such as aliphatic hydrocarbons, aromatic hydrocarbons, ethers, esters, nitriles, and alcohols. The solvent component of the solution preferably comprises a solvent selected from the group consisting of: glyme solvents having from 1 to 20 ethoxy -(C₂H₄O)-repeat units; C₂-C₁₂ alkanols, organic ethers selected from the group consisting of dialkyl ethers comprising C₁-C₆ alkyl moieties, C₄-C₈ cyclic ethers; C₁₂-C₆₀ crown O₄-O₂₀ ethers wherein the prefixed C_i range is the number i of carbon atoms in the ether compound and the suffixed O_i range is the number i of oxygen atoms in the ether compound; C₆-C₁₂ aliphatic hydrocarbons; C₆-C₁₈ aromatic hydrocarbons; organic esters; organic amines; and polyamines.

25

As used herein, the term "stable complex" means that the metal source complex in a pure state (unexposed to other materials, such as water, oxygen, etc.) is not susceptible to spontaneous degradation or decomposition at 25 degrees Centigrade and 1 atmosphere pressure. The term "complex" is intended to be broadly construed to encompass compounds as well as coordination complexes wherein at least one metal atom is coordinated (covalently, ionically and/or associatively) to at least one organic ligand group.

30

In yet another aspect, the source reagent compositions of the invention may comprise:

- (i) at least one, and preferably at least two, metal coordination complexes, each of the formula:



wherein:

- 10 M is a metal selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm, Fe, Ru, Eu, Co, Rh, Ir, Gd, Ni, Tb, Cu, Dy, Ho, Al, Tl, Er, Sn, Pb, Tm, Bi, Lu, Th, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, and Yb;

- 15 A is selected from the group consisting of β -diketonates and β -ketoesters, and their sulfur and nitrogen analogs;

- 20 R is selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and (fully or partially) fluorinated derivatives thereof (i.e., wherein hydrogen substituent(s) of the C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, or C₆-C₁₀ aryl ligand, is/are replaced by fluorine substituent(s));

- 25 B is selected from the group consisting of polyethers, polyamines, polythiols, bipyridines, glymes, alcohols, crown ethers, crown thioethers, cyclic polyamines (cyclenes), thioglymes, arylthiols, and aliphatic thiols (mercaptans).

- 30 Q is hydrocarbyl or halohydrocarbyl, e.g., a ligand selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof;

- 35 a, x, y, and z are stoichiometric coefficients for the ligands A, OR, B, and Q, respectively, wherein a is ≥ 1 ; each of x, y, and z is

independently ≥ 0 , and $A_a(OR)_x B_y Q_z$ is in stoichiometric relationship to metal M; and

(ii) a solvent for the metal coordination complex(es).

5

The solution compositions of the invention may include compounds comprised of β -diketonate and/or alkoxide ligands having a metal M, e.g., selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm, Fe, Ru, 10 Eu, Co, Rh, Ir, Gd, Ni, Tb, Cu, Dy, Ho, Al, Tl, Er, Sn, Pb, Tm, Bi, Lu, Th, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, and Yb, complexed to at least one alkoxide ligand and at least one β -diketonate ligand.

Such compounds may have the general formula:

15



wherein:

20 G is oxygen, sulfur, or imide of the formula: $=NR_b$, wherein R_b is H, C₁-C₈ alkyl, or C₁-C₈ perfluoroalkyl (e.g., trifluoroethyl);

$x + y = p$ where p is the valence of metal M;

25 $x + 2y = q$ where q is the coordination number of the metal M;

R^1 is C₁-C₆ hydrocarbyl or fluoroalkyl;

30 R^2 and R^3 are independently selected from C₁-C₁₄ hydrocarbyl, C₁-C₆ alkoxy, and C₂-C₆ fluoroalkyl groups, wherein hydrocarbyl groups may be selected from C₁-C₈ alkyl, C₆-C₁₀ cycloalkyl, C₂-C₁₂ alkenyl and C₆-C₁₄ aryl groups, and C₁-C₆ fluoroalkyl groups may be selected from perfluoroalkyls of 2 through 6 carbons.

35 As used herein, the following terms for ligand groups have the following meanings: acac = acetylacetonate, more specifically 2,4-

pentane dionate; hfacac (or hfac) = hexafluoroacetylacetonate, more specifically 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; tfacac (or tfac) = trifluoroacetylacetonate, more specifically 1,1,1-trifluoro-2,4-pentanedionate; thd = tetramethylheptanedionate, as hereinabove
5 identified, and more specifically 2,2,6,6-tetramethyl-3,5-heptanedionate; fod = fluorodimethyloctanedionate, more specifically 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate; hfod = heptafluoro-dimethyloctanedionate; and tg = tetraglyme. The corresponding β -thioketonate ligands are identified consistently therewith, by prefixation
10 of "s" to the corresponding β -diketonate ligand, e.g., shfac, sthd, etc.

More generally, various reagents and deposited products may be referred to sometimes hereinafter by alphabetic acronyms based on their constituent elements or moieties, e.g., PZT for lead zirconium titanate,
15 BST for barium strontium titanate, etc., and in such case, such acronymic designations are intended to be broadly construed to encompass all suitable stoichiometric forms of the composition under consideration.

20 It is to be appreciated that the compositions disclosed herein, in respect of constituent components and/or moieties of such compositions, may comprise, consist, and/or consist essentially of, such constituent components and/or moieties.

25 Other aspects and features of the invention will be more fully apparent from the ensuing disclosure and appended claims.

DETAILED DESCRIPTION OF THE INVENTION, AND PREFERRED EMBODIMENTS THEREOF

30

The disclosures of the following prior applications and appertaining patents hereby are incorporated herein in their entirety: U.S. Application Serial No. 08/181,800 filed January 18, 1994 and issued September 26, 1995 as U.S. Patent 5,453,494; U.S. Application Serial No.
35 07/981,141 filed July 22, 1992, and issued January 18, 1994 as U.S. Patent 5,280,012; U.S. Application Serial No. 08/414,504 filed March 31, 1995;

U.S. Application Serial No. 08/280,143 filed July 25, 1994; U.S. Patent Application Serial No. 07/927,134, filed August 7, 1992; U.S. Patent Application Serial No. 07/807,807, filed December 13, 1991, now issued as U.S. Patent No. 5,204,314; U.S. Patent Application Serial No. 5 07/549,389, filed July 6, 1990; U.S. Application Serial No. 07/981,141 filed July 22, 1992; U.S. Application Serial No. 07/615,303 filed November 19, 1990; U.S. Application Serial No. 07/581,631 filed September 12, 1990 in the names of Peter S. Kirlin, et al., and issued July 6, 1993 as U.S. Patent 5,225,561.

10

The present invention generally relates to metalorganic source reagent compositions, and liquid compositions containing such metal-organic source reagent compositions. More specifically, the metal source reagent compositions of the present invention comprise compounds or 15 coordination complexes in which the metal atoms are coordinated to ligand species which are organic in character, as discussed in the preceding Summary section herein.

The ligand groups of the metal source complexes in the broad 20 practice of the present invention may be variously substituted to realize a wide variety of materials to optimize volatility, stability and film purity. Preferably, when the metal source reagent comprises two or more metal source complexes in combination with one another, the ligands of the various metal source complexes should be either (a) 25 identical to result in degenerative ligand exchange (wherein any ligand exchange involves replacement of the ligand group by the same type ligand from another constituent of the composition), or (b) resistant to any detrimental non-degenerative ligand exchange in relation to one another which would substantially impair or preclude the efficacy of the 30 metal source complex for its intended purpose.

The ligand groups that are potentially useful in metal source reagents of the present invention include the ligands which are more 35 fully disclosed in U.S. Patent No. 5,225,561, the disclosure of which hereby is incorporated herein in its entirety.

The metal source reagents when utilized in solvent media are selected on the basis of the following criteria: (i) the metal centers in the coordinated complexes should be as coordinatively saturated as possible, and in such respect multidentate ligands are preferred which occupy multiple coordination sites in the source reagent complex; (ii) the ligands preferably comprise sterically bulky groups such as isopropyl, t-butyl, and neopentyl, which prevent close approach of the metal centers and thus hinder deleterious ligand exchange reactions which might otherwise occur; and (iii) each individual metal source reagent in the solution has a suitable vapor pressure characteristic, e.g., a vapor pressure of at least 0.001 Torr at the temperature and pressure conditions involved in their volatilization.

The solvent medium employed in source reagent solutions in accordance with the present invention may be any suitable organic solvent which is compatible with the metal complexes in the solution, has moderate volatility, and in which high concentrations of the metal complexes can be dissolved. Such solvent medium may suitably comprise one or more solvent species such as: glymes, aliphatic hydrocarbons, aromatic hydrocarbons, organic ethers (including dialkyl, cyclic and crown ethers), dialkyl esters, alkyl nitriles ($=NR_b$, wherein R_b is H, C₁-C₈ alkyl, or C₁-C₈ perfluoroalkyl, e.g., trifluoroethyl), and alkanols. Among these classes of solvents, preferred solvent species include glyme solvents having from 1 to 20 ethoxy $-(C_2H_4O)-$ repeat units; C₂-C₁₂ alkanols, organic ethers selected from the group consisting of dialkyl ethers comprising C₁-C₆ alkyl moieties, C₄-C₈ cyclic ethers, and C₁₂-C₆₀ crown O₄-O₂₀ ethers wherein the prefixed C_i range is the number i of carbon atoms in the ether compound and the suffixed O_i range is the number i of oxygen atoms in the ether compound; C₆-C₁₂ aliphatic hydrocarbons; and C₆-C₁₈ aromatic hydrocarbons. Particularly preferred crown ethers include 12-crown-4, 15-crown-5, and 18-crown-6 species.

Preferred metal source reagent species include compounds having as constituent moieties thereof β -diketonate and alkoxide ligands, and a metal selected from the group consisting of Mg, Ca, Sr, Ba,

Sc, Y, La, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm, Fe, Ru, Eu, Co, Rh, Ir, Gd, Ni, Tb, Cu, Dy, Ho, Al, Tl, Er, Sn, Pb, Tm, Bi, Lu, Th, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, and Yb, wherein the metal is coordinated to at least one alkoxide ligand and at least one β -diketonate ligand.

Illustrative β -diketonate ligands employed in metal source complexes of the present invention include acac, thd, fod, hfod, tfacac, and hfacac, and their corresponding thio analogs.

By way of example, the metal source reagent liquid solutions of the present invention may suitably comprise metal source reagent and solvent medium species identified in Table V set out below.

Table V

	<u>Metal Source Reagent(s)</u>	<u>Solvent Medium</u>
	Sr(thd) ₂	10:1 isopropanol/tetraglyme;
	Ir(acac) ₃ or Ir(thd) ₃	butyl acetate
	La(thd) ₃ (MeO) ₃ P=O	tetrahydrofuran
	Nb(OiPr) ₄ (thd)	8:2:1 tetrahydrofuran/isopropanol/ tetraglyme
	Pb(thd) ₂ La(thd) ₃ Ti(OiPr) ₂ (thd) ₂	9:1 tetrahydrofuran/tetraglyme;
	Pb(thd) ₂ Zr(thd) ₄ Ti(OiPr) ₂ (thd) ₂	8:2:1 tetrahydrofuran/isopropanol/ tetraglyme

	Ru(acac) ₃ or Ru(thd) ₃	butyl acetate
5	Sr(thd) ₂ (tetraglyme) BiPh ₃ Ta(OiPr) ₄ thd	8:2:1 tetrahydrofuran/isopropanol/ tetraglyme
10	[O=Ti(thd) ₂] _n wherein n is 1 or 2	butyl acetate or 25:1 butyl acetate/tetraglyme
	[O=Zr(thd) ₂] _n wherein n is 1 or 2	butyl acetate or 25:1 butyl acetate/tetraglyme
15	[O=Zr(thd) ₂] _n wherein n is 1 or 2	butyl acetate or 25:1 butyl acetate/tetraglyme
	Cu(shfac) ₂	25:1 butyl acetate/tetraglyme
20	Sr(shfac) ₂	25:1 butyl acetate/tetraglyme
	Sr(sthd) ₂	25:1 butyl acetate/tetraglyme
25	Sr(sthd) ₂	butyl acetate/tetrathiocyclodecane
	Ca(sthd) ₂ Sr(sthd) ₂ Ga(sthd) ₃ Ce(sthd) ₄	25:1 butyl acetate/tetraglyme
30	Ca(sthd) ₂ Ga(sthd) ₃ Ce(sthd) ₄	25:1 butyl acetate/tetraglyme
35	Cu(shfac) ₂	8:25:1 isopropanol/tetrahydrofuran/ tetraglyme

5	Ca(sthd) ₂	25:1 butyl acetate/tetrathiocyclodecane
	Sr(sthd) ₂	
	Ga(sthd) ₃	
	Ce(sthd) ₄	
10	Cu(hfac) ₂	25:1 butyl acetate/tetraglyme
	Sr(thd) ₂	25:1 butyl acetate/ tetrathiocyclodecane
	Cu(hfac) ₂	8:25:1 isopropanol/tetrahydrofuran/ tetraglyme
15	Ti(hfac) ₃	25:1 butyl acetate/tetraglyme
	Ti(hfac) ₃	butyl acetate
	Mo(hfac) ₃	butyl acetate
20	Mo(thd) ₃	butyl acetate

The metal source reagent solutions employed in the process of the present invention may be readily employed in CVD applications for forming a metal-containing film on a substrate, by the steps of volatilizing the metal source reagent liquid solution to yield a metal source vapor, and contacting the metal source vapor with the substrate, to deposit the metal-containing film thereon. Illustrative metal source reagent solutions and corresponding metal-containing film compositions are identified in Tables III and hereinabove in the "Summary of the Invention" section hereof.

The features and advantages of the invention are more fully shown by the following non-limiting examples, wherein all parts and percentages are by weight unless otherwise expressly stated.

Example 1. Synthesis of Ta(OEt)₄(η^2 -thd)

One equivalent (33.9 g) of 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd) was added directly to 74.6 g Ta(OEt)₅ in a 500 mL Schlenk flask; both starting materials were obtained commercially (Lancaster Chemicals, Inc.). The vessel was heated to 65°C under a slow nitrogen purge to a bubbler. After 2 hours, the ethanol generated was removed *in vacuo* to yield 99.8 g of the colorless liquid Ta(OEt)₄(η²-thd) in quantitative yield, which solidified upon cooling. The compound melted at 26°C and boiled at approximately 80°C at 140 mtorr. The ¹H and ¹³C NMR spectra in benzene-d₆ were consistent with an octahedral structure composed of two ethoxide ligands in axial positions and a second set of cis-ethoxide ligands in the equatorial plane across from the bidentate β-diketonate: δ 5.81 (s, 1 H, CH), 4.72 (q, 4 H, CH₂), 4.20 (q, 4 H, CH₂), 1.34 (tr, 6 H, CH₃), 1.14 (tr, 6 H, CH₃), 1.13 (s, 18 H, *t*-Bu); ¹³C{¹H} NMR (C₆D₆) δ 199.9 (C=O), 92.9 (CHdiket), 68.8 (CH₂CH₃), 65.4 (CH₂CH₃), 40.9 (CMe₃), 28.3 (CMe₃), 19.6 (CH₂CH₃), 19.0 (CH₂CH₃).

Example 2. Synthesis of Ta(OiPr)₄(η²-thd)

A nine-fold excess of isopropanol (170 mL) was added to 33.6 g Ta(OEt)₄(η²-thd). The solution was heated at 60°C for 45 min, following which the volatiles were removed *in vacuo*. The ligand exchange procedure was repeated a second time to yield 36.8 g of white, crystalline Ta(O-*i*-Pr)₄(η²-thd) in quantitative yield. The product was purified by sublimation at 100°C at 150 mtorr. The compound melted at 149°C. The ¹H and ¹³C NMR spectra in benzene-d₆ were consistent with an octahedral structure composed of two isopropoxide ligands in axial positions and a second set of cis-isopropoxide ligands in the equatorial plane across from the bidentate β-diketonate: δ 5.81 (s, 1 H, CH), 5.10 (sept, 2 H, CH), 4.51 (sept, 2 H, CH), 1.38 (d, 12 H, Me), 1.20 (d, 12 H, Me), 1.17 (s, 18 H, *t*-Bu); ¹³C{¹H} NMR (C₆D₆) δ 199.4 (C=O), 93.0 (CHdiket), 75.0 (CHMe₂), 71.4 (CHMe₂), 40.8 (CMe₃), 28.3 (CMe₃), 26.4 (CHMe₂), 25.8 (CHMe₂).

Example 3. Synthesis of Nb(OEt)₄(η²-thd)

The procedure of Example 1 is followed, using Nb(OEt)₅ as starting material rather than the tantalum ethoxide. One equivalent of

2,2,6,6-tetramethyl-3,5-heptanedione (Hthd) is added directly to Nb(OEt)₅ in a Schlenk flask. The vessel is heated to about 65°C under a slow nitrogen purge to a bubbler. After 2 hours the ethanol generated is removed *in vacuo* to yield Nb(OEt)₄(η²-thd) in quantitative yield.

5

Example 4. Synthesis of Nb(OiPr)₄(η²-thd)

A nine-fold molar excess of isopropanol is added to Nb(OEt)₄(η²-thd). The resulting solution is heated at 60°C for 45 min, following which the volatiles are removed *in vacuo*. The ligand
10 exchange procedure is repeated a second time to yield solid Nb(O-*i*-Pr)₄(η²-thd) in quantitative yield. The product is purified by sublimation at 100°C at 150 mtorr.

Example 5. Deposition of Niobia Film

15 Nb(O-*i*-Pr)₄(η²-thd) is used to deposit Nb₂O₅ ("niobia") on a silicon wafer held at 400°C in a CVD reactor. The Nb reagent is contained in a vessel ("bubbler") held at 185°C and Ar gas is flowed through the vessel at 100 sccm. Pressure in the "bubbler" is controlled at 80 torr using a manual throttle valve. Oxygen is flowed to the reactor
20 through a separate manifold at 300 sccm. Total pressure in the reactor is 1 torr and partial pressure of the Nb reagent in the reactor is 0.03 torr. Deposition rate is approximately 0.04 mm/minute.

Example 6. Deposition of Tantalum Film

25 Ta(O-*i*-Pr)₄(thd) is used to deposit Ta₂O₅ (tantala) on a fused silica (glass) envelope of a high intensity lamp by chemical vapor deposition. The glass surface is held at 450°C in a CVD reactor. The Ta(O-*i*-Pr)₄(thd) compound is dissolved in an organic solvent and this liquid solution is pumped to a vaporization zone of the reactor held at 200°C where Ar
30 carrier gas is also introduced at 100 sccm. At the vaporizer zone the solvent evaporates, the Ta compound sublimates and the gaseous reagents and Ar then flow to the chemical vapor deposition reactor. Oxygen is flowed to the reactor through a separate manifold at 300 sccm. Total pressure in the reactor is 1 torr and the deposition rate is 0.065
35 mm/minute.

Example 7. Deposition of Nb:BST

Nb(O-*i*-Pr)₄(η²-thd) is used to deposit Ba_{1-x}Sr_xTi_{1-y}Nb_yO₃ (Nb:BST) on a platinum metal layer on a silicon wafer in a CVD reactor.

5 The metal layer will act as a bottom electrode in a capacitor and the Nb:BST film will have a high dielectric constant with dc low leakage current density. The platinum surface is held at 650°C. Nb(O-*i*-Pr)₄(η²-thd) reagent is dissolved in an organic solvent along with Ba(thd)₂-tetraglyme, Sr(thd)₂-tetraglyme and Ti(OPr)₂(thd)₂, and this liquid

10 solution is pumped to a vaporization zone held at 220°C where Ar carrier gas is also introduced at 600 sccm. The solution is stable and no detrimental levels of ligand exchange occurred between the metallorganic compounds in the liquid phase or gas phase. At the vaporization zone the solvent evaporates and the Bi, Sr, and Ti

15 compounds sublime and pass into the vapor phase. The gaseous reagents and Ar then flow to the CVD reactor. A mixture of oxygen and nitrous oxide is flowed to the reactor through a separate manifold at 300 sccm each. Total pressure in the reactor is 0.700 torr and the (Nb:BST) is efficiently deposited.

20

Example 8. Deposition of Bi₂SrTa₂O₉

Ta(O-*i*-Pr)₄(thd) is used to deposit Bi₂SrTa₂O₉ on platinum metal layer on a silicon wafer in a CVD reactor. The Bi₂SrTa₂O₉ film will form a ferroelectric capacitor with remanent polarization that can

25 be switched greater than 10¹² times. The Bi₂SrTa₂O₉ is deposited at 650°C. Ta(O-*i*-Pr)₄(thd) is dissolved in an organic solvent along with triphenylbismuth and Sr(thd)₂-tetraglyme and this liquid solution is pumped to a vaporization zone held at 200°C where Ar carrier gas is also introduced at 100 sccm. The solution is stable and no detrimental

30 ligand exchange occurred between the metallorganic compounds in the liquid or gas phase. At the vaporization zone the solvent evaporates and the Bi, Sr, Na compounds sublime. The gaseous reagents and Ar then flow to the chemical vapor deposition reactor. A mixture of oxygen and nitrous oxide is flowed to the reactor through a separate

35 manifold at 300 sccm each. Total pressure in the reactor is 2.1 torr and the Bi₂SrTa₂O₉ is deposited at useful rates.

Example 9. Growth of GMR Oxide Films on LaAlO_3 (100), NdGaO_3 (110), and MgO (100) Substrates by CVD

$\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$ films were grown on LaAlO_3 (100), NdGaO_3 (110), and MgO (100) substrates by CVD in the CVD system that is shown schematically in Figure 1. Tris(tetramethylheptanedionato)lanthanum ($\text{La}(\text{thd})_3$), bis(tetra-methylheptanedionato)calcium ($\text{Ca}(\text{thd})_2$), and tris(tetramethylheptane-dionato)manganese ($\text{Mn}(\text{thd})_3$), all of which were purchased commercially (Strem Chemicals), were used as precursor materials. These three organic compounds, in appropriate amounts, were mixed and dissolved in a single organic solution of 25:1 butyl acetate:tetraglyme under an inert atmosphere. The concentrations of $\text{La}(\text{thd})_3$, $\text{Ca}(\text{thd})_2$ and $\text{Mn}(\text{thd})_3$ in the solution were 0.033, 0.017, and 0.05 moles/liter of solution, respectively. During deposition, the solution was constantly injected into a vaporizer by a liquid pump and the vapors were carried immediately into a chemical vapor deposition reactor by nitrogen gas. The films were deposited at a constant pressure of 1.5 Torr and at a substrate temperature ranging from 600°C to 700°C. Both oxygen and nitrous oxide were used as oxidants.

The films were characterized and showed a high transition temperature T_c in the as-deposited films, probably due to the higher oxygen partial pressure in the CVD process. The highest T_c attained was 300K. The peak value of resistivity r is observed to decrease from 34 m Ω -cm to 12 m Ω -cm in the film with $T_c = 300\text{K}$. Post annealing of these films in 1 atm of O_2 further reduced r and increased T_c . The oxygen content plays an important role in controlling the carrier concentration. All of the films prepared at different substrate temperatures between 600 and 750°C were highly (001) oriented. The grain size of films decreased as the substrate temperature decreased without a degradation of crystallinity determined by XRD in this temperature range. There was no correlation found between grain size and cusp temperature or magnetoresistance of the films. The preferred orientation of the films appear to affect on the temperature dependence of resistivity as shown in the case of a $(\text{LaCa})\text{MnO}_3$ film deposited on MgO substrate. A lower $\Delta R/R_H$ effect of as-deposited $(\text{LaCa})\text{MnO}_3$ films

by MOCVD than that of annealed (LaCa)MnO₃ films prepared by laser deposition is probably due to a relatively low resistivity of these MOCVD films.

5 Example 10. Growth of Zirconium Titanate

A number of PZT runs were performed with the objectives of optimizing vaporizer conditions and achieving desired film stoichiometry, from Zr(thd)₄ and Ti(O-iPr)₄ source reagents. The CVD reactor was constructed to permit preheating of the carrier gas using
10 heat tape around an in-line filter, and the delivery system for vaporization and transport of the source reagent vapor was arranged and constructed in accordance with the disclosure of U.S. Patent 5,204,314.

15 Initial experiments employed as the solvent a mixture of THF:tetraglyme in the ratio of 9:1. It was found that the effect of carrier gas preheat was minimal. Vaporizer temperature was a much stronger variable with increased vaporization temperature giving somewhat more consistent vaporization as judged by monitoring the pressure of
20 the vaporizer behind the frit (vaporization element). Lower temperatures ($T_{\text{vap}}=215^{\circ}\text{C}$) resulted in more erratic vaporizer pressure. In addition, increased relative Zr content in the solution caused wide swings in vaporizer pressure as the run progressed, even at $T_{\text{vap}}=230^{\circ}\text{C}$. (Total Zr content in all cases has been held at 0.15 to 0.145
25 moles/liter solution to prevent delivery tube clogging which was experienced at higher Zr concentrations.)

One variable studied in the test was the addition of isopropanol to the solvent. In such modification, the solvent used was
30 THF:isopropanol:tetraglyme in the ratio of 8:2:1. IPA affected the process remarkably favorably in respect of the desired film composition. Zr incorporation efficiency increased to the point where films of $\text{Zr}_x\text{Ti}_{1-x}\text{O}_4$ were produced. The deposition conditions were held constant during all of the experiments, evidencing the fact that transport of Zr is
35 significantly enhanced by the addition of IPA to the THF/tetraglyme solvent. This suggested that ligand exchange may have played a role,

e.g., with the reaction $\text{Zr}(\text{thd})_4 \rightarrow \text{Zr}(\text{OiPr})_x(\text{thd})_{4-x}$, leading to more volatile species. It was also observed that the swings in vaporizer pressure decreased (at $T_{\text{vap}} = 230^\circ\text{C}$ and with 40 mm frits) with the modified solvent. Ligand exchange may also have led to the provision of all liquid precursors at the vaporizer temperature rather than solid as is the case for $\text{Zr}(\text{thd})_4$.

Example 11. Growth of BiSrTa

Transport experiments for Bi-Sr-Ta were conducted in a CVD reactor to roughly determine vaporizer operating conditions, following which two Ta compounds were evaluated. The first was $\text{Ta}(\text{OiPr})_4(\text{thd})$, for which three vaporizer temperatures were investigated. The best condition was found to be 200°C . A second Ta compound, $\text{Ta}_2(\text{OEt})_4(\text{thd})$ also was tried under the same transport conditions, as summarized in Table V below.

Table V

20	Frit pore size	20 μm
	Carrier gas flow	450 sccm Ar (preheated)
25	Precursors	BiPh_3 , $\text{Sr}(\text{thd})_2$, and $\text{Ta}(\text{OiPr})_4(\text{thd})$ or $\text{Ta}(\text{OEt})_4(\text{thd})$
	Solvent	8:2:1 THF:isopropanol:tetraglyme
30	Reagent solution concentrations	Bi 0.40M - Sr 0.15M - Ta 0.40M
	Delivery rate	0.1 ml/min
35	System base pressure	2 torr

Ta(OiPr)₄(n²-thd)

The 180°C experiment resulted in a steep rise in pressure behind the frit, presumably due to unsublimed material (likely Sr(thd)₂) which
5 was consistent with the fact that the pressure behind the frit recovered by 93% to nearly its initial value in about 1.5 hours.

The 200°C experiment had a steep initial pressure rise, followed by the lowest steady-state rise of any of the conditions tried. A relatively
10 low pressure recovery after the experiment (29%) indicated that some decomposition of metalorganic material occurred at the frit.

The 220°C experiment behaved similarly to the 200°C experiment with two exceptions: the steady state rise was >2X higher and a steep
15 pressure rise occurred at the end of the experiment (~2 hours) which was accompanied by a clog in the delivery tube at the frit. The clog disappeared as the vaporizer cooled overnight and a significant amount (about a 5 mm dia. lump) of white material was present on top of the frit. This may have been due to the reagent being sucked into the
20 vaporizer from the delivery tube (with some leakage through the 20 psi check valve) from which the solvent had evaporated. An NMR analysis was conducted on the material, and it showed BiPh₃ and Ta(OiPr)₄(thd) precursors in about their original ratios but no Sr(thd)₂.

25 The frit residue was analyzed qualitatively by x-ray fluorescence (XRF). The results showed that the amount of Bi and Ta left on the frit increased with increasing vaporizer temperature, as expected.

Ta(OEt)₄(n²-thd)

30 This compound appeared fairly well behaved until near the end of the transport experiment, where a significant rise in pressure behind the frit occurred, accompanied by a clog in the delivery system. This clog disappeared within minutes of shutting off the solution flow. Vaporizer pressure recovered by about 62% after the experiment.
35

Several films were deposited on Pt/Ta/SiO₂/Si during the transport experiments. Deposition at 750°C susceptor temperature resulted in a film that was poorly crystallized. In contrast, films deposited at 800°C showed strong XRD peaks. Interestingly, all films had a striped appearance across the wafer indicating changing thickness. This may be attributable to a macroscopic manifestation of ledge motion during growth of the compound which is known to be a layered structure. Fringes were observed moving across the wafer at the early stages of growth.

10

Example 12. Growth of Bi₂SrTa₂O₉ Using Ta(OEt)₄(thd)

The combination of reagents Ta(OEt)₅ and Sr(thd)₂ also resulted in ligand exchange when the ligands were dissolved in solvent medium, as in Example 12. By using Ta(OEt)₄(thd) the aforementioned exchange problem is alleviated in solution. This enables a reproducible transport and CVD process.

15

The Ta(OEt)₄(thd) and Sr(thd)₂ solution can be used for depositing SrTaO or Bi₂SrTa₂O₉ materials.

20

Example 13. Use of Additive to Increase Reactant Solubility for LP CVD

Acetone, tetrahydrofuran, dimethoxyethane (DME) or dimethylformamide (DMF) are added to a solution containing Ba(thd)₂ to maximize its solubility.

25

Example 14. Addition of Excess Lewis Base to Increase Reactant Stability During LP CVD

Lewis base copper(I) β -diketonate complexes are useful for copper CVD. However, the Lewis base may be easily liberated from the molecule resulting in pre-mature decomposition and clogging of the vaporizer. To combat this problem, excess Lewis base is added. Similarly, excess Lewis base can be added to stop the formation of a less volatile dinuclear species and eliminate precipitation in the vaporizer. For example, liberation of 3-hexyne from 3-hexyne Cu(hfacac) leads to the formation of a dinuclear complex, 3-hexyne [Cu(hfacac)]₂, which is a solid at room temperature. The formation and precipitation of this

30

35

dinuclear solid can be controlled by forcing this equilibrium in the reverse direction. Thus, excess 3-hexyne not only enhances the thermal stability, but eliminates formation of a less volatile solid precipitate, which can lead to clogging and decomposition in the vaporizer.

5

Example 15. Addition of Polyether or Polyamine to Reduce Hydrolysis of Reactant During LP CVD

The coordination of H₂O to Ba(thd)₂ on thermal vaporization may be reduced or eliminated by coordinating a stronger Lewis Base to the barium center.

10

Example 16. Formation of CuS-Based Films

A solution consisting of copper (II) bis (1,1,1,5,5,5-hexafluoro-2-thio-pentane-4-one) was dissolved in an organic solvent containing n-butyl acetate and tetraglyme (25:1). The solution was delivered to a warm-walled reactor using a liquid delivery system and reacted with H₂S to produce a copper sulfide (CuS) based film. This approach can be used to produce complex copper sulfides by co-reaction with a third reactant to produce films such as CuInS, CuGaS and CuSeS films.

20

Example 17. Formation of SrS Films in Presence of H₂S

A solution consisting of strontium (II) bis (2,2,6,6-tetramethyl-3-thio-heptane-5-one) was dissolved in a solution of n-butyl acetate and tetraglyme (25:1). This solution was delivered, using a commercial liquid delivery system, to a CVD reactor and reacted with H₂S to produce high quality SrS films. These films can be used as a white phosphor layer for electroluminescent display applications.

25

Example 18. Formation of SrS Films With Thiol-Containing Source Solution

30

In a modification to Example 29, a solution consisting of strontium (II) bis (2,2,6,6-tetramethyl-3-thio-heptane-5-one) was dissolved in a solution of n-butyl acetate and tetraglyme (25:1). This solution also contained a sulfur source, such as t-butylthiol or cyclohexyl thiol and was delivered (using a commercial liquid delivery system) to a CVD reactor to produce high quality SrS films. The incorporation of the thiol

35

obviates the need for co-reaction with H_2S and therefore, is more desirable for health, safety and environmental reasons; this will facilitate manufacturing of SrS as a white phosphor layer for electroluminescent display applications.

5

Example 19. Formation of SrS Films in Presence of H_2S with Butyl Acetate/Tetrathiocyclodecane Solvent System

In a modification to Examples 29 and 30, a solution consisting of strontium (II) bis (2,2,6,6,-tetramethyl-3-thio-heptane-5-one) was dissolved in a solution of n-butyl acetate and tetrathiocyclodecane. This solution was delivered (using a commercial liquid delivery system) to a CVD reactor and co-reacted with H_2S to produce high quality SrS films. These films can be used as a white phosphor layer for electroluminescent display applications.

15

Example 20. Formation of Ce-Doped $(Ca, Sr)Ga_2S_4$ Films in Presence of H_2S

In a separate approach, multi-component phosphors, such as Ce doped $(Ca, Sr)Ga_2S_4$ can be deposited by liquid delivery of one or more solutions containing the following co-reactants; Ca (II) bis (2,2,6,6,-tetramethyl-3-thioheptane-5-one), Sr (II) bis (2,2,6,6,-tetramethyl-3-thioheptane-5-one), Ga (III) tris (2,2,6,6,-tetramethyl-3-thioheptane-5-one) and Ce (IV) tetrakis (2,2,6,6,-tetramethyl-3-thioheptane-5-one). These reactants are dissolved into n-butyl acetate and tetraglyme (25:1) and delivered to the CVD reactor for Ce doped $(Ca, Sr)Ga_2S_4$ film growth with H_2S as the sulfur source. The concentrations of each component can be controlled via the concentration of the individual components in solution or via mixing of individual solutions of the reactants. The resulting thiogallate film can be used for electroluminescent films in display applications.

25
30

Example 21. Formation of Ce-Doped $(Ca, Sr)Ga_2S_4$ Films With Thiol-Containing Solvent System

In a modification of Example 32, a Ce doped $(Ca, Sr)Ga_2S_4$ film can be deposited by liquid delivery of one or more solutions containing the

35

following co-reactants; Ca (II) bis (2,2,6,6,-tetramethyl-3-thio-heptane-5-one), Sr (II) bis (2,2,6,6,-tetramethyl-3-thio-heptane-5-one), Ga (III) tris (2,2,6,6,-tetramethyl-3-thio-heptane-5-one) and Ce (IV) tetrakis (2,2,6,6,-tetramethyl-3-thio-heptane-5-one). These reactants are dissolved into
5 n-butyl acetate, tetraglyme (25:1) and sulfur containing source, such as t-butyl thiol or cyclohexyl thiol. The incorporation of the thiol obviates the need for co-reaction with H₂S and therefore, is more desirable for manufacturing and environmental reasons.

10 **Example 22. Formation of Ce-Doped (Ca, Sr)Ga₂S₄ Films With Thiol-Containing Solvent System and Deposition in the Presence of Hydrogen Sulfide Gas**

In a modification of Examples 32 and 33, a Ce doped (Ca,Sr)Ga₂S₄ film can be deposited by liquid delivery of one or more solutions
15 containing the following co-reactants; Ca (II) bis (2,2,6,6,-tetramethyl-3-thioheptane-5-one), Sr (II) bis (2,2,6,6,-tetramethyl-3-thioheptane-5-one), Ga (III) tris (2,2,6,6,-tetramethyl-3-thioheptane-5-one) and Ce (IV) tetrakis (2,2,6,6,-tetramethyl-3-thioheptane-5-one). These reactants are dissolved into n-butyl acetate, tetrathiolcyclodecane and delivered to
20 the CVD reactor for Ce doped (Ca,Sr)Ga₂S₄ film growth with H₂S as the sulfur source. The concentrations of each component can be controlled via the concentration of the individual components in solution or via mixing of individual solutions of the reactants. The resulting thiogallate film can be used for electroluminescent films in display
25 applications.

Example 23. Formation of CuS Films, and Binary Metal Sulfide Films

A solution consisting of copper (II) bis (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) was dissolved in an organic solvent containing i-
30 propanol, tetrahydrofuranacetate and tetraglyme (2:8:1). The solution was delivered to a warm-walled reactor using a liquid delivery system and reacted with H₂S to produce a copper sulfide based film. In a modification of this method, the sulfur source is t-butylthiol, octanethiol or cyclohexylthiol and is a component of the solution. This
35 approach can be used to produce complex copper sulfides by co-reaction

with a third reactant to produce films such as CuInS, CuGaS and CuSeS films for a variety of applications.

Example 24. Formation of CuS Films, and Binary Metal Sulfide Films

5 A solution consisting of copper (II) bis (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) was dissolved in an organic solvent containing n-butyl acetate and tetraglyme (25:1). The solution was delivered to a warm-walled reactor using a liquid delivery system and reacted with H₂S to produce a copper sulfide (CuS) based film. This approach can be used to
10 produce complex copper sulfides by co-reaction with a third reactant to produce films such as CuInS, CuGaS and CuSeS films.

Example 25. Formation of SrS Films

15 A solution consisting of strontium (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione) was dissolved in a solution of n-butyl acetate and tetraglyme (25:1). This solution was delivered, using a commercial liquid delivery system, to a CVD reactor and reacted with H₂S to produce high quality SrS films. These films can be used as a white phosphor layer for electroluminescent display applications.

20

Example 26. Formation of SrS Films

25 In a modification to Example 29, a solution consisting of strontium (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione) was dissolved in a solution of n-butyl acetate and tetraglyme (25:1). This solution also contained a sulfur source, such as t-butylthiol or cyclohexyl thiol and was delivered (using a commercial liquid delivery system) to a CVD reactor to produce high quality SrS films. The incorporation of the thiol obviates the need for co-reaction with H₂S and therefore, is more desirable for health, safety and environmental reasons; this will
30 facilitate manufacturing of SrS as a white phosphor layer for electroluminescent display applications.

Example 27. Formation of SrS Films

35 In a modification to Examples 29 and 30, a solution consisting of strontium (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione) was dissolved

in a solution of n-butyl acetate and tetrathiocyclodecane. This solution was delivered (using a commercial liquid delivery system) to a CVD reactor and co-reacted with H₂S to produce high quality SrS films. These films can be used as a white phosphor layer for electroluminescent display applications.

Example 28. Formation of Ce-Doped (Ca, Sr)Ga₂S₄ Films in the Presence of Hydrogen Sulfide Gas

In a separate approach, multi-component phosphors, such as Ce doped (Ca,Sr)Ga₂S₄ can be deposited by liquid delivery of one or more solutions containing the following co-reactants; Ca (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione), Sr (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione), Ga (III) tris (2,2,6,6,-tetramethyl-3,5-heptanedione) and Ce (IV) tetrakis (2,2,6,6,-tetramethyl-3,5-heptanedione). These reactants are dissolved into n-butyl acetate and tetraglyme (25:1) and delivered to the CVD reactor for Ce doped (Ca,Sr)Ga₂S₄ film growth with H₂S as the sulfur source. The concentrations of each component can be controlled via the concentration of the individual components in solution or via mixing of individual solutions of the reactants. The resulting thiogallate film can be used for electroluminescent films in display applications.

Example 29. Formation of Ce-Doped (Ca, Sr)Ga₂S₄ Films With Thiol-Containing Solvent System

In a modification of Example 32, a Ce doped (Ca,Sr)Ga₂S₄ film can be deposited by liquid delivery of one or more solutions containing the following co-reactants; Ca (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione), Sr (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione), Ga (III) tris (2,2,6,6,-tetramethyl-3,5-heptanedione) and Ce (IV) tetrakis (2,2,6,6,-tetramethyl-3,5-heptane-dione). These reactants are dissolved into n-butyl acetate, tetraglyme (25:1) and sulfur containing source, such as t-butyl thiol, octylthiol or cyclohexyl thiol. The incorporation of the thiol obviates the need for co-reaction with H₂S and therefore, is more desirable for manufacturing and environmental reasons.

Example 30. Formation of Ce-Doped (Ca, Sr)Ga₂S₄ Films With Thiol-Containing Solvent System and Deposition in the Presence of Hydrogen Sulfide Gas

In a modification of Examples 32 and 33, a Ce doped (Ca,Sr)Ga₂S₄ film can be deposited by liquid delivery of one or more solutions containing the following co-reactants; Ca (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione), Sr (II) bis (2,2,6,6,-tetramethyl-3,5-heptanedione), Ga (III) tris (2,2,6,6,-tetramethyl-3,5-heptanedione) and Ce (IV) tetrakis (2,2,6,6,-tetramethyl-3,5-heptane-dione). These reactants are dissolved into n-butyl acetate, tetrathiacyclodecane and delivered to the CVD reactor for Ce doped (Ca,Sr)Ga₂S₄ film growth with H₂S as the sulfur source. The concentrations of each component can be controlled via the concentration of the individual components in solution or via mixing of individual solutions of the reactants. The resulting thiogallate film can be used for electroluminescent films in display applications.

Example 31. Formation of CuS Films With Thiol-Containing Solvent System and Deposition in the Presence of Hydrogen Sulfide Gas, and Production of Films of Binary Metal Sulfide Films

A solution consisting of copper (II) bis (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) in an organic solvent containing i-propanol, tetrahydrofuranacetate and tetraglyme (2:8:1). The solution was delivered to a warm-walled reactor using a liquid delivery system and reacted with H₂S to produce a copper sulfide based film. In a modification of this method, the sulfur source is t-butylthiol, octanethiol or cyclohexylthiol and is a component of the solution. This approach can be used to produce complex copper sulfides by co-reaction with a third reactant to produce films such as CuInS, CuGaS and CuSeS films for a variety of applications.

Example 32. Formation of TiS₂ Films With Thiol-Containing Solvent System or Deposition in the Presence of Hydrogen Sulfide Gas

A solution consisting of titanium (III) tris (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) dissolved in an organic solvent was delivered to a warm walled CVD reactor using a liquid delivery system. The precursor

was reacted with H₂S to deposit yellow films of TiS₂ as a lubricating layer onto metal parts. The process may be varied by using organic thiols in the solution and thus, obviates the need for H₂S co-reactant. This latter process is desirable for health, safety and environmental reasons.

Example 33. Formation of TiS₂ Films With Thiol-Containing Solvent System or Deposition in the Presence of Hydrogen Sulfide Gas

A solution consisting of titanium (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionato) dissolved in n-butylacetate and was delivered to a warm walled CVD reactor using a liquid delivery system. The precursor was reacted with H₂S to deposit yellow films of TiS₂ as a lubricating layer onto metal parts. The process may be modified by using organic thiols, such as t-butyl thiol, octylthiol and cyclohexylthiol, in the solution and thus, obviates the need for co-reactanting with H₂S. This latter process is desirable for health, safety and environmental reasons and enables full scale manufacturing to be safely realized.

Example 34. Formation of MoS₂ Films With Thiol-Containing Solvent System or Deposition in the Presence of Hydrogen Sulfide Gas

A solution consisting of molybdenum (III) tris (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) dissolved in n-butylacetate and was delivered to a warm walled CVD reactor using a liquid delivery system. The precursor was reacted with H₂S to deposit yellow films of MoS₂ as a lubricating layer onto metal parts. The process may be varied by using organic thiols in the solution and thus, obviates the need for H₂S co-reactant. This latter process is desirable for health, safety and environmental reasons.

Example 35. Formation of MoS₂ Films With Thiol-Containing Solvent System or Deposition in the Presence of Hydrogen Sulfide Gas

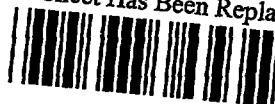
A solution consisting of molybdenum (III) tris (2,2,6,6-tetramethyl-3,5-heptanedionato) dissolved in n-butyl acetate and was delivered to a warm walled CVD reactor using a liquid delivery system. The precursor was reacted with H₂S to deposit films of MoS₂ as a lubricating layer

onto metal parts. The process may be varied by using organic thiols in the solution and thus, obviates the need for H₂S co-reactant. This latter process is desirable for health, safety and environmental reasons.

5

INDUSTRIAL APPLICABILITY

The metal source reagent compositions of the invention comprise thermally decomposable organometallic compounds, complexes, and solutions and suspensions thereof. These reagent compositions are
10 usefully employed in vapor-phase deposition processes such as chemical vapor deposition, to form films, layers, and coatings containing the metal, in applications such as formation of diffusion barriers, conductors, dielectrics, passivation or other protective coatings, phosphors, electroluminescent structures, ferroelectrics, giant
15 magnetoresistive films, corrosion-resistance films, and mixed metal films.



TSABR

43,48

THE CLAIMS**What is claimed is:**

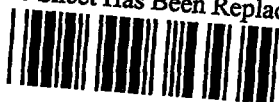
- 5 1. A metalorganic complex of the formula:



wherein:

- 10 M is a y-valent metal;
A is a monodentate or multidentate organic ligand
coordinated to M which allows complexing of MA_y with X;
y is an integer having a value of 2, 3 or 4;
each of the A ligands may be the same or different; and
15 X is a monodentate or multidentate ligand coordinated to M
and containing one or more atoms independently selected from
the group consisting of atoms of the elements C, N, H, S, O and F.
- 20 2. A complex according to claim 1, wherein M is selected from the
group consisting of Cu, Ba, Sr, La, Nd, Ce, Pr, Sm, Eu, Th, Gd, Tb, Dy,
Ho, Er, Tm, Yb, Lu, Bi, Tl, Y, Pb, Ni, Pd, Pt, Al, Ga, In, Ag, Au, Co, Rh, Ir,
Fe, Ru, Sn, Li, Na, K, Rb, Cs, Ca, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and
W.
- 25 3. A complex according to claim 1, wherein A is selected from the
group consisting of β -diketonates and their sulfur and nitrogen analogs,
 β -ketoesters and their sulfur and nitrogen analogs, cyclopentadienyls,
alkyls, perfluoroalkyls, alkoxides, perfluoroalkoxides, and Schiff bases.
- 30 4. A complex according to claim 1, wherein A is selected from the
group consisting of β -diketonates, β -thioketonates, β -ketoesters, β -
thioesters, and cyclopentadienyls.
5. A complex according to claim 1, wherein A is a β -diketonate.





CLMS 44-48

6. A complex according to claim 1, wherein A is selected from the group consisting of:
- (i) 2,2,6,6-tetramethyl-3,5-heptanedionate;
 - 5 (ii) 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate;
 - (iii) 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate;
 - (iv) cyclopentadienyl;
 - (v) 4,4'-(ethane-1,2-diyl-diimino) bis (3-pentene-2-one);
 - (vi) pentamethylcyclopentadienyl and other substituted
 - 10 cyclopentadienyls;
 - (vii) 2,4-pentanedionate; and
 - (viii) 1,1,1-trifluoro-2,4-pentanedionate.
7. A compound according to claim 1, wherein X is selected from the group consisting of:
- (i) oxyhydrocarbyl ligands;
 - (ii) nitrogenous oxyhydrocarbyl ligands;
 - (iii) fluorooxyhydrocarbyl ligands; and
 - 20 (iv) thiooxyhydrocarbyl ligands.
8. A complex according to claim 1, wherein X is selected from the group consisting of:
- 25 (a) amines and polyamines;
 - (b) bipyridines;
 - (c) ligands of the formula:
-
- 30 wherein G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;
- (d) crown ethers;
 - (e) thioethers; and
 - (f) ligands of the formula:
 - 35 $R^0(C(R^1)_2C(R^2)_2O)_nR^0$





wherein:

$R^0 =$ H, methyl, ethyl, n-propyl, cyanato, perfluoroethyl,

5 perfluoro-n-propyl, or vinyl;

$R^1 =$ H, F, or a sterically acceptable hydrocarbyl substituent;

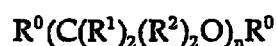
$R^2 =$ H, F, or a sterically acceptable hydrocarbyl substituent;

10 $n =$ 2, 3, 4, 5, or 6; and

each R^0 , R^1 , and R^2 may be the same as or different from the other R^0 , R^1 , and R^2 , respectively.

15 9. A complex according to claim 1, wherein X is selected from the group consisting of tetraglyme, tetrahydrofuran, bipyridine, and 18-crown-6 ethers.

20 10. A complex according to claim 1, wherein X comprises a liquid of the formula:



wherein:

25 $R^0 =$ H, methyl, ethyl, n-propyl, cyanato, perfluoroethyl,

perfluoro-n-propyl, or vinyl;

$R^1 =$ H, F, or a sterically acceptable hydrocarbyl substituent;

30 $R^2 =$ H, F, or a sterically acceptable hydrocarbyl substituent;

$n =$ 2, 3, 4, 5, or 6; and

35 each R^0 , R^1 , and R^2 may be the same as or different from the other R^0 , R^1 , and R^2 , respectively.





11. A complex according to claim 1, wherein X comprises a ligand of the formula:



wherein:

each R^0 , R^1 , and R^2 is selected independently, and

$R^0 = H, CH_3$, or C_2H_5 ;

10 R^1 and $R^2 = H$ or F .

12. A complex according to claim 1, wherein: A is a β -diketonate; and X is tetraglyme, 18-crown-6 ether, or bipyridine.

- 15 13. A complex according to claim 1, wherein each of the ligands A is a constituent moiety of a single group which is coordinatively attached to M thereby.

- 20 14. A complex according to claim 1, wherein the ligand X and at least one of said ligands A is a constituent moiety of a single group which is coordinatively attached to M thereby.

- 25 15. A metal source reagent solution comprising a metal source reagent and solvent medium, wherein the metal source reagent and the solvent medium are selected from the group of metal source reagent(s) and associated solvent media consisting of:

$Cu(shfac)_2$ 85-99% butyl acetate and 1-15% tetraglyme

30 $Sr(shfac)_2$ 85-99% butyl acetate and 1-15% tetraglyme

$Sr(sthd)_2$ 85-99% butyl acetate and 1-15% tetraglyme

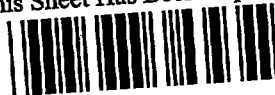
35 $Sr(sthd)_2$ 85-99% butyl acetate and 1-15% tetrathiocyclodecane





- | | | |
|----|------------------------|---|
| | Ca(sthd) ₂ | 85-99% butyl acetate and 1-15% tetraglyme |
| | Sr(sthd) ₂ | |
| | Ga(sthd) ₃ | |
| | Ce(sthd) ₄ | |
| 5 | | |
| | Ca(sthd) ₂ | 85-99% butyl acetate and 1-15% tetraglyme |
| | Ga(sthd) ₃ | |
| | Ce(sthd) ₄ | |
| 10 | Ca(sthd) ₂ | 85-99% butyl acetate and 1-15% tetrathiocyclodecane |
| | Sr(sthd) ₂ | butyl acetate and cyclohexylthiol |
| | Ga(sthd) ₃ | butyl acetate and t-butylthiol |
| | Ce(sthd) ₄ | |
| 15 | Cu(shfac) ₂ | 45-88% tetrahydrofuran |
| | | 10-35% isopropanol |
| | | 2-20 % tetraglyme |
| | | |
| | Sr(thd) ₂ | 85-99% butyl acetate and 1-15% tetraglyme |
| 20 | | |
| | Sr(thd) ₂ | 85-99% butyl acetate and 1-15% tetrathiocyclodecane |
| | | |
| | Ti(hfac) ₃ | 85-99% butyl acetate and 1-15% tetraglyme |
| | | butyl acetate and cyclohexylthiol |
| 25 | | |
| | Ti(hfac) ₃ | butyl acetate and t-butylthiol |
| | | |
| | Mo(hfac) ₃ | butyl acetate and t-butylthiol |
| | | |
| 30 | Mo(thd) ₃ | butyl acetate and cyclohexylthiol |
16. A composition according to claim 1, wherein MA_y comprises a metal β-thioketonate source compound.





17. A composition according to claim 16, wherein the metal moiety of said metal β -thioketone source compound is selected from the group consisting of Cu, Sr, Ca, Ga, Ce, Ti, and Mo.



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THE CLAIMSWhat is claimed is:

- 5 1. A metalorganic complex of the formula:



wherein:

- 10 M is a y-valent metal selected from the group consisting of Pd, Pt, Rh, Ir, Ru, V, Nb, Ta, Cr, Mo and W;
 A is a monodentate or multidentate organic ligand coordinated to M which allows complexing of MA_y with X;
 y is an integer having a value of 2, 3 or 4;
- 15 each of the A ligands may be the same or different; and
 X is a monodentate or multidentate ligand coordinated to M and containing one or more atoms independently selected from the group consisting of atoms of the elements C, N, H, S, O and F.
- 20 2. A complex according to claim 1, wherein A is selected from the group consisting of β -diketonates and their sulfur and nitrogen analogs, β -ketoesters and their sulfur and nitrogen analogs, cyclopentadienyls, alkyls, perfluoroalkyls, alkoxides, perfluoroalkoxides, and Schiff bases.
- 25 3. A complex according to claim 1, wherein A is selected from the group consisting of β -diketonates, β -thioketonates, β -ketoesters, β -thioesters, and cyclopentadienyls.
- 30 4. A complex according to claim 1, wherein A is a β -diketonate.
5. A complex according to claim 1, wherein A is selected from the group consisting of:
- 35 (i) 2,2,6,6-tetramethyl-3,5-heptanedionate;
 (ii) 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate;
 (iii) 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate;

- (iv) cyclopentadienyl;
- (v) 4,4'-(ethane-1,2-diyl)diimino) bis (3-pentene-2-one);
- (vi) pentamethylcyclopentadienyl and other substituted cyclopentadienyls;
- (vii) 2,4-pentanedionate; and
- (viii) 1,1,1-trifluoro-2,4-pentanedionate.

6. A compound according to claim 1, wherein X is selected from the group consisting of:

- (i) oxyhydrocarbyl ligands;
- (ii) nitrogenous oxyhydrocarbyl ligands;
- (iii) fluorooxyhydrocarbyl ligands; and
- (iv) thiooxyhydrocarbyl ligands.

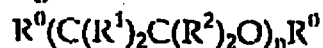
7. A complex according to claim 1, wherein X is selected from the group consisting of:

- (a) amines and polyamines;
- (b) bipyridines;
- (c) ligands of the formula:

G

wherein G is -O-, -S-, or -NR-, wherein R is H or hydrocarbyl;

- (d) crown ethers;
- (e) thioethers; and
- (f) ligands of the formula:



wherein:

$R^0 =$ H, methyl, ethyl, n-propyl, cyano, perfluoroethyl, perfluoro-n-propyl, or vinyl;



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$R^1 =$ H, F, or a sterically acceptable hydrocarbyl
substituent;

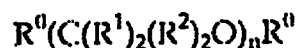
$R^2 =$ H, I, or a sterically acceptable hydrocarbyl
substituent;

5 $n =$ 2, 3, 4, 5, or 6; and

each R^0 , R^1 , and R^2 may be the same as or different from the other
 R^0 , R^1 , and R^2 , respectively.

10 8. A complex according to claim 1, wherein X is selected from the
group consisting of tetraglyme, tetrahydrofuran, bipyridine, and
18-crown-6 ethers.

15 9. A complex according to claim 1, wherein X comprises a liquid of
the formula:



wherein:

20 $R^0 =$ H, methyl, ethyl, n-propyl, cyano-,
perfluoroethyl,

perfluoro-n-propyl, or vinyl;

$R^1 =$ H, F, or a sterically acceptable hydrocarbyl
substituent;

25 $R^2 =$ H, I, or a sterically acceptable hydrocarbyl
substituent;

$n =$ 2, 3, 4, 5, or 6; and

30 each R^0 , R^1 , and R^2 may be the same as or different from the other
 R^0 , R^1 , and R^2 , respectively.

10. A complex according to claim 1, wherein X comprises a ligand of
the formula:



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wherein:

each R^0 , R^1 , and R^2 is selected independently, and

$R^0 = H$, CH_3 , or C_2H_5 ;

5 R^1 and $R^2 = H$ or F .

11. A complex according to claim 1, wherein: A is a β -diketonate; and X is tetraglyme, 18-crown-6 ether, or bipyridine.
- 10 12. A complex according to claim 1, wherein each of the ligands A is a constituent moiety of a single group which is coordinatively attached to M thereby.
- 15 13. A complex according to claim 1, wherein the ligand X and at least one of said ligands A is a constituent moiety of a single group which is coordinatively attached to M thereby.
14. A metal source reagent solution comprising a metal source reagent and solvent medium, wherein the metal source reagent and the
20 solvent medium are selected from the group of metal source reagent(s) and associated solvent media consisting of:

	Cu(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
25	Sr(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
30	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	
	Ga(sthd) ₃	
	Ce(sthd) ₄	
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	Ca(sthd) ₂ Ga(sthd) ₃ Ce(sthd) ₄	85-99% butyl acetate and 1-15% tetraglyme
5	Ca(sthd) ₂ Sr(sthd) ₂ Ga(sthd) ₃ Ce(sthd) ₄	85-99% butyl acetate and 1-15% tetrathiocyclodecane butyl acetate and cyclohexylthiol butyl acetate and t-butylthiol
10	Cu(shfac) ₂	45-88% tetrahydrofuran 10-35% isopropanol 2-20 % tetraglyme
	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetraglyme
15	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Ti(hfac) ₃	85-99% butyl acetate and 1-15% tetraglyme butyl acetate and cyclohexylthiol
20	Ti(hfac) ₃	butyl acetate and t-butylthiol
	Mo(hfac) ₃	butyl acetate and t-butylthiol
25	Mo(thd) ₃	butyl acetate and cyclohexylthiol

15. A composition according to claim 1, wherein MA_y comprises a metal β-thioketonate source compound.

30 16. A composition according to claim 16, wherein the metal moiety of said metal β-thioketonate source compound is selected from the group consisting of Cu, Sr, Ca, Ga, Ce, Ti, and Mo.

17. A composition comprising:

35

(i) metaforanic complex of the formula:



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wherein:

- 5 M is a y-valent metal selected from the group consisting of Pd, Pt, Rh, Ir, Ru, V, Nb, Ta, Cr, Mo and W;
A is a monodentate or multidentate organic ligand coordinated to M which allows complexing of MA_y with X;
y is an integer having a value of 2, 3 or 4;
10 each of the A ligands may be the same or different; and
X is a monodentate or multidentate ligand coordinated to M and containing one or more atoms independently selected from the group consisting of atoms of the elements C, N, H, S, O and F; and

15

- (ii) a solvent or suspending agent therefor.

18. A sulfur-based complex having utility for forming a metal sulfide film on a substrate, comprising a sulfur-containing metal source reagent
20 compound in a solvent medium, in which the sulfur-containing metal source reagent compound and solvent medium are selected from the group consisting of metal source compounds and associated solvent media consisting of:

25	<u>Metal Source Compound</u>	<u>Solvent Medium</u>
	Cu(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
30	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
35	Sr(sthd) ₂	



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Ga(sthd)3

Ce(sthd)4

5 Ca(sthd)2

Ga(sthd)3

Ce(sthd)4

85-99% butyl acetate and 1-15% tetraglyme

Ca(sthd)2

Sr(sthd)2

10 Ga(sthd)3

Ce(sthd)4

85-99% butyl acetate and 1-15% tetrathiocyclodecane

Cu(shfac)2

45-88% tetrahydrofuran

10-35% isopropanol

15

2-20 % tetraglyme.

19. A metal source reagent composition for forming a metal-containing film on a substrate, comprising a metal source reagent and a solvent medium, wherein the metal-containing film, metal source reagent and solvent medium are selected from the group consisting of:

	<u>Metal Containing Film</u>	<u>Metal Source Reagent</u>	<u>Solvent Medium</u>
25	Ir	Ir(acac)3 or Ir(thd)3	butyl acetate
	LaPO ₄	La(thd)3 O=I'(OMe) ₃	tetrahydrofuran
30	PbI _{1-x} Ti _{1-x} O ₃	Pb(thd) ₂ La(thd) ₃ Ti(OiPr) ₂ (thd) ₂	tetrahydrofuran/tetraglyme
35	PbZr _x Ti _{1-x} O ₃ x= 0 to 1	Pb(thd) ₂ [O=Zr(thd) ₂] _n [O=Ti(thd) ₂] _n	tetrahydrofuran/isopropanol/ tetraglyme, or butyl acetate/tetraglyme

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		n = 1 or 2	
	RuO ₂	Ru(acac) ₃ or Ru(thd) ₃	butyl acetate
5	SrBi ₂ Ta ₂ O ₉	Sr(thd) ₂ tetraglyme BiPh ₃ Ta(OiPr) ₄ thd	tetrahydrofuran/isopropanol/ tetraglyme
10	Ta ₂ O ₅	Ta(OR) ₄ (thd) R=ethyl, isopropyl	tetrahydrofuran/isopropanol/ tetraglyme
	TiO ₂	[O=Ti(thd) ₂] _n n = 1 or 2	butyl acetate/tetraglyme
15	V ₂ O ₅	O=V(thd) ₃	butyl acetate/tetraglyme.
	ZrO ₂	[O=Zr(thd) ₂] _n n = 1 or 2	butyl acetate/tetraglyme
20	CuS	Cu(shfac) ₂	butyl acetate/tetraglyme
	SrS	Sr(shfac) ₂	butyl acetate/tetraglyme
25	SrS	Sr(sthd) ₂	butyl acetate/tetraglyme
	SrS	Sr(sthd) ₂	butyl acetate/tetrathiocyclodecane
30	(Ca, Sr)Ga ₂ S ₄ , cerium-doped	Ca(sthd) ₂ Sr(sthd) ₂ Ga(sthd) ₃ Ce(sthd) ₄	butyl acetate/tetraglyme
35	(Ca, Sr)Ga ₂ S ₄ , cerium-doped	Ca(sthd) ₂ Sr(sthd) ₂ Ga(sthd) ₃	butyl acetate/ tetrathiocyclodecane

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Ce(sthd)₄

5	CuS	Cu(shfac) ₂	tetrahydrofuranacetate isopropanol tetraglyme
	CuS	Cu(hfac) ₂	butyl acetate/tetraglyme
10	SrS	Sr(thd) ₂	butyl acetate/tetraglyme
	SrS	Sr(thd) ₂	butyl acetate/tetrathiocyclodecane
15	CuS	Cu(hfac) ₂	tetrahydrofuranacetate isopropanol tetraglyme
	TiS ₂	Ti(hfac) ₃	butyl acetate/tetraglyme
20	TiS ₂	Ti(hfac) ₃	butyl acetate
	MoS ₂	Mo(hfac) ₃	butyl acetate
25	MoS ₂	Mo(thd) ₃	butyl acetate.

20. A metal coordination complexes of the formula:



30 wherein:

M is a metal selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, Lu, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm, Fe, Ru, Eu, Co, Rh, Ir, Gd, Ni, Tb, Th, Cu, Dy, Ho, Al, Tl, Er, Sn, Pb, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, Tm, Bi, and Yb;

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A is selected from the group consisting of β -diketonates and β -ketoesters, and their sulfur and nitrogen analogs;

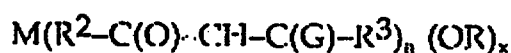
R is selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and (fully or partially) fluorinated derivatives thereof;

B is selected from the group consisting of polyethers, polyamines, polythiols, bipyridines, glymes, alcohols, crown ethers, crown thioethers, cyclic polyamines (cyclenes), thioglymes, arylthiols, and aliphatic thiols (mercaptans).

Q is hydrocarbyl or halohydrocarbyl, e.g., a ligand selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof;

a, x, y, and z are stoichiometric coefficients for the ligands A, OR, B, and Q, respectively, wherein a is ≥ 1 ; each of x, y, and z is independently > 0 ; and $A_a(OR)_x B_y Q_z$ is in stoichiometric relationship to metal M.

21. A source reagent complex of the formula:



wherein:

a is ≥ 1 ;

x is ≥ 0 ;

M is a metal selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, Lu, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm, Fe, Ru, Eu, Co, Rh, Ir, Gd, Ni, Tb, Th, Cu, Dy, Ho, Al, Tl, Li, Sn, Pb, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, Tm, Bi, and Yb;

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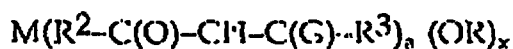
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R is selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and (fully or partially) fluorinated derivatives thereof;

- 5 R² and R³ are independently selected from C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof; and

- 10 G is oxygen, sulfur, or nitrogen moiety of the formula =NR_b in which R_b is selected from the group consisting of H, C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and fluorinated derivatives thereof.

22. A source reagent solution, comprising:
15 a source reagent complex of the formula:



- 20 wherein:

a is ≥ 1 ;

x is ≥ 0 ;

25

M is a metal selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, La, Lu, Ce, Ti, Zr, Hf, Pr, V, Nb, Ta, Nd, Cr, W, Pm, Mn, Re, Sm, Fe, Ru, Rh, Co, Rh, Ir, Gd, Ni, Tb, Th, Cu, Dy, Ho, Al, Tl, Er, Sn, Pb, Pd, Pt, Ga, In, Au, Ag, Li, Na, K, Rb, Cs, Mo, Tm, Bi, and Yb;

30

R is selected from the group consisting of C₁-C₈ alkyl, C₂-C₈ cycloalkyl, C₂-C₁₀ alkenyl, C₂-C₁₅ cycloalkenyl, C₆-C₁₀ aryl, and (fully or partially) fluorinated derivatives thereof;



R^2 and R^3 are independently selected from C_1 - C_8 alkyl, C_2 - C_8 cycloalkyl, C_2 - C_{10} alkenyl, C_2 - C_{15} cycloalkenyl, C_6 - C_{10} aryl, and fluorinated derivatives thereof; and

- 5 G is oxygen, sulfur, or nitrogen moiety of the formula $=NR_b$, in which R_b is selected from the group consisting of H, C_1 - C_8 alkyl, C_2 - C_8 cycloalkyl, C_2 - C_{10} alkenyl, C_2 - C_{15} cycloalkenyl, C_6 - C_{10} aryl, and fluorinated derivatives thereof; and
- 10 a solvent or suspending agent for the source reagent complex, selected from the group consisting of aliphatic hydrocarbons, aromatic hydrocarbons, ethers, esters, nitriles, and alcohols.
23. A source reagent solution according to claim 22, wherein the
15 solvent or suspending agent of the solution comprises a solvent selected from the group consisting of: glyme solvents having from 1 to 20 ethoxy $-(C_2H_4O)-$ repeat units; C_2 - C_{12} alkanols, organic ethers selected from the group consisting of dialkyl ethers comprising C_1 - C_6 alkyl moieties, C_4 - C_8 cyclic ethers; C_{12} - C_{60} crown O_4 - O_{20} ethers
20 wherein the prefixed C_i range is the number i of carbon atoms in the ether compound and the suffixed O_i range is the number i of oxygen atoms in the ether compound; C_6 - C_{12} aliphatic hydrocarbons; C_6 - C_{18} aromatic hydrocarbons; organic esters; organic amines; and polyamines.
- 25 24. A metal source reagent solution comprising at least one metalorganic complex in a solvent or suspending agent for the complex(es), wherein the metal source reagent(s) and the solvent medium are selected from the group consisting of:

30	<u>Metal Source Reagent(s)</u>	<u>Solvent Medium</u>
	Ba(thd) ₂ (tetraglyme)	85-98% butyl acetate and 1-15% tetraglyme
	Sr(thd) ₂ (tetraglyme)	
	Ti(OiPr) ₂ (thd) ₂	

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	Ca(thd) ₂ (tetraglyme) Sr(thd) ₂ (tetraglyme)	75-95% isopropanol with 5-25% tetraglyme
5	Ir(acac) ₃ or Ir(thd) ₃	butyl acetate
	La(thd) ₃ (MeO) ₃ P=O	tetrahydrofuran
10	Nb(OiPr) ₄ thd	45-88% tetrahydrofuran 10-35% isopropanol 2-20% tetraglyme
15	Pb(thd) ₂ La(thd) ₃ Ti(OiPr) ₂ (thd) ₂	80-98% tetrahydrofuran and 2-20% tetraglyme
20	Pb(thd) ₂ Zr(thd) ₄ Ti(OiPr) ₂ (thd) ₂	45-88% tetrahydrofuran 10-35% isopropanol 2-20 % tetraglyme
	Ru(acac) ₃ or Ru(thd) ₃	butyl acetate
25	Sr(thd) ₂ (tetraglyme) BiPh ₃ Ta(OiPr) ₄ (thd)	45-88% tetrahydrofuran 10-35% isopropanol 2-20 % tetraglyme
30	[O=Ti(thd) ₂] _n wherein n is 1 or 2	butyl acetate
	Zr(thd) ₄ Y(thd) ₃	80-98% tetrahydrofuran and 2-20% tetraglyme
35	[O=Zr(thd) ₂] _n wherein n is 1 or 2	butyl acetate or butyl acetate/tetraglyme



	Cu(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(shfac) ₂	85-99% butyl acetate and 1-15% tetraglyme
5	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
10	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Sr(sthd) ₂	
	Ga(sthd) ₃	
	Ce(sthd) ₄	
15	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetraglyme
	Ga(sthd) ₃	
	Ce(sthd) ₄	
20	Ca(sthd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Sr(sthd) ₂	
	Ga(sthd) ₃	
	Ce(sthd) ₄	
25	Cu(shfac) ₂	45-88% tetrahydrofuranacetate 10-35% isopropanol 2-20 % tetraglyme
	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetraglyme
30	Sr(thd) ₂	85-99% butyl acetate and 1-15% tetrathiocyclodecane
	Ti(hfac) ₃	85-99% butyl acetate and 1-15% tetraglyme
35	Ti(hfac) ₃	butyl acetate
	Mo(hfac) ₃	butyl acetate



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Mo(thd)₃

butyl acetate

- 5 wherein when the solvent medium contains multiple solvent components, the percentages specified are percentages by weight, based on the weight of the total solvent medium, and with the total percentage of all solvent components being 100%.

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