

Group 13 Metal Compounds for ALD Applications

Field

The present invention relates to aluminum, gallium and indium metal complexes and a method of using these complexes as precursors for deposition of metal-containing films, in particular by atomic layer deposition.

Background Art

Metal-containing films are used in semiconductor and electronics applications. Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) have been applied as the main deposition techniques for producing thin films for semiconductor devices. These methods enable the achievement of conformal films (metal, metal oxide, metal nitride, metal silicide, and the like) through chemical reactions of metal-containing compounds (precursors). The chemical reactions occur on surfaces which may include metals, metal oxides, metal nitrides, metal silicides, and other surfaces. In CVD and ALD, the precursor molecule plays a critical role in achieving high quality films with high conformality and low impurities. The precursor needs to have an appropriate vapor pressure and sufficient thermal stability. Furthermore, it needs to be vaporizable in a stable supply amount for forming a thin film by CVD or ALD method. The temperature of the substrate in CVD and ALD processes is an important consideration in selecting a precursor molecule. The precursor molecules should preferably be stable at typical substrate temperatures, e.g. in the range of 150 to 600 °C. Furthermore, the preferred precursor is capable of being delivered to the reaction vessel in a liquid or gaseous phase. The liquid phase of precursors at volatilization temperature generally provides a more uniform delivery of the precursor to the reaction vessel than solid phase precursors. While it is sufficient that the precursor is a liquid at delivery temperature, it is preferable that the precursor is a liquid at room temperature. This has the advantage that condensation is less likely to occur if there is any cold spot in the precursor delivery system. Furthermore, the handling of a compound which is a liquid at room temperature is technically easier, e.g. the filling of the vessels from which the precursor is applied.

The ALD process deposits thin layers of solid materials using two or more different vapor phase precursors. The surface of a substrate onto which the film is to be deposited is exposed to a dose of vapor of a first precursor. Then any excess unreacted vapor from that precursor is pumped away, e.g. by inert gas purges. Next, a vapor dose of a second precursor is brought to the surface and allowed to react. This cycle of steps can be repeated to build up thicker films. One particularly important aspect of this process is that the ALD reactions are self-limiting in that only a certain maximum thickness can form in

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each cycle, after which no further deposition occurs during that cycle, even if excess reactant is available. Because of this self-limiting character, ALD reactions produce coatings with highly uniform thicknesses not only on flat substrate surfaces, but also into narrow holes and trenches as well as other three-dimensional surfaces, which renders this technique indispensable for the semiconductor industry.

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Thin films containing indium have enormous technological significance. Such thin films can contain metallic indium or indium compounds, such as indium oxide, indium nitride, indium sulfide, etc.. In thin-film photovoltaics, mixed oxide-sulfides of indium act as electron-transport layers, and copper-indium-gallium-sulfide serves as an absorber layer. By far the most common use is in indium tin oxide (ITO), a transparent conducting oxide (TCO) widely used in flat-panel and touch-sensitive displays as well as thin-film solar cells. Furthermore, indium gallium zinc oxide (IGZO) from the group of TCOs is gaining more and more interest in the semiconductor industry. Due to increasing demand for highly conformal, very thin films containing indium as part of a multi-component composition, it would be advantageous to have highly volatile compounds with a low melting point having a low and wide ALD window as precursors for ALD of indium containing films.

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Possible applications for Ga containing films are for example thin films of IGZO in the semiconductor industry or thin films of gallium nitride as an important III-V semiconductor in the display industry. Aluminum oxide films formed by ALD can for example be used as gate dielectric or as protective coating, such as for example gas barrier layers. Metallic aluminum can for examples be used as metal for interconnects.

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Precursors for ALD of thin films comprising group 13 metals are widely dominated by alkyl precursors, such as trimethyl indium (TMI), trimethyl gallium (TMG) or trimethyl aluminum (TMA). These precursors have in common that they have a very high volatility and extreme reactivity enabling a large variety of ALD processes for a multitude of materials, such as for the respective metals, metal oxides, metal nitrides, metal sulfides and several inorganic-organic hybrid materials. However, the largest disadvantage is their high pyrophoricity which bears a high risk in handling these compounds and which necessitates strong safety regulations and renders them hazardous in case of accidents. Therefore, it is highly desirable to replace these compounds with compounds which do not show this disadvantage. Furthermore, the thermal stability is an issue in particular in the case of TMI which results in a non-existing or only very narrow ALD window and a maximum deposition temperature of 250 °C. Furthermore, TMI is solid at room temperature, thus resulting in fluctuating evaporation rates.

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Furthermore, metal amidinates (AMD) are known as precursors for ALD applications. WO2004/046417 discloses the use of volatile metal amidinates for ALD applications embracing a large variety of metals wherein the amidinate ligands can be substituted by a large variety of substituents, such as H, alkyl, aryl, alkynyl, etc.. The examples disclose
5 complexes with various transition metals, as well as with the main group metals Bi and Sr, wherein the amidinate ligands are substituted with isopropyl, sec-butyl and/or tert-butyl groups. This document suggests to use longer alkyl chains and/or alkyl chains with more than one stereo-isomer as substituents on the amidinate to lower the melting point.

10 GB2295392 A1 discloses metal amidinate complexes ML_3 wherein $M = Al, Ga$ or In , and L is an amidinate ligand substituted with substituents such as H, alkyl, haloalkyl, cycloalkyl, phenyl, etc.. These complexes are disclosed for use in CVD. The examples disclose only complexes wherein the N atoms of the amidinate ligands are substituted with phenyl groups. As can be seen from the TGA curves, these complexes are not
15 volatile, as evident from the high $T_{50\%}$ temperature around $400\text{ }^{\circ}C$, and are not thermally stable, as indicated by the high residual masses of more than 10% that can be explained by partial decomposition already during or before evaporation.

EP4134372 discloses metal amidinate complexes wherein the amidinate ligand is substituted with C_{1-5} alkyl groups and wherein at least one H atom of the substituents is
20 replaced by F. By using a fluorinated ligand, complexes with large vapor pressure and low melting points are obtained. However, due to the toxicity of fluorinated hydrocarbons, as well as their detrimental effect on the environment, it is desirable to avoid the use of fluorinated compounds. A further disadvantage of fluorinated compound is that it is generally known that fluorine can get incorporated into the thin films which strongly
25 changes the properties of that film.

US2016/0017485 discloses indium-tris(N,N'-diisopropylacetamidinate) as precursor for ALD of indium sulfide. However, no melting point was observed for this precursor up to $320\text{ }^{\circ}C$ when the material started to decompose, i.e. it is not possible to handle this
30 precursor in liquid form.

Furthermore, indium-tris(N,N'-diisopropylformamidinate) and indium-tris(N,N'-diisopropylacetamidinate) as precursors for ALD are disclosed in various scientific publications (e.g. S. B. Kim et al., Chem. Eur. J. 2018, 24, 9525-9529 and further publications) and were
35 shown to be more stable than TMI. While indium-tris(N,N'-diisopropylformamidinate) enables ALD of indium oxide using H_2O as the co-reactant on surfaces at a temperature

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range of 150-275 °C, it has the drawback of a low volatility compared to TMI, as well as a high melting point of 270 °C. Indium-tris(N,N'-diisopropylacetamidinate) has a considerably higher and narrower ALD window of 225-300 °C in the analogous reaction with H₂O, and lacks a melting point without decomposition, as described above.

5 Gallium-tris(N,N'-diisopropylamidinate) complexes as precursors for ALD applications are known from US2023/0167548. Aluminum-tris(N,N'-diisopropylacetamidinate) as precursor for ALD applications is known from A. L. Brazeau, Inorg. Chem. 2006, 45, 2276-2281. As can be seen from the thermogravimetric analysis, this aluminum complex does not show clean evaporation without decomposition.

10 In a method of forming a thin-film through the vaporization of a compound such as the CVD or ALD method, important properties that the compound to be used as a thin-film forming precursor (reactant) is required to have are as follows: its vapor pressure is high; its melting point is low, and the compound is preferably a liquid at room temperature; its thermal stability is high; and the compound can produce a high-quality thin-film with high
15 productivity, i.e. the reactivity towards the surface, the co-reactant and the deposited material is high and the reactions are clean, i.e. the reactions do essentially not produce any undesired byproducts on the surface. As discussed above, there is still room for improvement with respect to the amidinate compounds of the prior art. Accordingly, an object of the present invention is to provide novel compounds, which have high vapor
20 pressures, low melting points, and can each produce high-quality thin-films with high productivity when used as a thin-film forming raw material as compared to the related-art amidinate compounds.

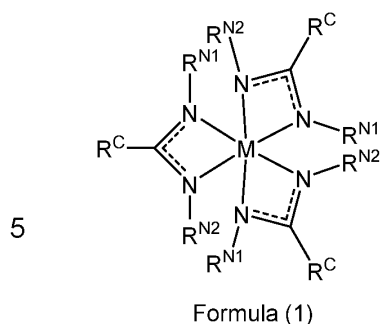
Surprisingly, it was found that modification of the alkyl substituents on the amidinate ligand
25 in metal amidinate complexes could significantly decrease the melting temperature and evaporation temperature of the resulting metal compounds compared to the metal complexes known in the prior art. These compounds furthermore have appropriate thermal stability and volatility and can be employed in a CVD or ALD method to form a metal-containing film. Such compounds are therefore the object of the present invention.

30 **Summary**

The disclosed and claimed subject matter is directed to a compound of the following formula (1):

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wherein the symbols used are as follows:

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M is Al, Ga or In;

R^{N1} , R^{N2} are on each occurrence, identically or differently, an alkyl group with 1, 2 or 3 carbon atoms;

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R^C are on each occurrence, identically or differently, H, D, methyl or ethyl;

with the proviso that the substituents R^{N1} and R^{N2} which are bound in the same amidinate ligand are not simultaneously isopropyl (iPr) groups when M is In or Ga;

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and with the proviso that the substituents R^{N1} and R^{N2} which are bound in the same amidinate ligand are not simultaneously isopropyl (iPr) groups when M is Al and R^C is methyl or ethyl.

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Each of the groups $[R^{N1}N-C(R^C)-NR^{N2}]^-$ in the compound of formula (1) is referred to as a "ligand" or "amidinate ligand".

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The disclosed and claimed subject further includes compositions and formulations comprising the compound of formula (1), methods of using the compound of formula (1) as precursor for deposition of metal-containing films, and metal-containing films derived from the compound of formula (1).

Detailed description

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All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

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5 The use of the terms "a", "an", "the" and similar referents in the context of describing the disclosed and claimed subject matter (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms "comprising," "having," "including," and "containing" are to be construed as open-ended terms (*i.e.*, meaning "including, but not limited to") unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it was individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, "such as") provided herein, is intended merely to better illuminate the disclosed and claimed subject matter and does not pose a limitation on the scope of the disclosed and claimed subject matter unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the disclosed and claimed subject matter. The use of the term "comprising" or "including" in the specification and the claims includes the narrower language of "consisting essentially of" and "consisting of."

20 Embodiments of the disclosed and claimed subject matter are described herein, including the best mode known to the inventors for carrying out the disclosed and claimed subject matter. Variations of those embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the disclosed and claimed subject matter to be practiced otherwise than as specifically described herein. Accordingly, the disclosed and claimed subject matter includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the disclosed and claimed subject matter unless otherwise indicated herein or otherwise clearly contradicted by context.

30 The compound according to the present invention is also referred to as "precursor" or "reactant" when the use of the compound in CVD or ALD deposition techniques is described.

35 For ease of reference, "microelectronic device" or "semiconductor device" corresponds to semiconductor wafers having integrated circuits, memory, and other electronic

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structures fabricated thereon, and flat panel displays, phase change memory devices, solar panels and other products including solar substrates, photovoltaics, and microelectromechanical systems (MEMS), manufactured for use in microelectronic, integrated circuit, or computer chip applications. Solar substrates include, but are not limited to, silicon, amorphous silicon, polycrystalline silicon, monocrystalline silicon, 5 CdTe, copper indium selenide, copper indium sulfide, and gallium arsenide on gallium. The solar substrates may be doped or undoped. It is to be understood that the term "microelectronic device" or "semiconductor device" is not meant to be limiting in any way and includes any substrate that will eventually become a microelectronic device or microelectronic assembly.

10 As defined herein, the term "barrier material" corresponds to any material used in the art to seal the metal lines, e.g., copper interconnects, to minimize the diffusion of said metal, e.g., copper, into the dielectric material. Preferred barrier layer materials include tantalum, titanium, ruthenium, hafnium, and other refractory metals and their nitrides and silicides.

15 Unless otherwise indicated, "alkyl" refers to hydrocarbon groups which can be linear (e.g. methyl, ethyl, n-propyl) or branched (e.g., isopropyl).

"Substantially free" is defined herein as less than 0.001 wt.%. "Substantially free" also includes 0.000 wt.%. The term "free of" means 0.000 wt.%. As used herein, "about" or 20 "approximately" are intended to correspond to within $\pm 5\%$ of the stated value.

In all such compositions, wherein specific components of the composition are discussed in reference to weight percentage (or "weight %" or "wt.%") ranges including a zero lower limit, it will be understood that such components may be present or absent in various specific 25 embodiments of the composition, and that in instances where such components are present, they may be present at concentrations as low as 0.001 wt.%, based on the total weight of the composition in which such components are employed. All percentages of the components are weight percentages and are based on the total weight of the composition, that is, 100%.

30 Moreover, when referring to the compositions described herein in terms of weight % or wt.%, it is understood that in no event shall the wt.% of all components, including non-essential components, such as impurities, add to more than 100 wt.%. In compositions "consisting essentially of" recited components, such components may add up to 100 wt.% of the composition or may add up to less than 100 wt.%. Where the components add up to 35 less than 100 wt.%, such composition may include some small amounts of a non-essential

contaminants or impurities. For example, in one such embodiment, the formulation can contain 2 wt.% or less of impurities. In another embodiment, the formulation can contain 1 wt.% or less than of impurities. In a further embodiment, the formulation can contain 0.05 wt.% or less than of impurities. In other such embodiments, the constituents can form at least 90 wt.%, more preferably at least 95 wt.% , more preferably at least 99 wt.%, more preferably at least 99.5 wt.%, most preferably at least 99.9 wt.%, and can include other ingredients that do not or not significantly affect the deposition process. Otherwise, if no significant non-essential impurity component is present, it is understood that the composition of all essential constituent components will essentially add up to 100 wt.%.

Any reference to “one or more” or “at least one” includes “two or more” and “three or more” and so on.

The headings employed herein are not intended to be limiting; rather, they are included for organizational purposes only.

In a preferred embodiment of the invention, M is indium or aluminum. In a particularly preferred embodiment, M is indium.

In a further preferred embodiment of the invention, the three amidinate ligands in the compound of formula (1) are identical. It is therefore preferred that all groups R^{N1} are identical, all groups R^{N2} are identical, and all groups R^C are identical.

In one embodiment of the invention, the substituents R^{N1} and R^{N2} which are bound in the same amidinate ligand are not simultaneously isopropyl (iPr) groups when M is Al.

Suitable combinations of R^{N1} , R^{N2} and R^C are therefore the compounds no. 1 to 82 of Table 1. Preferred are the compounds no. 1 to 55 in Table 1, i.e. In or Al compounds, and particularly preferred are the compounds no. 1 to 27 in Table 1, i.e. In compounds.

Table 1:

Compound no.	M	R^{N1}	R^{N2}	R^C
1	In	methyl	methyl	H
2	In	methyl	ethyl	H
3	In	methyl	n-propyl	H
4	In	methyl	isopropyl	H
5	In	ethyl	ethyl	H
6	In	ethyl	n-propyl	H

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5	7	In	ethyl	isopropyl	H
	8	In	n-propyl	n-propyl	H
	9	In	n-propyl	isopropyl	H
	10	In	methyl	methyl	methyl
	11	In	methyl	ethyl	methyl
10	12	In	methyl	n-propyl	methyl
	13	In	methyl	isopropyl	methyl
	14	In	ethyl	ethyl	methyl
	15	In	ethyl	n-propyl	methyl
	16	In	ethyl	isopropyl	methyl
15	17	In	n-propyl	n-propyl	methyl
	18	In	n-propyl	isopropyl	methyl
	19	In	methyl	methyl	ethyl
	20	In	methyl	ethyl	ethyl
	21	In	methyl	n-propyl	ethyl
20	22	In	methyl	isopropyl	ethyl
	23	In	ethyl	ethyl	ethyl
	24	In	ethyl	n-propyl	ethyl
	25	In	ethyl	isopropyl	ethyl
	26	In	n-propyl	n-propyl	ethyl
25	27	In	n-propyl	isopropyl	ethyl
	28	Al	methyl	methyl	H
	29	Al	methyl	ethyl	H
	30	Al	methyl	n-propyl	H
	31	Al	methyl	isopropyl	H
30	32	Al	ethyl	ethyl	H
	33	Al	ethyl	n-propyl	H
	34	Al	ethyl	isopropyl	H
	35	Al	n-propyl	n-propyl	H
	36	Al	n-propyl	isopropyl	H
35	37	Al	isopropyl	isopropyl	H
	38	Al	methyl	methyl	methyl
	39	Al	methyl	ethyl	methyl
	40	Al	methyl	n-propyl	methyl
	41	Al	methyl	isopropyl	methyl
	42	Al	ethyl	ethyl	methyl
	43	Al	ethyl	n-propyl	methyl

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5	44	Al	ethyl	isopropyl	methyl
	45	Al	n-propyl	n-propyl	methyl
	46	Al	n-propyl	isopropyl	methyl
	47	Al	methyl	methyl	ethyl
	48	Al	methyl	ethyl	ethyl
10	49	Al	methyl	n-propyl	ethyl
	50	Al	methyl	isopropyl	ethyl
	51	Al	ethyl	ethyl	ethyl
	52	Al	ethyl	n-propyl	ethyl
	53	Al	ethyl	isopropyl	ethyl
15	54	Al	n-propyl	n-propyl	ethyl
	55	Al	n-propyl	isopropyl	ethyl
	56	Ga	methyl	methyl	H
	57	Ga	methyl	ethyl	H
	58	Ga	methyl	n-propyl	H
20	59	Ga	methyl	isopropyl	H
	60	Ga	ethyl	ethyl	H
	61	Ga	ethyl	n-propyl	H
	62	Ga	ethyl	isopropyl	H
	63	Ga	n-propyl	n-propyl	H
25	64	Ga	n-propyl	isopropyl	H
	65	Ga	methyl	methyl	methyl
	66	Ga	methyl	ethyl	methyl
	67	Ga	methyl	n-propyl	methyl
	68	Ga	methyl	isopropyl	methyl
30	69	Ga	ethyl	ethyl	methyl
	70	Ga	ethyl	n-propyl	methyl
	71	Ga	ethyl	isopropyl	methyl
	72	Ga	n-propyl	n-propyl	methyl
	73	Ga	n-propyl	isopropyl	methyl
35	74	Ga	methyl	methyl	ethyl
	75	Ga	methyl	ethyl	ethyl
	76	Ga	methyl	n-propyl	ethyl
	77	Ga	methyl	isopropyl	ethyl
	78	Ga	ethyl	ethyl	ethyl
	79	Ga	ethyl	n-propyl	ethyl
	80	Ga	ethyl	isopropyl	ethyl

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81	Ga	n-propyl	n-propyl	ethyl
82	Ga	n-propyl	isopropyl	ethyl

5 In a further preferred embodiment of the invention, the total number of carbon atoms in R^{N1} , R^{N2} and R^C in each ligand is between 2 and 6, more preferably between 3 and 6 and even more preferred 4, 5 or 6.

In a further preferred embodiment of the invention, R^C is H or methyl, and particularly preferred R^C is H.

10 In one embodiment of the invention, R^{N1} and R^{N2} are identical. In a further embodiment of the invention, R^{N1} and R^{N2} are different from each other.

15 Preferred embodiments of the invention are the compounds 5, 6, 7, 8, 11, 14 and 23 with M = indium, the compounds 32, 33, 34, 35, 37, 39, 42 and 51 with M = aluminum and the compounds 60, 61, 62, 63, 66, 69 and 78 with M = gallium. Preferred are the compounds 5, 6, 7, 8, 11, 14 and 23 with M = indium and the compounds 32, 33, 34, 35, 37, 39, 42 and 51 with M = aluminum, and more preferred are the compounds 5, 6, 7, 8, 11, 14 and 23 with M = indium. Particularly preferred is the compound 5 with M = indium and the compound 32 with M = aluminum, i.e. a compound with M = indium or aluminum, R^C = H and $R^{N1} = R^{N2}$ = ethyl, and compound 8 with M = indium and the compound 35
20 with M = aluminum, i.e. a compound with M = indium or aluminum, R^C = H and $R^{N1} = R^{N2}$ = n-propyl. A further preferred embodiment of the invention is the compound 37 with M = aluminum, R^C = H and $R^{N1} = R^{N2}$ = isopropyl.

25 It is preferable that the compound of formula (1) or the preferred embodiments is essentially free of impurities. This refers in particular to metal impurities, organic by-products and halogen impurities. The content of each of the impurity metal elements is preferably 10 ppm or less, more preferably 1 ppm or less, and the total content thereof is preferably 50 ppm or less, more preferably 10 ppm or less. The total content of the impurity halogens is preferably 100 ppm or less, more preferably 10 ppm or less, and
30 most preferably 1 ppm or less.

The compound of formula (1) and the preferred embodiments can be synthesized by reaction of an appropriate metal precursor MX_3 wherein M is Al, Ga or In and X is a counteranion, such as halogen (F, Cl, Br, I, preferably Cl), triflate or tosylate, with the desired amidinate salt, such as LiAMD, NaAMD or KAMD, preferably LiAMD, where
35 AMD stands for amidinate. The amidinate salt can be prepared in situ from the

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corresponding amidine by deprotonation in a solvent, wherein polar or non-polar aprotic solvents, such as THF dioxane, diethylether, methyl-tert-butylether, dibutylether, hexane, pentane or toluene or mixtures thereof, are preferred. Examples for suitable bases for the deprotonation are alkylolithium, such as butyllithium or hexyllithium, alkali hydrides, such as LiH, NaH or KH, or hexamethyldisilazane salts, such as LiHMDS, NaHMDS or KHMDS.

The present invention is therefore further directed to a method of manufacturing a compound of formula (1) or the preferred embodiments wherein a compound MX_3 with $M = Al, Ga$ or In and X is a counterion, preferably F, Cl, Br, I , triflate or tosylate and particularly preferably Cl , is reacted with an amidinate salt, preferably a Li, Na or K salt and particularly preferably a Li salt.

Method of Use

The disclosed compounds can be used as precursors (reactants) for the deposition of metal-containing films using any chemical vapor deposition process known to those of skill in the art. The precursor for forming a thin film, also referred to as "thin film forming precursor" comprises the compound according to the present invention and optionally further compounds, depending on the production process to which the precursor is applied. For example, when a thin film containing only a metal atom M as a metal is produced, the thin film forming precursor of the present invention is free of metal compounds other than the compound represented by the general formula (1). Meanwhile, when a thin film containing two or more kinds of metals is produced, the thin film forming precursor of the present invention may contain a compound containing a desired metal in addition to the compound represented by the general formula (1). The thin film forming precursor of the present invention may further contain an organic solvent. As described above, the physical properties of the compound represented by the general formula (1) are suitable for serving as the precursor for a CVD method, and hence the thin film forming precursor of the present invention is useful as a CVD precursor. In particular, the thin-film forming precursor of the present invention is particularly suitable for an ALD method because the compound represented by the general formula (1) has a self-limiting reaction behavior at the surface, i.e. is not reacting with the adsorbed surface precursor species.

As used herein, the term "chemical vapor deposition process" (CVD) refers to any process wherein a substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposition. As used herein, the term "atomic layer deposition process" (ALD) refers to a self-limiting (e.g., the amount

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of film material deposited in each reaction cycle is constant), sequential surface chemistry that deposits films of materials onto substrates of varying compositions. Although the precursors, reagents and co-reagents used herein may be sometimes described as "gaseous," it is understood that the precursors can be either liquid or solid at room temperature and/or at elevated temperature and are transported with or without an inert gas into the reactor via direct vaporization, bubbling or sublimation. In some case, the vaporized precursors can pass through a plasma generator. The term "reactor" as used herein, includes without limitation, the reaction chamber (reaction vessel, deposition chamber).

Chemical vapor deposition processes in which the disclosed and claimed compounds can be utilized as precursors include, but are not limited to, those used for the manufacture of semiconductor type microelectronic devices, such as ALD, CVD, pulsed CVD, plasma enhanced ALD (PEALD) and/or plasma enhanced CVD (PECVD). Examples of suitable deposition processes for the method disclosed herein include, but are not limited to, cyclic CVD (CCVD), MOCVD (Metal Organic CVD), thermal chemical vapor deposition, plasma enhanced chemical vapor deposition ("PECVD"), high density PECVD, photon assisted CVD, plasma-photon assisted ("PPECVD"), cryogenic chemical vapor deposition, chemical assisted vapor deposition, hot-filament chemical vapor deposition, CVD of a liquid polymer precursor, deposition from supercritical fluids, low energy CVD (LECVD), roll-to-roll ALD, spatial ALD and atmospheric pressure ALD. In certain embodiments, the metal containing films are deposited via atomic layer deposition (ALD), plasma enhanced ALD (PEALD) or plasma enhanced cyclic CVD (PECCVD) process.

In one embodiment, the metal-containing film is deposited using an ALD process. In another embodiment, the metal-containing film is deposited using a CCVD process. In a further embodiment, the metal-containing film is deposited using a thermal CVD process.

Suitable substrates on which the disclosed and claimed precursors can be deposited are not particularly limited and vary depending on the intended final use. For example, the substrate may be chosen from oxides, such as HfO₂ based materials, TiO₂ based materials, ZrO₂ based materials, rare earth oxide-based materials, ternary oxide-based materials, etc., or from nitride-based materials. Other substrates may include solid substrates, such as metal substrates (e.g., Au, Pd, Rh, Ru, W, Al, Ni, Ti, Co, Pt), metal silicide containing substrates (e.g., TiSi₂, CoSi₂, and NiSi₂), metal nitride containing substrates (e.g., TaN, TiN, WN, TaCN, TiCN, TaSiN, and TiSiN), semiconductor materials (e.g., Si, SiGe, GaAs, InP, diamond, GaN, and SiC), insulators (e.g., SiO₂,

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Si₃N₄, SiON, HfO₂, Ta₂O₅, ZrO₂, TiO₂, Al₂O₃, and barium strontium titanate), and combinations thereof. Preferred substrates include TiN, Ru and Si type substrates.

5 In such deposition methods and processes, usually a co-reactant is used, such as an oxidizing agent. An "oxidizing agent" in the sense of this application is understood to mean a chemical compound which transfers oxygen to the metal-containing film. The oxidizing agent is typically introduced in gaseous form. Examples of suitable oxidizing agents include, but are not limited to, oxygen gas, water vapor, ozone, oxygen plasma, or mixtures thereof.

10 Further possible co-reactants are reducing agents, such as H₂, H₂ plasma, hydrazine or aminoboranes, nitrogen-containing co-reactants, such as hydrazine, NH₃, N₂ or N₂ plasma, sulfur-containing co-reactant, such as H₂S or elemental sulfur, or peroxides, such as H₂O₂ or HOOtBu.

15 The deposition methods and processes may also involve purge steps, which are usually done by using one or more purge gases. The purge gas, which is used to purge away unconsumed reactants and/or reaction byproducts, is an inert gas that does not react with the precursors and with the formed thin film. Exemplary purge gases include, but are not limited to, argon (Ar), nitrogen (N₂), helium (He), neon (Ne), and mixtures thereof. For example, a
20 purge gas, such as Ar, is supplied into the reactor at a flow rate ranging from about 10 to about 2000 sccm for about 0.1 to 10000 seconds, thereby purging the unreacted material and any byproduct that may remain in the reactor.

25 The deposition methods and processes require that energy be applied to the at least one of the precursors according to the present invention, co-reactants or combination thereof to induce reaction and to form the metal-containing film or coating on the substrate. Such energy can be provided by, but not limited to, temperature (thermally induced), plasma, pulsed plasma, helicon plasma, high density plasma, inductively coupled plasma, X-ray, e-beam, photon, remote plasma methods, and combinations thereof. In some processes, a secondary RF frequency source can be used to modify the plasma characteristics at
30 the substrate surface. When utilizing plasma, the plasma-generated process may include a direct plasma-generated process in which plasma is directly generated in the reactor, or alternatively a remote plasma-generated process in which plasma is generated outside of the reactor and supplied into the reactor.

35 When utilized in such deposition methods and processes, suitable precursors, such as the compounds of the present invention, may be delivered to the reaction chamber, such

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as a CVD or ALD reactor, in a variety of ways. A preferred method of delivering the precursors to the reaction chamber is by vaporization of the precursor, *e.g.* either by vacuum driven thermal vaporization or by active vaporization using a carrier gas. In other instances, a liquid delivery system or a combined liquid delivery and flash vaporization process unit may be employed to enable low volatility materials to be volumetrically delivered, which leads to reproducible transport and deposition without thermal decomposition of the precursor. The precursor compositions described herein can be effectively used as reagents via direct liquid injection (DLI) or via vacuum driven vaporization to provide a vapor stream of these metal precursors into an ALD or CVD reactor. Vacuum driven vaporization is the preferred method of delivery for the precursors according to the present invention.

When used in these deposition methods and processes, the disclosed and claimed compounds may include hydrocarbon solvents which are particularly desirable due to their ability to be dried to sub-ppm levels of water. Exemplary hydrocarbon solvents that can be used in the precursors include, but are not limited to, toluene, mesitylene, cumene (isopropylbenzene), *p*-cymene (4-isopropyl toluene), 1,3-diisopropylbenzene, octane, dodecane, 1,2,4-trimethylcyclohexane, *n*-butylcyclohexane, and decahydronaphthalene (decalin). The disclosed and claimed compounds can also be stored and used in stainless steel containers. In certain embodiments, the hydrocarbon solvent is a high boiling point solvent or has a boiling point of 100 °C or greater. The disclosed and claimed compounds can also be mixed with other suitable metal compounds, which can be utilized as precursors, and the mixture used to deliver both metals simultaneously for the growth of a binary metal-containing films.

A flow of argon and/or other gas may be employed as a carrier gas to help deliver a vapor containing at least one of the disclosed and claimed precursors to the reaction chamber during the precursor pulsing. When delivering the precursors, the reaction chamber process pressure is between 1 and 50 torr, preferably between 5 and 20 torr.

Substrate temperature can be an important process variable in the deposition of high-quality metal-containing films. Typical substrate temperatures range from about 100 °C to about 550 °C. Higher temperatures can promote higher film growth rates, but might result in bulk CVD rather than ALD. Furthermore, there is the risk at higher substrate temperatures that the precursor desorbs from the substrate, thus resulting in lower growth rates. If the substrate temperature is not high enough, the temperature might be too low for a sufficient reaction of the precursor with the surface, which also results in

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lower growth rates, and/or the precursor might condense on the surface resulting in increasing growth rates.

In view of the forgoing, those skilled in the art will recognize that the disclosed and claimed subject matter further includes the use of the disclosed and claimed compounds
5 as precursors in chemical vapor deposition (CVD) processes as follows.

In one embodiment, the disclosed and claimed subject matter includes a method for forming a metal-containing film, wherein the metal is Al, Ga or In, on at least one surface of a substrate that includes the steps of:

- 10 (a) providing the at least one surface of the substrate in a reaction vessel; and
(b) forming a metal-containing film on the at least one surface by a deposition process selected from a chemical vapor deposition (CVD) process and an atomic layer deposition (ALD) process using at least one compound of formula (1) or the preferred embodiments as precursor of a metal source compound for the deposition process.

15 In a further aspect of this embodiment, the method includes introducing at least one co-reactant into the reaction vessel. A co-reactant is a reactant which is used in addition to the precursor of the present invention for the deposition of the metal-containing film. In a further aspect of this embodiment, the method includes introducing at least one co-reactant into the reaction vessel where the at least one co-reactant is selected from the
20 group of water, oxygen (O₂), oxygen plasma, ozone (O₃), NO, N₂O, NO₂, CO, CO₂ and combinations thereof. These co-reactants are typically used for forming a metal oxide thin film. In another aspect of this embodiment, the method includes introducing at least one co-reactant into the reaction vessel where the at least one co-reactant is selected from the group of ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen,
25 nitrogen/hydrogen, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma, and combinations thereof. These co-reactants are typically used for forming a metal nitride thin film, but ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, ammonia plasma, and combinations thereof, might also be used for forming a metallic film, if the metal is indium. In another aspect of this embodiment, the method includes introducing
30 at least one co-reactant into the reaction vessel where the at least one co-reactant is selected from the group of hydrogen, hydrogen plasma, a mixture of hydrogen and helium, a mixture of hydrogen and argon, hydrogen/helium plasma, hydrogen/argon plasma, boron-containing compounds, silicon-containing compounds and combinations thereof. These co-reactants are typically used for forming metallic film, i.e. formation of the elemental metal.

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In one embodiment, the disclosed and claimed subject matter includes a method of forming a metal-containing film wherein the metal is Al, Ga or In via an atomic layer deposition (ALD) process or ALD-like process that includes the steps of:

- (a) providing a substrate in a reaction vessel;
- (b) introducing into the reaction vessel one or more of the compounds of formula (1) or the preferred embodiments as precursor;
- (c) a purging step, in particular purging the reaction vessel with a first purge gas;
- (d) introducing into the reaction vessel a co-reactant;
- (e) a purging step, in particular purging the reaction vessel with a second purge gas;
- (f) sequentially repeating steps (b) through (e) until a desired thickness of the metal-containing film is obtained.

Depending on the desired composition of the produced metal-containing thin film, the steps (b), (c), (d) and (e) may also be repeated with a second co-reactant in step (d) and optionally a third or further co-reactant and a purging step with the third purge gas and optionally a fourth or further purge gases.

Furthermore, it is possible in step (b) to introduce two or more precursors, wherein at least one precursor is a compound of formula (1) or the preferred embodiments. These two or more precursors may be introduced as a mixture from the same container or may be introduced from different containers.

Furthermore, it is possible in step (d) to introduce two or more co-reactants. These two or more co-reactants may be introduced as a mixture from the same source vessel or may be introduced from different containers.

In a further aspect of this embodiment, the co-reactant is one or more of an oxygen-containing co-reactant selected from water, O₂, oxygen plasma, O₃, NO, N₂O, NO₂, CO, CO₂ and combinations thereof. In another aspect of this embodiment, the co-reactant is one or more of a nitrogen-containing co-reactant selected from ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma and mixture thereof. In another aspect of this embodiment, the co-reactant is selected from hydrogen, hydrogen plasma, a mixture of hydrogen and helium, a mixture of hydrogen and argon, hydrogen/helium plasma, hydrogen/argon plasma, boron-containing compounds, silicon-containing compounds and combinations thereof. In a further aspect of this embodiment, the method the first and second purge gases are each independently selected one or more of argon, nitrogen, helium, neon, and combinations thereof. Additionally or alternatively, vacuum may be

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applied for one or more purging steps. In a further aspect of this embodiment, the method further includes applying energy to at least one of the precursor, the co-reactant, the substrate, and combinations thereof, wherein the energy is one or more of thermal, plasma, pulsed plasma, helicon plasma, high density plasma, inductively coupled plasma, capacitively coupled plasma, X-ray, e-beam, photon, remote plasma methods and combinations thereof. In a preferred aspect of this embodiment, step (b) of the method includes introducing into the reaction vessel the precursor using thermal energy and vacuum. In a further aspect of this embodiment, step (b) of the method further includes introducing into the reaction vessel the precursor using a stream of carrier gas to deliver a vapor of the precursor into the reaction vessel. In a further aspect of this embodiment, step (b) of the method further includes use of a solvent medium comprising one or more of toluene, mesitylene, isopropylbenzene, 4-isopropyl toluene, 1,3-diisopropylbenzene, octane, dodecane, 1,2,4-trimethylcyclohexane, n-butylcyclohexane, and decahydronaphthalene and combinations thereof.

The shape of the substrate is not particularly limited and can be, for example, a plate shape, a spherical shape, a fibrous shape, or a scaly shape. The surface of the substrate may be planar, or may have a three-dimensional structure such as a trench structure.

In addition, examples of the above-mentioned production conditions include a reaction temperature (substrate temperature), a reaction pressure, and a deposition rate. The reaction temperature is preferably from room temperature to 500 °C, more preferably from 100°C to 300°C. In addition, the reaction pressure is preferably from 10 Pa to an atmospheric pressure in the case of the thermal CVD or the optical CVD, and is preferably from 10 Pa to 2,000 Pa in the case of using plasma. For ALD, the pressure of a system (in the film formation chamber) when this step is performed is preferably from 1 Pa to 10,000 Pa, more preferably from 10 Pa to 1,000 Pa.

In addition, the deposition rate may be controlled by the supply conditions (vaporization temperature and vaporization pressure) of the precursor, the reaction temperature, and the reaction pressure. When the deposition rate is large, the characteristics of a thin-film to be obtained may deteriorate. When the deposition rate is small, a problem may occur in productivity. Accordingly, for CVD processes, the deposition rate is preferably from 0.01 nm/min to 100 nm/min, more preferably from 1 nm/min to 50 nm/min. In addition, in the case of the ALD method, the deposition rate is controlled by the number of cycles so that a desired film thickness may be obtained. In an ALD process, typical deposition rates are from 0.01 nm/cycle to 0.2 nm/cycle, more typically from 0.05 nm/cycle to 1.3

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nm/cycle. Further, as the above-mentioned production conditions, there are given a temperature and a pressure when the thin-film forming precursor is vaporized to obtain a precursor gas. The step of vaporizing the thin-film forming precursor to obtain a precursor gas may be performed in the precursor vessel or in the vaporization chamber. In any case, it is preferred that the thin-film forming precursor of the present invention be
5 evaporated at a temperature between 0 °C and 150 °C. In addition, when the thin-film forming precursor is vaporized to obtain a precursor gas in the precursor vessel or in the vaporization chamber, the pressure in the precursor vessel and the pressure in the vaporization chamber are each preferably from 1 Pa to 10,000 Pa.

10 In addition, in the method of producing a thin-film of the present invention, after the thin-film deposition, annealing treatment may be performed under an inert atmosphere, an oxidizing atmosphere, or a reducing atmosphere in order to obtain more satisfactory electrical characteristics. The temperature for annealing is from 200 °C to 1,000 °C, preferably from 250 °C to 500 °C.

15 **Brief description of the drawings**

Fig. 1 shows the TGA curves for various indium compounds according to the invention as well as a comparative indium compound.

20 Fig. 2 shows the TGA curves for various aluminum compounds according to the invention as well as a comparative aluminum compound.

Fig. 3 shows the result of the thermal decomposition study of $\text{In}(\text{Et}_2\text{-fAMD})_3$ on SiO_2 and TiN .

25 Fig. 4 shows the saturation study of $\text{In}(\text{Et}_2\text{-fAMD})_3$ with O_3 as co-reactant on SiO_2 at 300 °C substrate temperature.

30 Fig. 5 shows the SEM micrographs of the top, middle and bottom position of a Si (native oxide) trenched substrate with an aspect ratio of 17:1, coated with indium oxide from $\text{In}(\text{Et}_2\text{-fAMD})_3$ and O_3 at 300 °C and estimated thin film thicknesses (from SEM) at the indicated positions with calculated step coverage values.

Examples

35 Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples are

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given below to more fully illustrate the disclosed subject matter and should not be construed as limiting the disclosed subject matter in any way.

It will be apparent to those skilled in the art that various modifications and variations can be made in the disclosed subject matter and specific examples provided herein without
5 departing from the spirit or scope of the disclosed subject matter. Thus, it is intended that the disclosed subject matter, including the descriptions provided by the following examples, covers the modifications and variations of the disclosed subject matter that come within the scope of any claims and their equivalents.

10 **Materials and Methods:**

All solvents and starting materials were purchased from Sigma-Aldrich unless otherwise indicated.

General synthetic procedure:

15 In a Schlenk flask the respective amidine (AMDH) (3eq) to prepare the below shown complexes was solved in THF (27 eq) and cooled to -78 °C. n-Butyl lithium (nBuLi), 1.6 M in hexane (3 eq), was added dropwise to the solution. The mixture was allowed to warm up to room temperature and was stirred for 2h. The mixture was cooled to 0 °C and was transferred slowly via a cannula into a 0 °C cold solution of the respective metal chloride (InCl₃, GaCl₃ or AlCl₃) (1eq) in THF (18 eq). After addition, the reaction mixture
20 was stirred at room temperature overnight. The solvent was removed under reduced pressure and the crude mixture was extracted with toluene. The suspension was filtered, and solvent of the filtrate was removed under reduced pressure. The crude product was sublimed under the below given conditions to obtain spectroscopically pure complexes. In the following, fAMD stands for formamidinate, and MeAMD stands for acetamidinate.
25 The employed amidines are known in the literature.

Example 1: In(Et₂-fAMD)₃

Compound with M = In, R^{N1} = R^{N2} = ethyl and R^C = H.

¹H NMR (500 MHz, C₆D₆) δ 7.37 (s, 3H), 3.25 (q, J = 7.2 Hz, 12H), 1.17 (t, J = 7.2 Hz, 18H).
30

TGA: T_{1%} = 111 °C, T_{50%} = 193 °C, m_{Rest} = 1.5%

Vapor pressure from TGA: $\text{Lg}(p[\text{Pa}]) = -2822.2 \cdot 1/T[\text{K}] + 9.6281 \rightarrow T_{1\text{Torr}} = 103 \text{ °C}$

DSC: T_{melting point} = 38.0 °C

35 **Example 2: In(nPr₂-fAMD)₃**

Compound with M = In, R^{N1} = R^{N2} = n-propyl and R^C = H.

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^1H NMR (500 MHz, C_6D_6) δ 7.38 (s, 3H), 3.19 (t, J = 6.8 Hz, 12H), 1.56 (q, J = 7.1 Hz, 12H), 0.95 (t, J = 7.4 Hz, 18H).

TGA: $T_{1\%}$ = 102 °C, $T_{50\%}$ = 233 °C, m_{Rest} = 1.0 %

Vapor pressure from TGA: $\text{Lg}(p[\text{Pa}]) = -3628.2 \cdot 1/T[\text{K}] + 10.825 \rightarrow T_{1\text{Torr}} = 144$ °C

DSC: $T_{\text{melting point}} < -50$ °C

5

Example 3: In(Et-Me-MeAMD)₃

Compound with $M = \text{In}$, $R^{\text{N1}} = \text{ethyl}$, $R^{\text{N2}} = \text{methyl}$ and $R^{\text{C}} = \text{methyl}$.

^1H NMR (500 MHz, C_6D_6) δ 3.31 – 3.19 (m, 6H), 3.05 – 2.92 (m, 9H), 1.57 – 1.39 (m, 9H), 1.34 – 1.18 (m, 9H).

10

TGA: $T_{1\%}$ = 137 °C, $T_{50\%}$ = 216 °C, m_{Rest} = 4.4 %

DSC: $T_{\text{melting point}} = 110$ °C

Example 4: In(Me₂-MeAMD)₃

Compound with $M = \text{In}$ and $R^{\text{N1}} = R^{\text{N2}} = R^{\text{C}} = \text{methyl}$.

^1H NMR (500 MHz, C_6D_6) δ 3.01 (s, 18H), 1.42 (s, 9H).

15

TGA: $T_{1\%}$ = 115 °C, $T_{50\%}$ = 215 °C, m_{Rest} = 12.9 %

DSC: $T_{\text{melting point}} = 183$ °C

Example 5: Al(Et₂-fAMD)₃

Compound with $M = \text{Al}$ and $R^{\text{N1}} = R^{\text{N2}} = \text{ethyl}$ and $R^{\text{C}} = \text{H}$.

20

^1H NMR (500 MHz, C_6D_6) δ 7.33 (s, 3H), 3.14 (q, J = 7.1 Hz, 12H), 1.15 (t, J = 7.2 Hz, 18H).

TGA: $T_{1\%}$ = 98 °C, $T_{50\%}$ = 179 °C, m_{Rest} = 0.2 %

DSC: $T_{\text{melting point}} = \text{not observed}$

25

Example 6: Al(nPr₂-fAMD)₃

Compound with $M = \text{Al}$ and $R^{\text{N1}} = R^{\text{N2}} = \text{n-propyl}$ and $R^{\text{C}} = \text{H}$.

^1H NMR (500 MHz, C_6D_6) δ 7.35 (s, 3H), 3.06 (t, J = 7.1 Hz, 12H), 1.54 (q, J = 7.3 Hz, 12H), 0.94 (t, J = 7.4 Hz, 18H).

TGA: $T_{1\%}$ = 130 °C, $T_{50\%}$ = 231 °C, m_{Rest} = 0.2 %

30

DSC: $T_{\text{melting point}} = < -50$ °C

Example 7: Al(iPr₂-fAMD)₃

Compound with $M = \text{Al}$, $R^{\text{N1}} = R^{\text{N2}} = \text{isopropyl}$ and $R^{\text{C}} = \text{H}$.

^1H NMR (500 MHz, C_6D_6) δ 7.58 (s, 3H), 3.47 (hept, J = 6.5 Hz, 6H), 1.21 (d, J = 6.5 Hz, 36H).

35

TGA: $T_{1\%}$ = 152 °C, $T_{50\%}$ = 235 °C, m_{Rest} = 0.4 %

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DSC: $T_{\text{melting point}} = 132\text{ }^{\circ}\text{C}$

Comparative example 1: $\text{In}(\text{iPr}_2\text{-fAMD})_3$

Compound with $\text{M} = \text{In}$, $\text{R}^{\text{N1}} = \text{R}^{\text{N2}} = \text{isopropyl}$ and $\text{R}^{\text{C}} = \text{H}$.

^1H NMR (500 MHz, C_6D_6) δ 7.44 (s, 3H), 3.53 (hept, $J = 6.4\text{ Hz}$, 6H), 1.24 (d, $J = 6.4\text{ Hz}$, 36H).

TGA: $T_{1\%} = 159\text{ }^{\circ}\text{C}$, $T_{50\%} = 236\text{ }^{\circ}\text{C}$, $m_{\text{Rest}} = 0.5\%$

DSC: $T_{\text{melting point}} = 260\text{ }^{\circ}\text{C}$

Analysis by TGA

TGA curves were determined for the indium precursors of examples 1 to 4 and comparative example 1, as well as for the aluminum precursors of examples 5 to 7. The sample mass of each compound was 10 mg for the TGA experiment. The TGA curves for the indium complexes are shown in Figure 1, and the TGA curves for the aluminum complexes are shown in Figure 2.

Discussion of results

The compound of Comparative example 1 is known, e.g. from S. B. Kim et al., Chem. Eur. J. 2018, 24, 9525-9529. The melting point of this compound is $260\text{ }^{\circ}\text{C}$. Surprisingly it was found, by introducing small, non-branched alkyl rests instead of the isopropyl groups, the melting point can be drastically lowered to substances with a melting point below $40\text{ }^{\circ}\text{C}$ or even liquid at RT. Furthermore, TGA experiments are indicating that the volatility of the precursors is improved as compared to $\text{In}(\text{iPr}_2\text{-fAMD})_3$ as evident from the $T_{1\%}$ and $T_{50\%}$ values (see Figure 1 and Table 1). It is a particular advantage if the compound is a liquid at evaporation temperature, and in particular liquid at room temperature, as condensation is less likely to occur if there is any cold spot in the precursor delivery system. Furthermore, the handling of a compound which is a liquid at room temperature is technically easier, e.g. the filling of the vessels from which the precursor is applied.

Table 1. Comparison of the amidinate In precursors of Examples 1 to 4 with $\text{In}(\text{iPr}_2\text{-fAMD})_3$ from comparative example 1 in terms of onset of evaporation ($T_{1\%}$), 50 % mass loss ($T_{50\%}$) and melting point.

Example	Complex	$T_{1\%}\text{ [}^{\circ}\text{C]}$	$T_{50\%}\text{ [}^{\circ}\text{C]}$	$T_{\text{m.p.}}\text{ [}^{\circ}\text{C]}$
1	$\text{In}(\text{Et}_2\text{-fAMD})_3$	111	193	38
2	$\text{In}(\text{nPr}_2\text{-fAMD})_3$	102	233	liquid at RT
3	$\text{In}(\text{Et-Me-MeAMD})_3$	137	216	110
4	$\text{In}(\text{Me}_2\text{-MeAMD})_3$	115	215	183

comp. ex. 1	In(iPr ₂ -fAMD) ₃	159	236	260
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The properties of the aluminum compounds are summarized in Table 2. All compounds are stable during evaporation and show clean evaporation curves (Fig. 2). The volatility of the compounds with n-propyl (Example 6) and isopropyl (Example 7) substituents on the N atoms are similar. Surprisingly, it was found that by introducing n-propyl residues instead of the isopropyl groups, the melting point can be drastically lowered and a compound which is liquid at RT is obtained. The volatility can be further improved when using ethyl substituents instead of propyl substituents on the N atoms, as evident from the T_{1%} and T_{50%} values (Figure 2 and Table 2).

10

Table 2. Results obtained with the amidinate Al precursors of Examples 5 to 7.

Example	Complex	T _{1%} [°C]	T _{50%} [°C]	T _{m.p.} [°C]
5	Al(Et ₂ -fAMD) ₃	98	179	not observed
6	Al(nPr ₂ -fAMD) ₃	130	231	liquid at RT
7	Al(iPr ₂ -fAMD) ₃	152	235	132

15

ALD of Indium Oxide Films with In(Et₂-fAMD)₃ – General Procedure

An Atomic Premium CN-1 200 mm reactor was employed to demonstrate atomic layer deposition of indium oxide films with the precursors of this invention. The precursor In(Et₂-fAMD)₃ was delivered from SS316 ampoule (container) kept at 88 °C (ampoule wall temperature). 25 sccm of argon carrier gas flow was used to deliver precursor vapor to the reactor chamber. Reactor chamber pressure was 1.2 -1.5 torr. Ozone was used as the co-reagent. Si with native oxide as well as TiN substrates were used to deposit indium oxide films. Indium oxide film thickness was measured by X-ray fluorescence (XRF) calibrated using XRR of deposited indium oxide films.

25

Example 7: Precursor Thermal Decomposition Test on Si and TiN Wafer

In this experiment In(Et₂-fAMD)₃ precursor vapors were delivered to the deposition chamber in a pulsed mode separated by argon purge. Pulse sequence was: 6 s precursor pulse and 30 s of argon purge. The total number of precursor/Ar purge cycles was 50. No oxidant pulse was used in this experiment to demonstrate good thermal stability of the precursor in the absence of the oxidant. Good thermal stability (lack of deposition in the absence of oxidant) is an important precursor property for atomic layer deposition process. Wafer temperature was varied from 150 to 400 °C. After the experiment, the indium layer density on the surface was measured by X-Ray fluorescence analysis and is shown in Fig. 3. No increase in indium concentration on the silicon with native oxide and TiN wafers was observed up to at least 400 °C suggesting

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very good thermal stability of this precursor in the vapor phase and its utility for vapor deposition applications.

Example 8: Precursor saturation behavior during deposition process

In this experiment indium oxide films were deposited by atomic layer deposition method comprising the following steps:

- 5 a. providing Si or SiO₂ substrate in a reaction vessel;
- b. introducing into the reaction vessel In(Et₂-fAMD)₃ precursor;
- c. purging the reaction vessel with argon;
- d. introducing into the reaction vessel ozone;
- 10 e. purging the reaction vessel with pumping and argon; and
- f. sequentially repeating steps b through e until a desired thickness of the indium-containing film is obtained.

15 In(Et₂-fAMD)₃ precursor pulse varied from 2 s to 8 s seconds to demonstrate saturation behavior with increasing pulse time. Ar purge after precursor pulse was 30 s, ozone pulse was 2 s, followed by a 30 s pump step and 30 s Ar purge. The number of ALD cycles was 50. Fig. 4 shows very good saturation behavior at 300 °C temperature from a 6 s pulse of In(Et₂-fAMD)₃. Saturation behavior is one of the key features of atomic layer deposition process.

Example 9: Deposition of indium oxide film on trenched substrates (Aspect Ratio 17:1)

20 In this experiment indium oxide films were deposited by atomic layer deposition method comprising the following steps:

- a. providing Si or SiO₂ substrate in a reaction vessel;
- b. introducing into the reaction vessel In(Et₂-fAMD)₃ precursor;
- 25 c. purging the reaction vessel with argon;
- d. introducing into the reaction vessel ozone;
- e. purging the reaction vessel with pumping and argon; and
- f. sequentially repeating steps b through e until a desired thickness of the indium-containing film is obtained.

30 In(Et₂-fAMD)₃ precursor pulse was 6 s. Ar purge after precursor pulse was 30 s, ozone pulse was 2 s, and 30 s pump followed by 30 s Ar purge. The number of ALD cycles was 260. Wafer temperature was 300 °C. Figure 5 shows the cross section SEM image of indium oxide film deposited on structured wafer at 300 °C. Figure 5 shows film thickness on top, middle and bottom of the trench of the patterned wafer. TEM shows deposition of smooth and dense films. The experiment also shows only minor change in the thickness at the
35 different spots suggesting good ALD behavior. Without being bound by theory it is believed

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that step coverage could be further improved by process optimization, such as for example longer precursor pulse and purge times.

5 The foregoing description is intended primarily for purposes of illustration. Although the disclosed and claimed subject matter has been shown and described with respect to an exemplary embodiment thereof, it should be understood by those skilled in the art that the foregoing and various other changes, omissions, and additions in the form and detail thereof may be made therein without departing from the spirit and scope of the disclosed and claimed subject matter.

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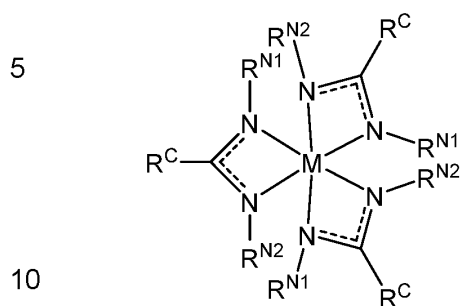
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Claims

1. Compound of formula (1):



Formula (1)

wherein the symbols used are as follows:

15

M is Al, Ga or In;

R^{N1} , R^{N2} are on each occurrence, identically or differently, an alkyl group with 1, 2 or 3 carbon atoms;

20

R^C are on each occurrence, identically or differently, H, D, methyl or ethyl;

with the proviso that the substituents R^{N1} and R^{N2} which are bound in the same amidinate ligand are not simultaneously isopropyl (iPr) groups when M is In or Ga;

25

and with the proviso that the substituents R^{N1} and R^{N2} which are bound in the same amidinate ligand are not simultaneously isopropyl (iPr) groups when M is Al and R^C is methyl or ethyl.

30

2. Compound according to claim 1 characterized in that M is indium or aluminum, preferably indium.

3. Compound according to claim 1 or 2, characterized in that all three amidinate ligands are identical.

35

4. Compound according to one or more of claim 1 to 3, characterized in that the total number of carbon atoms in R^{N1} , R^{N2} and R^C in each ligand is between 2 and 6.

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5. Compound according to claim 4, characterized in that the total number of carbon atoms in R^{N1} , R^{N2} and R^C in each ligand is 4, 5 or 6.
6. Compound according to one or more of claims 1 to 5, characterized in that R^C is H.
7. Compound according to one or more of claims 1 to 6 wherein the following applies to the symbols:
 - $M = \text{In}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{H}$; or
 - $M = \text{In}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{n-propyl}$, $R^C = \text{H}$; or
 - $M = \text{In}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{isopropyl}$, $R^C = \text{H}$; or
 - $M = \text{In}$, $R^{N1} = \text{n-propyl}$, $R^{N2} = \text{n-propyl}$, $R^C = \text{H}$; or
 - $M = \text{In}$, $R^{N1} = \text{methyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{methyl}$; or
 - $M = \text{In}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{methyl}$; or
 - $M = \text{In}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{ethyl}$; or
 - $M = \text{Al}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{H}$; or
 - $M = \text{Al}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{n-propyl}$, $R^C = \text{H}$; or
 - $M = \text{Al}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{isopropyl}$, $R^C = \text{H}$; or
 - $M = \text{Al}$, $R^{N1} = \text{n-propyl}$, $R^{N2} = \text{n-propyl}$, $R^C = \text{H}$; or
 - $M = \text{Al}$, $R^{N1} = \text{isopropyl}$, $R^{N2} = \text{isopropyl}$, $R^C = \text{H}$; or
 - $M = \text{Al}$, $R^{N1} = \text{methyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{methyl}$; or
 - $M = \text{Al}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{methyl}$; or
 - $M = \text{Al}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{ethyl}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{H}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{n-propyl}$, $R^C = \text{H}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{isopropyl}$, $R^C = \text{H}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{n-propyl}$, $R^{N2} = \text{n-propyl}$, $R^C = \text{H}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{methyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{methyl}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{methyl}$; or
 - $M = \text{Ga}$, $R^{N1} = \text{ethyl}$, $R^{N2} = \text{ethyl}$, $R^C = \text{ethyl}$.
8. Method of manufacturing a compound according to one or more of claim 1 to 7, characterized that a compound MX_3 with $M = \text{Al}$, Ga or In and $X = \text{F}$, Cl , Br , I , triflate or tosylate is reacted with an amidinate salt.
9. Use of a compound according to one or more of claim 1 to 7 for the deposition of a metal-containing film.

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10. Method for forming a metal-containing film on at least one surface of a substrate wherein the metal is Al, Ga or In, comprising the steps:
- (a) providing at least one surface of the substrate in a reaction vessel; and
 - (b) forming a metal-containing film on the at least one surface by a deposition process selected from a chemical vapor deposition (CVD) process and an atomic layer deposition (ALD) process using at least one compound according to one or more of claim 1 to 7 as precursor of a metal source compound for the deposition process.
11. Method according to claim 10, further comprising introducing into the reaction vessel at least one co-reactant.
12. Method according to claim 11, characterized in that the co-reactant is selected from the group of water, oxygen, oxygen plasma, ozone, NO, N₂O, NO₂, CO, CO₂, ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, ammonia plasma, nitrogen plasma, nitrogen/hydrogen plasma, hydrogen, hydrogen plasma, a mixture of hydrogen and helium, a mixture of hydrogen and argon, hydrogen/helium plasma, hydrogen/argon plasma, boron-containing compounds, silicon-containing compounds and combinations thereof.
13. Method for forming a metal-containing film wherein the metal is Al, Ga or In via an atomic layer deposition (ALD) process or ALD-like process, the method comprising the steps of:
- (a) providing a substrate in a reaction vessel;
 - (b) introducing into the reaction vessel one or more compounds according to one or more of claims 1 to 7 as precursor;
 - (c) a purging step, in particular purging the reaction vessel with a first purge gas;
 - (d) introducing into the reaction vessel a co-reactant;
 - (e) a purging step, in particular purging the reaction vessel with a second purge gas;
 - (f) sequentially repeating steps (b) through (e) until a desired thickness of the metal-containing film is obtained.
14. Method according to claim 13, characterized in that at least one co-reactant in step (d) is selected from water, O₂, O₃, NO, N₂O, NO₂, CO, CO₂, ammonia, hydrazine, monoalkylhydrazine, dialkylhydrazine, nitrogen, nitrogen/hydrogen, hydrogen, a mixture of hydrogen and helium, a mixture of hydrogen and argon, hydrogen/helium

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plasma, boron-containing compounds, silicon-containing compounds and combinations thereof or a plasma of these co-reactants.

15. Method according to one or more of claims 10 to 14, characterized in that the compound according to one of more of claims 1 to 7 is introduced into the reaction
5 vessel by vaporization using thermal energy and vacuum.

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