

**INTRAMOLECULAR STABILIZED MONO ALKYL METAL COMPOUNDS WITH
IMPROVED THERMAL AND LIGHT STABILITY AND THEIR USE THEREOF****[0001] BACKGROUND****[0002] Field**

[0003] The disclosed and claimed subject matter relates to mono alkyl metal compounds and their use in methods for depositing metal-containing films.

[0004] Related Art

[0005] Thin films, and in particular thin metal-containing films, have a variety of important applications, such as in nanotechnology and the fabrication of semiconductor devices. Examples of such applications include high-refractive index optical coatings, corrosion-protection coatings, photocatalytic self-cleaning glass coatings, biocompatible coatings, dielectric capacitor layers and gate dielectric insulating films in field-effect transistors (FETs), capacitor electrodes, gate electrodes, adhesive diffusion barriers, EUV photoresist patterning materials, hard mask, transparent conducting electrodes, and integrated circuits.

[0006] Various precursors may be used to form metal-containing thin films and a variety of deposition techniques can be employed. Such techniques include reactive sputtering, ion-assisted deposition, sol-gel deposition, chemical vapor deposition (CVD) (also known as metalorganic CVD or MOCVD), and atomic layer deposition (ALD) (also known as atomic layer epitaxy). CVD and ALD processes are increasingly used as they have the advantages of enhanced compositional control, high film uniformity, and effective control of doping.

[0007] CVD is a chemical process whereby precursors are used to form a thin film on a substrate surface. In a typical CVD process, the precursors are passed over the surface of a substrate (*e.g.*, a wafer) in a low pressure or ambient pressure reaction reactor. The precursors react and/or decompose on the substrate surface creating a thin film of deposited material. Volatile by-products are removed by gas flow through the reaction chamber. The deposited film thickness can be difficult to control because it depends on coordination of many parameters such as temperature, pressure, gas flow volumes and uniformity, chemical depletion effects, and time.

[0008] ALD is also a method for the deposition of thin films. It is a self-limiting, sequential, unique film growth technique based on surface reactions that can provide precise thickness control and deposit conformal thin films of materials provided by precursors onto surfaces substrates of varying compositions. In ALD, the precursors are admitted separately during the reaction, resulting in a reaction sequence. The first precursor is passed over the substrate surface producing a monolayer on the substrate surface. Any excess unreacted precursor is pumped out of the reaction reactor. A

second precursor is then passed over the substrate surface and reacts with the first precursor, forming a second monolayer of film over the first-formed monolayer of film on the substrate surface. This cycle is repeated to create a film of desired thickness.

[0009] However, the continual decrease in the size of microelectronic components, such as semiconductor devices, presents several technical challenges and has increased the need for improved thin film technologies. In particular, microelectronic components may include features on or in a substrate, which require filling, *e.g.*, to form a conductive pathway or to form interconnections. Filling such features, especially in smaller and smaller microelectronic components, can be challenging because the features can become increasingly thin or narrow. Consequently, a complete filling of the feature, *e.g.*, via ALD, would require infinitely long cycle times as the thickness of the feature approaches zero. Moreover, once the thickness of the feature becomes narrower than the size of a molecule of a precursor, the feature cannot be completely filled. As a result, a hollow seam can remain in a middle portion of the feature when ALD is performed. The presence of such hollow seams within a feature is undesirable because they can lead to failure of the device. Accordingly, there exists significant interest in the development of thin film deposition methods, particularly ALD methods that can selectively grow a film on one or more substrates and achieve improved filling of a feature on or in a substrate, including depositing a metal-containing film in a manner which substantially fills a feature without any voids.

[0010] In CVD and ALD, the precursor molecule plays a critical role in achieving high quality films with high conformality and low impurities. Suitable metal precursors include those which are thermally stable to preclude any thermal decomposition but activation for initial chemisorption and yet are chemically reactive towards added reagent. Additionally, it is important that the metal precursors are monomeric for maximum volatility, thermally stable and of high purity to ensure clean evaporation leaving only traces of involatile residue. It is also desirable that the precursors are liquid at room temperature. The temperature of the substrate in CVD and ALD processes is an important consideration in selecting a precursor molecule. Higher substrate temperatures usually promote a higher film growth rate. The preferred precursor molecules must be stable in this temperature range. The preferred precursor is capable of being delivered as gas to the reaction vessel from a liquid phase. This way a constant evaporation surface is ensured, which generally provides a more uniform delivery of the precursor to the reaction vessel than solid phase precursors. The preferred precursor needs to be thermally stable during the use on deposition tool and have sufficient vapor pressure to be delivered to deposition tool without significant decomposition. The precursor is typically delivered from a container stored on a deposition tool for extended period of time, often greater than 3 months. The impurities

formed by thermal decomposition of precursor may have negative effect on the deposition process. In some application it is also preferred that the precursor has low sensitivity to light for a longer shelf-life.

[0011] There is a need in the art to provide a thermally stable composition and method for using organometallic (Sn and Ge) compounds as precursors for the deposition of organotin- and organogermanium-containing films for certain applications in semiconductor industry such as EUV photoresist materials, hardmasks for patterning process and transparent conducting electrodes. The resulting organotin or organogermanium oxide films using organometallic compounds featuring the thermally stable composition may result in organotin and organogermanium oxide films having different physical and electrical properties needed in semi-conductor fabrication compared with that disclosed in the prior art, *i.e.*, organotin oxide films derived from organotin precursors having *i*Pr-Sn or *t*Bu-Sn groups.

[0012] There have been only a few prior art describing organogermanium trisamides incorporating Me, Et, *n*Bu and *t*Bu groups and as well their use as precursors for vapor deposition of organogermanium oxide films. These include: (i) WO2007140012; (ii) EP1464724; (iii) Thornten, P., "Germylamines," *Science of Synthesis*, Vol. 5, 97-100 (2003); (iv) Shutov, P. L. *et al.* (2001), "Syntheses and Characterization of 1-Haloazagermatranes," *Zeitschrift fuer Naturforschung, B: Chemical Sciences*, Vol. 56, 2, 137-140 (2001); and (v) U.S. Patent No. 5,344,948. Organogermanium trisamide complexes with alkyl chains with an additional coordination site which enhances the thermal stability do not appear to have been described in the literature.

[0013] Organotin trisamides having Me, Et, *i*Pr, *n*Bu, and *t*Bu groups and dialkylamide groups such as dimethylamido, ethylmethylamido, and diethylamido as well as their use as precursors for vapor deposition of organotin oxide thin films have been described. For example: (i) Lorberth, J. and M. R. Kula, "Methyltin Amides," *Chem. Ber.*, 98(2): 520-525 (1965); (ii) Jones, K. and M. F. Lappert, "Amino Derivatives of Metals and Metalloids: Preparation of Aminostannanes, Stannylamines, and Stannazanes," *J. Chem. Soc.*, 1944-1951 (1965); (iii) Haenssger, D., *et al.*, "Synthesis of the First Mono-*tert*-butyltin Compounds," *J. Organomet. Chem.*, 293(2): 191-195 (1985); (iv) U.S. Patent Application Publication No. 2022306657; (v) Kula, M.-R., *et al.*, "Proton Magnetic Resonance Spectra of Organotindiethylamides," *Chem. Ber.*, 97(5): 1294-1297 (1964); (vi) U.S. Patent Application Publication No. 2022242888; (vii) U.S. Patent Application Publication No. 2019/337969; (viii) WO2022/016128; and (ix) U.S. Patent No. 10,732,505.

[0014] Further organotin trisamides having hydrocarbyl groups have been described as precursors for solution phase deposition of organotin oxide films. For example: U.S. Patent Application Publication No. 10228618; U.S. Patent Application Publication No. 2022/0064192.

[0015] The above references, however, use either complex synthesis routes or starting material which are expensive or complicated to synthesize. Another issue is the selectivity of different syntheses for these monoalkylated tin species. These references also demonstrate the difficulty of synthesizing monoalkyl tin complexes without impurities, namely organotin compounds with more than one alkyl ligand as a side product (which is why multistep syntheses with low yields are often applied to achieve high purities). In contrast, disclosed and claimed herein is a one-step synthesis using a Grignard reagent of the form MgRX/MgR_2 and $\text{Sn}(\text{NMe}_2)_4$ as the starting material. The Grignard reagent is synthesized following by literature known synthetic procedures and $\text{Sn}(\text{NMe}_2)_4$ can either be commercially purchased or synthesized by using SnCl_4 , HNMe_2 and $n\text{BuLi}$. This one step synthesis gives selectively the mono alkylated product and shows only 4-5% overalkylation.

[0016] Other references disclose the introduction of alkyl chains with heteroatoms or heterocycles with oxygen and nitrogen atoms but did not show any synthetic work or the influence of the hetero atoms on the thermal stability or light stability of the precursor. *See, e.g.*, Pieper, N. *et al.*, "Aminoalkyl Tin Compounds," *Organometallics*, 16:1043-1052 (1997), U.S. Patent Application Publication No. 20230072538, and U.S. Patent Application Publication No. 2023/0374338.

[0017] Similarly, different types of alkyl chains with heteroatoms attached to a Sn center used for the deposition (MOCVD and related methods) of tin metal films or films of mixtures of tin and arsine, antimony, or phosphor but not oxygen has been shown. However, only structures where R is specifically a linear chain are shown, and the unexpected stabilizing effects of branched systems with quaternary carbon in α - or β - or γ -position relative to tin is not considered or suggested. *See, e.g.*, DE4213292. Another patent claims similar compounds for usage as coordination catalysts. In this case similar alkyl chains with heteroatoms attached to a Sn center are claimed, however, the three other ligands at the Sn center are not claimed to be amides. *See, e.g.*, EP0690748.

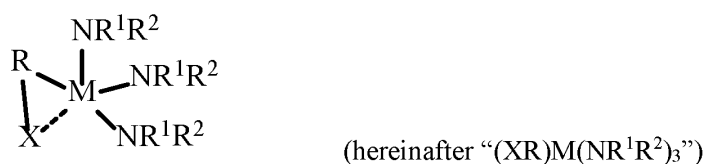
[0018] Another reference discloses mono alkyl tin amides with nitrogen in the alkyl chain for the application as photoresist precursors. Branched alkyl chains are included; however, all compounds contain alkyl chains with secondary and tertiary carbons at maximum so that at least one hydrogen is present at every carbon of the alkyl chain. Again, the unexpected stabilizing effects of branched systems with at least one quaternary carbon in α - or β - or γ -position relative to tin is not considered or suggested. *See, e.g.*, U.S. Patent Application Publication No. 2024/0201586.

[0019] Although organotin trisamides are often highly volatile and liquid, they typically show a high sensitivity towards light and relatively low thermal stabilities, making them less suitable for vapor phase deposition applications. The disclosed and claimed subject matter includes compounds

having an additional donating function (oxygen or nitrogen) at the alkyl chain, which has a chelating effect and can stabilize the complex. In addition, by utilizing branched alkyl chains with at least one quaternary carbon in one or more of the α - or β - or γ -position, hydrogens are excluded and potential α - or β - or γ -hydrogen elimination is suppressed. Both features increase the thermal and light stability of the claimed compounds compared to known monoalkyltin trisamide complexes like $\text{MeSn}(\text{NMe}_2)_3$ or $\text{iPrSn}(\text{NMe}_2)_3$ making the claimed complexes beneficial for the usage in CVD and ALD processes for deposition of Sn-containing thin films of high purity.

[0020] SUMMARY

[0021] In one embodiment, the disclosed and claimed subject matter relates to compounds of Formula (I):



where

- (i) M = Sn or Ge;
- (ii) R is a branched C₅ to C₁₀ alkylene linker group where (i) three to eight main chain carbon moieties connect M and X and (ii) at least one of the first three main chain carbon moieties (*i.e.*, the α - or β - or γ -carbon moieties) that connect M and X is a quaternary carbon moiety that is free of hydrogen;
- (iii) R¹ and R² are each independently selected from a linear C₁ to C₆ alkyl group, a branched C₄ to C₆ alkyl group or a cyclic C₃ to C₆ alkyl group; and
- (iv) X is selected is one of -OR³ or -NR⁴R⁵ where R³, R⁴ and R⁵ are each independently selected from a linear C₁ to C₆ alkyl group, a branched C₄ to C₆ alkyl group or a cyclic C₃ to C₆ alkyl group. In one aspect of this embodiment, the compound of Formula (I) includes, consists essentially of or consists of $(\text{NMe}_2\text{CH}_2\text{CMe}_2\text{CH}_2)\text{Sn}(\text{NMe}_2)_3$. In one aspect of this embodiment, the compound of Formula (I) includes, consists essentially of or consists of $(\text{OMeCH}_2\text{CH}_2\text{CMe}_2)\text{Sn}(\text{NMe}_2)_3$.

[0022] The disclosed and claimed compounds of Formula (I) include three amides (-NR¹R²) and one alkylene group (-R) with one additional coordination site (X) which can be an amine or ether group. This amine or ether group (X) is coordinated to the metal via a dative bond (shown as dotted line above) to stabilize the disclosed and claimed compounds and is not a covalent bond like the amides

(-NR¹R²) have (shown as a full line). As such, the disclosed and claimed compounds do not include compounds with the formula M(NR¹R²)₄ as disclosed in U.S. Patent No. 11,500,284 and related organotin compounds discussed therein having formula RM(NR¹R²)₃.

[0023] In one embodiment, the disclosed and claimed subject matter relates to compositions that include, consist essentially of or consist of one or more compounds of Formula (I).

[0024] In another embodiment, the above-described compounds and/or compositions are used in method(s) for depositing tin-containing films and/or germanium-containing films. In a further aspect of this embodiment, the deposited films include, consist essentially of or consist of one or more of organotin oxide, tin oxide, organogermanium oxide and germanium oxide.

[0025] This summary section does not specify every embodiment and/or incrementally novel aspect of the disclosed and claimed subject matter. Instead, this summary only provides a preliminary discussion of different embodiments and corresponding points of novelty over conventional techniques and the known art. For additional details and/or possible perspectives of the disclosed and claimed subject matter and embodiments, the reader is directed to the Detailed Description section and corresponding figures of the disclosure as further discussed below.

[0026] The order of discussion of the different steps described herein has been presented for clarity's sake. In general, the steps disclosed herein can be performed in any suitable order. Additionally, although each of the different features, techniques, configurations, etc. disclosed herein may be discussed in different places of this disclosure, it is intended that each of the concepts can be executed independently of each other or in combination with each other as appropriate. Accordingly, the disclosed and claimed subject matter can be embodied and viewed in many different ways.

[0027] BRIEF DESCRIPTION OF THE DRAWINGS

[0028] The accompanying drawings, which are included to provide a further understanding of the disclosed subject matter and are incorporated in and constitute a part of this specification, illustrate embodiments of the disclosed subject matter and together with the description serve to explain the principles of the disclosed subject matter. In the drawings:

[0029] FIG. 1 illustrates the ¹H NMR of (DMDMP)Sn(NMe₂)₃ (compound "3");

[0030] FIG. 2 illustrates the ¹³C NMR of compound 3;

[0031] FIG. 3 illustrates the ¹¹⁹Sn NMR of compound 3;

[0032] FIG. 4 illustrates the ¹H NMR of compound 3 made by the traditional synthetic method;

[0033] FIG. 5 illustrates the ¹³C NMR of compound 3 made by the traditional synthetic method;

[0034] FIG. 6 illustrates the thermal gravimetric analysis (TGA) of compound 3 and 7;

- [0035] FIG. 7 illustrates the differential scanning calorimetry (DSC) of compound **3**;
- [0036] FIG. 8 illustrates the ^{119}Sn NMR spectra of compound **3** recorded at room temperature at various time intervals;
- [0037] FIG. 9 illustrates the ^{119}Sn NMR spectra of $\text{iPrSn}(\text{NMe}_2)_3$ after exposing to light for 24 days;
- [0038] FIG. 10 illustrates the ^1H NMR of $(\text{MODMP})\text{Sn}(\text{NMe}_2)_3$ (compound “7”);
- [0039] FIG. 11 illustrates the ^{119}Sn NMR of compound **7**;
- [0040] FIG. 12 illustrates shows the DSC of compound **7**;
- [0041] FIG. 13 illustrates the growth rate vs number of cycles for $(\text{DMDMP})\text{Sn}(\text{NMe}_2)_3$ and H_2O at 90 °C with an ALD-like cycle comprising $(\text{DMDMP})\text{Sn}(\text{NMe}_2)_3$ (5 sec) – purge (60 sec) - H_2O (0.1 sec)- purge (90 sec), demonstrating ALD-like linear growth; and
- [0042] FIG. 14 illustrates the growth rate vs number of cycles for $(\text{DMDMP})\text{Sn}(\text{NMe}_2)_3$ and H_2O at 110 °C with an ALD-like cycle comprising $(\text{DMDMP})\text{Sn}(\text{NMe}_2)_3$ (5 sec) – purge (60 sec) - H_2O (0.1 sec)- purge (90 sec), demonstrating ALD-like linear growth.
- [0043] **DEFINITIONS**
- [0044] Unless otherwise stated, the following terms used in the specification and claims shall have the following meanings for this application.
- [0045] For purposes of this invention and the claims hereto, the numbering scheme for the Periodic Table Groups is according to the IUPAC Periodic Table of Elements.
- [0046] The term “and/or” as used in a phrase such as “A and/or B” herein is intended to include “A and B,” “A or B,” “A” and “B.”
- [0047] As used herein, “ C_{x-y} ” designates the number of carbon atoms in a chain. For example, C_{1-6} alkyl refers to an alkyl chain having a chain of between 1 and 6 carbons (*e.g.*, methyl, ethyl, propyl, butyl, pentyl and hexyl). Unless specifically stated otherwise, the chain can be linear or branched.
- [0048] Unless otherwise indicated, “alkyl” refers to hydrocarbon groups which can be linear, branched (*e.g.*, methyl, ethyl, propyl, isopropyl, tert-butyl and the like), cyclic (*e.g.*, cyclohexyl, cyclopropyl, cyclopentyl and the like) or multicyclic (*e.g.*, norbornyl, adamantyl and the like). Suitable acyclic groups can be methyl, ethyl, n- or iso-propyl, n-, iso, or tert-butyl, linear or branched pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl. Unless otherwise stated, alkyl refers to 1-10 carbon atom moieties. The cyclic alkyl groups may be mono cyclic or polycyclic. Suitable examples of mono-cyclic alkyl groups include substituted cyclopentyl, cyclohexyl, and cycloheptyl groups. As mentioned herein the cyclic alkyl groups may have any of the acyclic alkyl groups as substituent. These alkyl moieties may be substituted or unsubstituted.

[0049] “Hydroxy” (a.k.a. “hydroxyl”) refers to an –OH group.

[0050] Unless otherwise indicated, the term “substituted” when referring to an alkyl, alkoxy, fluorinated alkyl and the like refers to one of these moieties which also contains one or more substituents including, but not limited, to the following substituents: alkyl, substituted alkyl, unsubstituted aryl, substituted aryl, alkyloxy, alkylaryl, haloalkyl, halide, hydroxy, amino and amino alkyl. Similarly, the term “unsubstituted” refers to these same moieties where no substituents apart from hydrogen are present.

[0051] Alkylene groups are bivalent saturated aliphatic radical (such as ethylene) regarded as derived from an alkane (such as those described above) by removal of two hydrogen atoms from different carbon atoms. When referring to alkylene groups, these include an alkylene chain substituted with (C₁-C₁₈) alkyl groups in the main carbon chain of the alkylene group. Alkylene groups can also include one or more alkyne groups in the alkylene moiety, where alkyne refers to a triple bond. Essentially an alkylene is a divalent hydrocarbon group as the backbone. Accordingly, a divalent acyclic group may be methylene, 1,1- or 1,2-ethylene, 1,1-, 1,2-, or 1,3 propylene, 2,5-dimethyl-hexene, 2,5-dimethyl-hex-3-yne, and so on. Similarly, a divalent cyclic alkyl group may be 1,2- or 1,3-cyclopentylene, 1,2-, 1,3-, or 1,4-cyclohexylene, and the like.

[0052] The terms “substituent,” “radical,” “group” and “moiety” may be used interchangeably.

[0053] As used herein, the terms “metal-containing complex” (or more simply, “complex”) and “precursor” are used interchangeably and refer to metal-containing molecule or compound which can be used to prepare a metal-containing film by a vapor deposition process such as, for example, ALD or CVD. The metal-containing complex may be deposited on, adsorbed to, decomposed on, delivered to, and/or passed over a substrate or surface thereof, as to form a metal-containing film. In one or more embodiments, the metal-containing complexes disclosed herein are metal halide complexes, particularly molybdenum chloride complexes.

[0054] As used herein, the term “metal-containing film” includes not only an elemental metal film as more fully defined below, but also a film which includes a metal along with one or more elements, for example in form of a metal oxide film, metal nitride film, metal silicide film, a metal carbide film and the like. As used herein, the terms “elemental metal film” and “pure metal film” are used interchangeably and refer to a film which consists of, or consists essentially of, pure metal. For example, the elemental metal film may include 100% pure metal, or the elemental metal film may include at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 96%, at least about 97%, at least about 98%, at least about 99%, at least about 99.9%, or at least about 99.99% pure metal along with one or more impurities. Unless context dictates otherwise, the term

“metal film” shall be interpreted to mean an elemental metal film.

[0055] As used herein, the term “vapor deposition process” is used to refer to any type of vapor deposition technique, including but not limited to, CVD and ALD. In various embodiments, CVD may take the form of conventional (*i.e.*, continuous flow) CVD, liquid injection CVD, or photo-assisted CVD. CVD may also take the form of a pulsed technique, *i.e.*, pulsed CVD. ALD is used to form a metal-containing film by vaporizing and/or passing at least one metal complex disclosed herein over a substrate surface. For conventional ALD processes see, for example, George S. M., *et al.* *J. Phys. Chem.*, 1996, *100*, 13121–13131. In other embodiments, ALD may take the form of conventional (*i.e.*, pulsed injection) ALD, liquid injection ALD, photo-assisted ALD, plasma-assisted ALD, or plasma-enhanced ALD. The term “vapor deposition process” further includes various vapor deposition techniques described in *Chemical Vapour Deposition: Precursors, Processes, and Applications*; Jones, A. C.; Hitchman, M. L., Eds. The Royal Society of Chemistry: Cambridge, 2009; Chapter 1, pp. 1–36.

[0056] Throughout the description, the term “ALD or ALD-like” refers to a process including, but not limited to, the following processes: a) each reactant including organotin compound precursor and reactive gas is introduced sequentially into a reactor such as a single wafer ALD reactor, semi-batch ALD reactor, or batch furnace ALD reactor; b) each reactant including organotin compound precursor and reactive gas is exposed to a substrate by moving or rotating the substrate to different sections of the reactor and each section is separated by inert gas curtain, *i.e.*, spatial ALD reactor or roll to roll ALD reactor. The ALD-like is defined herein as a cyclic CVD process that provides a high conformal metal-containing film on a substrate as shown by having at least one of the following: percentage of non-uniformity of about 5% or less as measured by ellipsometry, a deposition rate of 1 Å or greater per cycle or a combination thereof.

[0057] As used herein, the term “feature” refers to an opening in a substrate which may be defined by one or more sidewalls, a bottom surface, and upper corners. In various aspects, the feature may be a via, a trench, contact, dual damascene, *etc.*

[0058] As used herein, the terms “selective growth,” “selectively grown” and “selectively grows” may be used synonymously and refer to film growth on at least a portion of a first substrate and no substantial film growth on a remaining portion of the first substrate as well as more film growth on at least a portion of the first substrate compared to film growth on a remaining portion of the first substrate. For example, selective growth may include growth of a film on a lower portion of a feature while less film growth or no film growth may occur in an upper portion of that feature or outside that feature. With respect to more than one substrate, the terms “selective growth,” “selectively grown” and “selectively grows” also encompass film growth on a first substrate and substantially no film growth on a second substrate (or a

third substrate, or fourth substrate or a fifth substrate, *etc.*) as well as more film growth on the first substrate than on the second substrate (or a third substrate, or fourth substrate or a fifth substrate, *etc.*).

[0059] The term “about” or “approximately,” when used in connection with a measurable numerical variable, refers to the indicated value of the variable and to all values of the variable within $\pm 5\%$ of the indicated value.

[0060] “Halo” or “halide” refers to a halogen (*e.g.*, F, Cl, Br and I).

[0061] “Tin-containing film” refers to organotin oxide or tin oxide which can be employed as material in semi-conductor or display device fabrication process.

[0062] The section headings used herein are for organizational purposes and are not to be construed as limiting the subject matter described. All documents, or portions of documents, cited in this application, including, but not limited to, patents, patent applications, articles, books, and treatises, are hereby expressly incorporated herein by reference in their entirety for any purpose. In the event that any of the incorporated literature and similar materials defines a term in a manner that contradicts the definition of that term in this application, this application controls.

DETAILED DESCRIPTION

[0063] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. The objects, features, advantages and ideas of the disclosed subject matter will be apparent to those skilled in the art from the description provided in the specification, and the disclosed subject matter will be readily practicable by those skilled in the art on the basis of the description appearing herein. The description of any “preferred embodiments” and/or the examples which show preferred modes for practicing the disclosed subject matter are included for the purpose of explanation and are not intended to limit the scope of the claims.

[0064] It will also be apparent to those skilled in the art that various modifications may be made in how the disclosed subject matter is practiced based on described aspects in the specification without departing from the spirit and scope of the disclosed subject matter disclosed herein.

[0065] In the below-described embodiments directed to methods or processes, it is understood that in some embodiments the steps of the methods may be performed in a variety of orders, may be performed sequentially or concurrently (*e.g.*, during at least a portion of another step), and any combination thereof. The respective step of supplying the precursors and the nitrogen-containing source gases may be performed by varying the duration of the time for supplying them to change the stoichiometric composition of the resulting dielectric film.

[0066] As noted above, the disclosed and claimed subject matter relates to mono alkyl metal

compounds and their use in methods for depositing metal-containing films. During the typical preparation of such materials, overalkylation typically takes place either due to the strong alkylation agent or through rearrangements of the corresponding products where 2 RSnL_3 are slowly reacting to R_2SnL_2 and SnL_4 . This particular redistribution behavior has not been observed for germanium in literature. One approach to thermally stabilize these types of compounds is to insert another coordination site to the alkyl ligand. This can enhance the overall stability, but also lead to a decreased volatility and even to solidification at room temperature.

[0067] The disclosed and claimed subject matter overcomes the above issues. Namely it provides an easy method for synthesizing compounds of Formula (I): $(\text{XR})\text{M}(\text{NR}^1\text{R}^2)_3$ where

(i) $\text{M} = \text{Sn}$ or Ge ;

(ii) R is a branched C_5 to C_{10} alkylene linker group where (i) three to eight main chain carbon moieties connect M and X and (ii) at least one of the first three main chain carbon moieties (*i.e.*, the α - or β - or γ -carbon moieties) that connect M and X is a quaternary carbon moiety that is free of hydrogen;

(iii) R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_4 to C_6 alkyl group or a cyclic C_3 to C_6 alkyl group; and

(iv) X is selected is one of $-\text{OR}^3$ or $-\text{NR}^4\text{R}^5$ where R^3 , R^4 and R^5 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_4 to C_6 alkyl group or a cyclic C_3 to C_6 alkyl group. These compounds remain liquids at room temperature and provide high thermal and light stabilities making them ideal for the utilization in vapor phase deposition processes. The introduction of alkyl groups with additional heteroatoms (*i.e.*, $-\text{OR}^3$ and $-\text{NR}^4\text{R}^5$) results in a dative bond to the metal center, which increase thermal and light stability. Furthermore, blocking the α - or β - or γ -C position of the alkylene related to the metal atom with alkyl groups such as one or two methyl groups would block potential α - or β - or γ -hydrogen elimination decomposition pathway as well as introduces a higher asymmetry to the resulting metal complex. Thus, the thermal stability, volatility and viscosity is improved.

[0068] Organotin and Organogermanium Compounds

[0069] In one embodiment, the disclosed and claimed subject matter relates to compounds of Formula (I): $(\text{XR})\text{M}(\text{NR}^1\text{R}^2)_3$ where

(i) $\text{M} = \text{Sn}$ or Ge ;

(ii) R is a branched C_5 to C_{10} alkylene linker group where (i) three to eight main chain carbon moieties connect M and X and (ii) at least one of the first three main chain carbon moieties (*i.e.*, the α - or β - or γ -carbon moieties) that connect M and X is a quaternary carbon moiety

that is free of hydrogen;

(iii) R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_4 to C_6 alkyl group or a cyclic C_3 to C_6 alkyl group; and

(iv) X is selected is one of $-OR^3$ or $-NR^4R^5$ where R^3 , R^4 and R^5 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_4 to C_6 alkyl group or a cyclic C_3 to C_6 alkyl group.

[0070] Metals

[0071] In one embodiment, $M = Sn$.

[0072] In one embodiment, $M = Ge$.

[0073] R Group

[0074] As noted above, R is a branched C_5 to C_{10} alkylene linker group wherein (i) three to eight main chain carbon moieties connecting M and X and (ii) at least one of the first three main chain carbon moieties (*i.e.*, the α - or β - or γ -positions or α - or β - or γ -carbons) connecting M and X is a quaternary carbon moiety that is free of hydrogen. As those skilled in the art will understand, although the R group includes a total of five to ten carbon moieties, at least three to eight of those carbon moieties must form the main chain (*i.e.*, the “backbone”) connecting M and X, and at least one of the first three carbon moieties (*i.e.*, the α -carbon moiety, β -carbon moiety and γ -carbon moiety) in the main chain starting from M must be a hydrogen-free quaternary carbon moiety. Thus, for example, an embodiment where R has three carbon moieties in main chain connecting M and X has the formula/structure $(NR^1R^2)_3M-C^\alpha-C^\beta-C^\gamma-X$ (note that the sidechains/hydrogens on the three backbone carbon moieties are not shown).

[0075] It is further to be understood that the requirement that at least one of the first three carbon moieties (*i.e.*, the α -carbon moiety, β -carbon moiety and γ -carbon moiety) in the main chain starting from M must be a hydrogen-free quaternary carbon moiety refers only to the carbon atoms of carbon moieties in the main chain (*i.e.*, the “backbone”) connecting M and X; it does not exclude the presence of hydrogens on other atoms attached or otherwise appended to such main chain carbon moieties (*i.e.*, side chains appended to the main chain carbons such as a $-CH_3$ group).

[0076] In one embodiment, in R the C_5 to C_{10} alkylene linker group consist of three main chain carbons moieties connecting M and X.

[0077] In one embodiment, in R the C_5 to C_{10} alkylene linker group consist of four main chain carbon moieties connecting M and X.

[0078] In one embodiment, in R the C_5 to C_{10} alkylene linker group consist of five main chain carbon moieties connecting M and X.

[0079] In one embodiment, in R the C₅ to C₁₀ alkylene linker group consist of six main chain carbon moieties connecting M and X.

[0080] In one embodiment, in R the C₅ to C₁₀ alkylene linker group consist of seven main chain carbon moieties connecting M and X.

[0081] In one embodiment, in R the C₅ to C₁₀ alkylene linker group consist of eight main chain carbon moieties connecting M and X.

[0082] In one embodiment, in R the α -carbon moiety is a hydrogen-free quaternary carbon moiety.

[0083] In one embodiment, in R the β -carbon moiety is a hydrogen-free quaternary carbon moiety.

[0084] In one embodiment, in R the γ -carbon moiety is a hydrogen-free quaternary carbon moiety.

[0085] In one embodiment, in R two or more of the α -carbon moiety, β -carbon moiety and γ -carbon moiety are hydrogen-free quaternary carbon moieties.

[0086] In one embodiment, R is a -C(Me₂)CH₂CH₂- group starting from M and connecting to X (*i.e.*, (NR¹R²)₃M-C(Me₂)CH₂CH₂-X).

[0087] In one embodiment, R is a -CH₂C(Me₂)CH₂- group starting from M and connecting to X (*i.e.*, (NR¹R²)₃M-CH₂C(Me₂)CH₂-X).

[0088] In one embodiment, R is a -CH₂CH₂C(Me₂)- group starting from M and connecting to X (*i.e.*, (NR¹R²)₃M-CH₂CH₂C(Me₂)-X).

[0089] **R¹ and R² Groups**

[0090] In one embodiment, one or both of R¹ and R² is a linear C₁ to C₆ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a linear C₁ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a linear C₂ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a linear C₃ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a linear C₄ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a linear C₅ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a linear C₆ alkyl group.

[0091] In one embodiment, one or both of R¹ and R² is a branched C₄ to C₆ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a branched C₄ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a branched C₅ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a branched C₆ alkyl group.

[0092] In one embodiment, one or both of R¹ and R² is a cyclic C₃ to C₆ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a cyclic C₃ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a cyclic C₄ alkyl group. In one aspect of this embodiment, one or both of R¹ and R² is a cyclic C₅ alkyl group. In one aspect of this embodiment, one or both of

R¹ and R² is a cyclic C₆ alkyl group.

[0093] X Group

[0094] In one embodiment, X is a -OR³ group. In one aspect of this embodiment, R³ is a linear C₁ to C₆ alkyl group. In one aspect of this embodiment, R³ is a linear C₁ alkyl group. In one aspect of this embodiment, R³ is a linear C₂ alkyl group. In one aspect of this embodiment, R³ is a linear C₃ alkyl group. In one aspect of this embodiment, R³ is a linear C₄ alkyl group. In one aspect of this embodiment, R³ is a linear C₅ alkyl group. In one aspect of this embodiment, R³ is a linear C₆ alkyl group. In another aspect of this embodiment, R³ is a branched C₄ to C₆ alkyl group. In one aspect of this embodiment, R³ is a branched C₄ alkyl group. In one aspect of this embodiment, R³ is a branched C₅ alkyl group. In one aspect of this embodiment, R³ is a branched C₆ alkyl group. In a further aspect of this embodiment, R³ is a cyclic C₃ to C₆ alkyl group. In one aspect of this embodiment, R³ is a cyclic C₃ alkyl group. In one aspect of this embodiment, R³ is a cyclic C₄ alkyl group. In one aspect of this embodiment, R³ is a cyclic C₅ alkyl group. In one aspect of this embodiment, R³ is a cyclic C₆ alkyl group.

[0095] In one embodiment, X is a -NR⁴R⁵ group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₁ to C₆ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₁ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₂ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₃ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₄ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₅ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a linear C₆ alkyl group. In another aspect of this embodiment, one or both of R⁴ and R⁵ is a branched C₄ to C₆ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a branched C₄ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a branched C₅ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a branched C₆ alkyl group. In a further aspect of this embodiment, one or both of R⁴ and R⁵ is a cyclic C₃ to C₆ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a cyclic C₃ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a cyclic C₄ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a cyclic C₅ alkyl group. In one aspect of this embodiment, one or both of R⁴ and R⁵ is a cyclic C₆ alkyl group.

[0096] In one embodiment, the compound of Formula (I) includes, consists essentially of or consists of (NMe₂CH₂CMe₂CH₂)Sn(NMe₂)₃.

[0097] In one embodiment, the compound of Formula (I) includes, consists essentially of or consists of (OMeCH₂CMe₂CH₂)Sn(NMe₂)₃.

[0098] In one embodiment, the compound of Formula (I) includes, consists essentially of or consists of $(\text{NMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2)\text{Sn}(\text{NMe}_2)_3$.

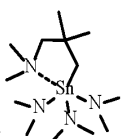
[0099] In one embodiment, the compound of Formula (I) includes, consists essentially of or consists of $(\text{OMeCH}_2\text{CH}_2\text{CMe}_2)\text{Sn}(\text{NMe}_2)_3$.

[0100] **Exemplary Embodiments**

[0101] In one embodiment, in Formula (I) M is Sn, R is one of $-\text{C}(\text{Me}_2)\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{C}(\text{Me}_2)-$, R^1 and R^2 each are independently one of Me and Et and X is $-\text{NR}^4\text{R}^5$ where R^4 and R^5 each are independently one of Me and Et.

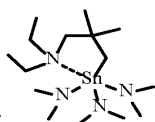
[0102] In one embodiment, in Formula (I) M is Sn, R is one of $-\text{C}(\text{Me}_2)\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{C}(\text{Me}_2)-$, R^1 and R^2 each are independently one of Me and Et and X is $-\text{OR}^3$ where R^3 is one of Me and Et.

[0103] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 and R^2 are Me



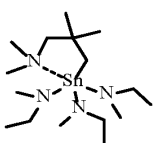
and X is $-\text{NMe}_2$ as follows: (i.e., 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin).

[0104] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 and R^2 are Me



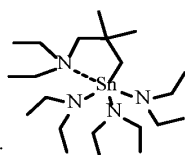
and X is $-\text{NEt}_2$ as follows: (i.e., 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin).

[0105] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 is Me and R^2 is



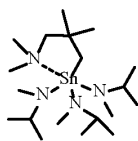
Et and X is $-\text{NMe}_2$ as follows: (i.e., 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-ethylmethylamidotin).

[0106] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 and R^2 are Et



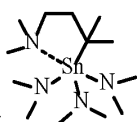
and X is $-\text{NEt}_2$ as follows: (i.e., 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-diethylamidotin).

[0107] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 is Me and R^2 is



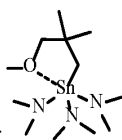
iPr and X = $-\text{NMe}_2$ as follows: (*i.e.*, 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-methyl-iso-propylamidotin).

[0108] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{CH}_2\text{C}(\text{Me}_2)-$, R^1 and R^2 Me and



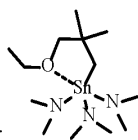
X is $-\text{NMe}_2$ as follows: (*i.e.*, 3-(N,N-dimethylamino)-1,1-dimethyl-propyl-tris-dimethylamidotin).

[0109] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 and R^2 Me and



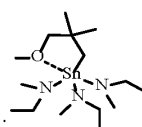
X is $-\text{OMe}$ as follows: (*i.e.*, 3-methoxy-2,2-dimethyl-propyl-tris-dimethylamidotin).

[0110] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 and R^2 Me and



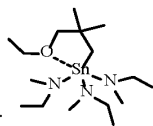
X is $-\text{OEt}$ as follows: (*i.e.*, 3-ethoxy-2,2-dimethyl-propyl-tris-dimethylamidotin).

[0111] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 Me and R^2 is Et



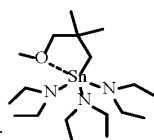
and X is $-\text{OMe}$ as follows: (*i.e.*, 3-methoxy-2,2-dimethyl-propyl-tris-ethylmethylamidotin).

[0112] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 Me and R^2 is Et



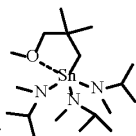
and X is $-\text{OEt}$ as follows: (*i.e.*, 3-ethoxy-2,2-dimethyl-propyl-tris-ethylmethylamidotin).

[0113] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 and R^2 are Et ,

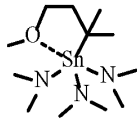


and X is $-\text{OMe}$ as follows: (*i.e.*, 3-methoxy-2,2-dimethyl-propyl-tris-diethylamidotin).

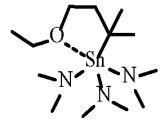
[0114] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{C}(\text{Me}_2)\text{CH}_2-$, R^1 is Me and R^2 is

iPr and X is -OMe as follows:  (i.e., 3-ethoxy-2,2-dimethyl-propyl-tris-methylisopropylamidotin).

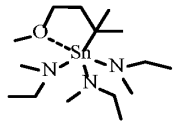
[0115] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{CH}_2\text{C}(\text{Me})_2-$, R^1 and R^2 are Me

and X is -OMe as follows:  (i.e., 3-methoxy-1,1-dimethyl-propyl-tris-dimethylamidotin).

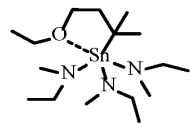
[0116] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{CH}_2\text{C}(\text{Me})_2-$, R^1 and R^2 are Me

and X is -OEt as follows:  (i.e., 3-ethoxy-1,1-dimethyl-propyl-tris-dimethylamidotin).

[0117] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{CH}_2\text{C}(\text{Me})_2-$, R^1 is Me and R^2 is

Et and X is -OMe as follows:  (i.e., 3-methoxy-1,1-dimethyl-propyl-tris-ethylmethylamidotin).

[0118] In one embodiment, in Formula (I) M is Sn, R is $-\text{CH}_2\text{CH}_2\text{C}(\text{Me})_2-$, R^1 is Me and R^2 is

Et and X is -OEt as follows:  (i.e., 3-ethoxy-1,1-dimethyl-propyl-tris-ethylmethylamidotin).

[0119] Compositions of Organotin Compounds

[0120] In one embodiment, the disclosed and claimed subject matter relates to compositions that include, consist essentially of or consist of (a) one or more of the compounds of Formula (I) described above and (b) one or more solvents.

[0121] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of one or more of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-ethylmethylamidotin, 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-diethylamidotin, 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-methyl-iso-

propylamidotin, 3-(N,N-dimethylamino)-1,1-dimethyl-propyl-tris-dimethylamidotin, 3-methoxy-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-ethoxy-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-methoxy-2,2-dimethyl-propyl-tris-ethylmethyamidotin, 3-ethoxy-2,2-dimethyl-propyl-tris-ethylmethyamidotin, 3-methoxy-2,2-dimethyl-propyl-tris-diethylamidotin, 3-ethoxy-2,2-dimethyl-propyl-tris-methylisopropylamidotin, 3-methoxy-1,1-dimethyl-propyl-tris-dimethylamidotin, 3-ethoxy-1,1-dimethyl-propyl-tris-dimethylamidotin, 3-methoxy-1,1-dimethyl-propyl-tris-ethylmethyamidotin and 3-ethoxy-1,1-dimethyl-propyl-tris-ethylmethyamidotin.

[0122] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin.

[0123] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin.

[0124] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-ethylmethyamidotin.

[0125] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-diethylamidotin.

[0126] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-methyl-iso-propylamidotin.

[0127] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-(N,N-dimethylamino)-1,1-dimethyl-propyl-tris-dimethylamidotin.

[0128] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-methoxy-2,2-dimethyl-propyl-tris-dimethylamidotin.

[0129] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-ethoxy-2,2-dimethyl-propyl-tris-dimethylamidotin.

[0130] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-methoxy-2,2-dimethyl-propyl-tris-ethylmethyamidotin.

[0131] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-ethoxy-2,2-dimethyl-propyl-tris-ethylmethanimidotin.

[0132] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-methoxy-2,2-dimethyl-propyl-tris-diethylimidotin.

[0133] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-ethoxy-2,2-dimethyl-propyl-tris-methylisopropylimidotin.

[0134] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-methoxy-1,1-dimethyl-propyl-tris-dimethylimidotin.

[0135] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-ethoxy-1,1-dimethyl-propyl-tris-dimethylimidotin.

[0136] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-methoxy-1,1-dimethyl-propyl-tris-ethylmethanimidotin.

[0137] In one embodiment, the one or more the compounds of Formula (I) of the compositions includes, consists essentially of or consists of 3-ethoxy-1,1-dimethyl-propyl-tris-ethylmethanimidotin.

[0138] The compositions of the disclosed and claimed subject matter further include (b) one or more solvent(s). Suitable solvents 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 compositions include, but are not limited to, toluene, mesitylene, cumene (iso-propylbenzene), p-cymene (4-iso-propyl toluene), 1,3-di-iso-propylbenzene, octane, dodecane, 1,2,4-trimethylcyclohexane, n-butylcyclohexane, decahydronaphthalene (decalin) and combinations thereof. In certain embodiments, the hydrocarbon solvent is a high boiling point solvent or has a boiling point of 100 °C or greater.

[0139] **Methods of Depositions**

[0140] In another embodiment, the above-described tin compounds and/or compositions are used in method(s) for depositing tin-containing films.

[0141] In one embodiment, the method for deposition of organotin oxide or tin oxide films of the disclosed and claimed subject matter includes, consists essentially of or consists of the steps of:

- a. providing one or more substrates in a reactor, where the reactor is heated to temperature of from about 25 °C to about 600 °C and optionally maintained at a pressure of about 100 torr or less;
- b. introducing into the reactor a vapor including, consisting essentially of or consisting of one or more compounds of Formula (I) or a composition of such

compounds that forms a metal-containing (*i.e.*, a tin-containing or a germanium-containing) layer on a surface of the substrate;

- c. purging the reactor with an inert gas;
- d. introducing one or more oxygen source to convert the tin-containing layer to an organotin oxide or tin oxide layer; and
- e. purging the reactor with an inert gas.

[0142] In one embodiment, the oxygen source can be one or more of water vapor, hydrogen peroxide, organic peroxides and mixtures thereof for a thermal ALD or ALD-like process to deposit organotin oxide. In other one embodiment, the oxygen source can be one or more of water plasma, ozone, oxygen, oxygen plasma, oxygen/helium plasma, oxygen/argon plasma, nitrogen oxides plasma, carbon dioxide plasma, and mixtures thereof for formation of tin oxide materials. In a particular embodiment, the oxygen source includes, consists essentially of or consists of water vapor.

[0143] In a preferred embodiment of the above method, the step (d) one or more oxygen source includes, consists essentially of or consists of water vapor and the process further includes, consists essentially of or consists of the additional steps of introducing a carboxylic acid vapor and purging the same. In particular, the method for deposition of organotin oxide films of the disclosed and claimed subject matter includes, consists essentially of or consists of the steps of:

- a. providing one or more substrates in a reactor, where the reactor is heated to temperature of from about 25 °C to about 600 °C and optionally maintained at a pressure of about 100 torr or less;
- b. introducing into the reactor a vapor including, consisting essentially of or consisting of one or more compounds of Formula (I) or a composition of such compounds that forms a metal-containing (*i.e.*, a tin-containing or a germanium-containing) layer on a surface of the substrate;
- c. purging any unreacted precursor from the reactor using an inert gas;
- d. introducing one or more oxygen source including, consisting essentially of or consisting of water vapor to convert the tin-containing layer to an organotin oxide or tin oxide layer;
- e. purging the reactor with an inert gas;
- f. introducing one or more carboxylic acid vapor having the formula R^3COOH where R^3 is selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_3 to C_6 alkynyl

group, and a C₄ to C₁₀ aryl group to react with the organotin oxide layer; and

g. purging the reactor with an inert gas.

[0144] Step (b) Delivery of Organotin and/or Organogermanium Precursor

[0145] As noted above, step (b) of the disclosed and claimed methods includes introducing into the reactor a vapor including, consisting essentially of or consisting of one or more compounds of Formula (I) or a composition of such compounds that forms a metal-containing (*i.e.*, a tin-containing or a germanium-containing) layer on a surface of the substrate.

[0146] In one embodiment, the vapor includes, consists essentially of or consists of one or more organotin compound of Formula (I). In one embodiment, the vapor includes, consists essentially of or consists of one or more organogermanium compound of Formula (I).

[0147] In one embodiment, the precursor vapor pulse time is from about 0.1 seconds to about 3 seconds. In another embodiment, the precursor vapor pulse time is from about 0.3 seconds to about 3 seconds. In another embodiment, the precursor vapor pulse time is about 0.1 second. In another embodiment, the precursor vapor pulse time is about 0.25 second. In another embodiment, the precursor vapor pulse time is about 0.5 second. In another embodiment, the precursor vapor pulse time is about 1 second. In another embodiment, the precursor vapor pulse time is about 1.5 seconds. In another embodiment, the precursor vapor pulse time is about 2 seconds. In yet another embodiment, the precursor vapor pulse time is longer than 2 seconds depending on the volume/design of the reactor chamber.

[0148] In one embodiment, the precursor vapor is separated from other precursor materials prior to and/or during the introduction to the reactor. This process avoids any premature reaction of the metal precursor with any other materials.

[0149] In another embodiment, the precursor vapor is alternatively exposed to the substrate with other reactants (*e.g.*, other precursors or reagents). This process enables film growth to proceed by self-limiting control of the surface reactions, the pulse length of each precursor or reagent and the deposition temperature. It should be noted, however, that film growth ceases once the surface of the substrate is saturated with organotin precursor vapor.

[0150] In another embodiment, a flow of argon and/or other gas is employed as a carrier gas to help deliver the organotin precursor vapor to the reaction reactor during the precursor pulsing.

[0151] Step (d) Oxygen Source

[0152] As noted above, step (d) of the disclosed and claimed method includes introducing one or more oxygen source to convert the metal-containing layer to an organometal oxide or metal oxide layer. In one embodiment, the metal-containing layer includes, consists essentially of or consists of tin. In one

embodiment, the metal-containing layer includes, consists essentially of or consists of germanium.

[0153] In one embodiment, the one or more oxygen source includes one or more of oxygen (O_2), ozone (O_3), nitric oxide (NO), water (H_2O) vapor, hydrogen peroxide (H_2O_2), oxygen plasma (O^*), N_xO_y (where $x = 1$ or 2 and $y = 1, 2, 3$ or 4) and combinations thereof. In one aspect of this embodiment, the one or more oxygen source includes oxygen. In one aspect of this embodiment, the one or more oxygen source includes ozone. In one aspect of this embodiment, the one or more oxygen source includes nitric oxide. In one aspect of this embodiment, the one or more oxygen source includes water vapor. In one aspect of this embodiment, the one or more oxygen source includes hydrogen peroxide. In one aspect of this embodiment, the one or more oxygen source includes oxygen and ozone. In one aspect of this embodiment, the one or more oxygen source includes oxygen plasma. In one aspect of this embodiment, the one or more oxygen source includes N_xO_y where $x = 1$ or 2 and $y = 1, 2, 3$ or 4 . In one embodiment, the one or more oxidant is a vapor.

[0154] As noted above, in one preferred embodiment, for example, the one or more oxygen source includes, consists essentially of or consists of water vapor. In one aspect of this embodiment, the one or more oxygen source includes water vapor. In one aspect of this embodiment, the one or more oxygen source consists essentially of water vapor. In one aspect of this embodiment, the one or more oxygen source consists of water vapor.

[0155] In one embodiment, the one or more oxygen source pulse time varies from about 0.5 seconds to about 5 seconds. In one embodiment, for example, the one or more oxygen source pulse time is about 2.5 seconds. In one embodiment, for example, the one or more oxygen source pulse time is about 5 seconds. Yet, in another embodiment, the one or more oxygen source pulse time is longer than 5 seconds depending on the volume/design of the reactor chamber.

[0156] Step (f) Carboxylic Acid-Containing Vapor

[0157] As noted above, a preferred embodiment of the disclosed and claimed method includes step (f) introducing one or more carboxylic acid vapor having the formula R^3COOH where R^3 is selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_3 to C_6 alkynyl group, and a C_4 to C_{10} aryl group to react with the organotin oxide layer.

[0158] In another embodiment, the carboxylic acid includes one or more of formic acid, acetic acid, propionic acid, butyric acid, iso-butyric acid, valeric acid, 2-methylbutyric acid, 3-methylbutyric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, fluoroacetic acid, chloroacetic acid, iodoacetic acid, dichloroacetic acid, 4,4,4-trifluorobutanoic acid, 3,3,3-

trifluoropropanoic acid, cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, 4,4-difluorocyclohexanecarboxylic acid, tetrahydro-3-furancarboxylic acid and combinations thereof. In one aspect of this embodiment, the carboxylic acid includes formic acid. In one aspect of this embodiment, the carboxylic acid includes acetic acid. In one aspect of this embodiment, the carboxylic acid includes propionic acid. In one aspect of this embodiment, the carboxylic acid includes butyric acid. In one aspect of this embodiment, the carboxylic acid includes iso-butyric acid. In one aspect of this embodiment, the carboxylic acid includes valeric acid. In one aspect of this embodiment, the carboxylic acid includes 2-methylbutyric acid. In one aspect of this embodiment, the carboxylic acid includes 3-methylbutyric acid. In one aspect of this embodiment, the carboxylic acid includes caproic acid. In one aspect of this embodiment, the carboxylic acid includes enanthic acid. In one aspect of this embodiment, the carboxylic acid includes caprylic acid. In one aspect of this embodiment, the carboxylic acid includes pelargonic acid. In one aspect of this embodiment, the carboxylic acid includes capric acid. In one aspect of this embodiment, the carboxylic acid includes fluoroacetic acid. In one aspect of this embodiment, the carboxylic acid includes chloroacetic acid. In one aspect of this embodiment, the carboxylic acid includes iodoacetic acid. In one aspect of this embodiment, the carboxylic acid includes dichloroacetic acid. In one aspect of this embodiment, the carboxylic acid includes 4,4,4-trifluorobutanoic acid. In one aspect of this embodiment, the carboxylic acid includes 3,3,3-trifluoropropanoic acid. In one aspect of this embodiment, the carboxylic acid includes cyclobutanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes cyclopentanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes cyclohexanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes 4,4-difluorocyclohexanecarboxylic acid. In one aspect of this embodiment, the carboxylic acid includes tetrahydro-3-furancarboxylic acid.

[0159] In another embodiment, the carboxylic acid includes, consists essentially of or consists of one more carboxylic acid having a boiling point of 250 °C or lower. In a further aspect of this embodiment, the carboxylic acid includes, consists essentially of or consists of one more carboxylic acid having a boiling point of 200 °C or lower.

[0160] In another embodiment, the carboxylic acid vapor is substantially free of any carboxylic acids having boiling points of greater 250 °C. In a further aspect of this embodiment, the carboxylic acid vapor is substantially free of any carboxylic acids having boiling points of greater 200 °C.

[0161] In another embodiment, the carboxylic acid vapor is free of any carboxylic acids having boiling points of greater 250 °C. In a further aspect of this embodiment, the carboxylic acid vapor is

substantially free of any carboxylic acids having boiling points of greater 200 °C.

[0162] Steps (c), (e) and (g) Purging

[0163] As noted above, steps (c), (e) and (g) of the disclosed and claimed methods include purging the reactor vessel with inert gas. Purging with an inert gas removes unabsorbed excess materials and by products from the process reactor. In one embodiment, the purge gas includes argon. In another embodiment, the purge gas includes nitrogen.

[0164] In one embodiment, for example, the purge time varies from about 1 seconds to about 90 seconds. In one embodiment, for example, the purge time varies from about 15 seconds to about 90 seconds. In one embodiment, for example, the purge time varies from about 15 seconds to about 60 seconds. In another embodiment, the purge time is about 30 seconds. In another embodiment, the purge time is about 60 seconds. In another embodiment, the purge time is about 90 seconds.

[0165] In one embodiment, the purge gas includes argon. In another embodiment, the purge gas includes nitrogen.

[0166] Operating Conditions

[0167] As noted above, the disclosed and claimed tin-containing film deposition process can be effectively conducted under very favorable ALD or ALD-like conditions.

[0168] In one embodiment the substrate (*e.g.*, aluminum oxide (Al₂O₃), titanium nitride (TiN), silicon oxide (SiO₂), zirconium oxide (ZrO₂), amorphous carbon, silicon-containing underlayer) is heated on a heater stage in a reaction reactor that is exposed to the organotin precursor initially to allow the complex to chemically adsorb onto the surface of the substrate. In one embodiment, the substrate temperature is from about 25 °C to about 600 °C. In a further aspect of this embodiment, the substrate temperature is from about 25 °C to about 500 °C. In a further aspect of this embodiment, the substrate temperature is from about 25 °C to about 400 °C. A preferred substrate temperature for water only process is from 25 °C to about 200 °C.

[0169] In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 100 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 75 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 50 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 40 torr. In another embodiment, the reactor pressure for depositions according to the disclosed and claimed process is $\leq$ about 30 torr. In a further aspect of this embodiment, the reactor pressure is $\leq$ about 20 torr. In a further aspect of this embodiment, the reactor pressure is $\leq$ about 10 torr. In a

further aspect of this embodiment, the reactor pressure is $\leq$ about 5 torr.

[0170] Cycles and Order of Steps

[0171] In the above-described embodiments, as well as the other embodiments described herein, the described steps (*e.g.*, (a) through (e)) define one cycle of the method. It is to be understood that a cycle can be repeated until the desired thickness of a film is obtained.

[0172] In the embodiments described herein, it is understood that the steps of the methods may be performed in a variety of orders, may be performed sequentially or concurrently (*e.g.*, during at least a portion of another step), and any combination thereof. In addition, the respective steps of supplying the reactants (*i.e.*, the organotin precursor, the water-containing vapor and the carboxylic acid-containing vapor) and or the subsequent purges thereof may be performed by varying the duration of the time for supplying them to change film composition.

[0173] Films

[0174] The disclosed and claimed subject matter further includes films prepared by the methods described herein. In one embodiment, the films include, consist essentially of or consist of tin. In one embodiment, the films include, consist essentially of or consist of germanium.

[0175] In one embodiment, the films formed by the methods described herein have trenches, vias or other topographical features with an aspect ratio of about 1 to about 60. In a further aspect of this embodiment, the aspect ratio is about 1 to about 50. In a further aspect of this embodiment, the aspect ratio is about 1 to about 40. In a further aspect of this embodiment, the aspect ratio is about 1 to about 30. In a further aspect of this embodiment, the aspect ratio is about 1 to about 20. In a further aspect of this embodiment, the aspect ratio is about 1 to about 10. In a further aspect of this embodiment, the aspect ratio is greater than about 1. In a further aspect of this embodiment, the aspect ratio is greater than about 2. In a further aspect of this embodiment, the aspect ratio is greater than about 5. In a further aspect of this embodiment, the aspect ratio is greater than about 10. In a further aspect of this embodiment, the aspect ratio is greater than about 15. In a further aspect of this embodiment, the aspect ratio is greater than about 20. In a further aspect of this embodiment, the aspect ratio is greater than about 30. In a further aspect of this embodiment, the aspect ratio is greater than about 40. In a further aspect of this embodiment, the aspect ratio is greater than about 50.

[0176] The steps of the described and claimed processes may be repeated to provide a desired thickness of the films. The thickness of the films can range from about 10 Å to about 5000 Å, or about 10 Å to about 1000 Å, or about 10 Å to about 500 Å, or about 10 Å to about 300 Å or about 10 Å to about 200 Å, or about 50 Å to about 1000 Å, or about 50 Å to about 500 Å, or about 50 Å to about 300 Å or

about 50 Å to about 200 Å. In one embodiment, the films formed by the methods described herein have a thickness of about 10 Å to about 5000 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about 10 Å to 1000 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about 10 Å to 500 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 10 Å to 300 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 10 Å to 200 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 50 Å to 1000 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 50 Å to 500 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 50 Å to 300 Å. In another aspect of this embodiment, the films formed by the methods described herein have a thickness of about, 50 Å to 200 Å.

[0177] In some embodiments, a super-cycle ALD or ALD-like process may be performed, one super-cycle includes the following: steps (b) to (e) may be repeated to provide a desired thickness of the films which can range from about 50 Å to about 1000 Å, about 50 Å to about 500 Å, about 50 Å to about 300 Å or about 50 Å to about 200 Å, followed by steps (f) to (g) to modify the resulting films. The super-cycle can be repeated to provide a desired thickness of film. It is believed that reaction between the carboxylic acid and the resulting film from steps (b) to (e) may improve/stabilize the film, thus allowing the films to be more resistant to environment changes such as moisture or carbon dioxide during semi-conductor fabrication processes. Additionally, in some embodiments, steps (f) to (g) are performed before steps (d) to (e) to provide a desired thickness of the film.

[0178] Examples

[0179] Reference will now be made to more specific embodiments of the present disclosure and experimental results that provide support for such embodiments. The examples given below more fully illustrate the disclosed and claimed subject matter and should not be construed as limiting the disclosed subject matter in any way.

[0180] 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 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.

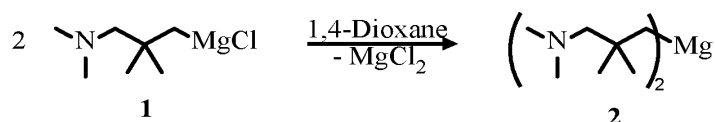
[0181] Working Example 1: Synthesis of (DMDMP)Sn(NMe)₃ (DMDMP = 3-(N,N-

dimethylamino)-2,2-dimethyl-propyl) (3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin) in which the β -carbon is quaternary

[0182] All reactions were carried out with the strict exclusion of moisture and oxygen by using standard inert-atmosphere and Schlenk techniques. Solvents such as tetrahydrofuran (THF), 1,4-dioxane and *n*-pentane were dried by standard methods before use. Commercially available $\text{Sn}(\text{NMe}_2)_4$ (Strem) was used without further purification. 3-(N,N-dimethylamino)-2,2-dimethylpropyl magnesiumchloride (**1**) was synthesized following a general synthetic procedure for Grignard reagents using 3-(N,N-dimethylamino)-2,2-dimethyl-propylchlorid and magnesium powder. $\text{iPrSn}(\text{NMe}_2)_3$ was synthesized by using iPrSnCl_3 and LiNMe_2 .

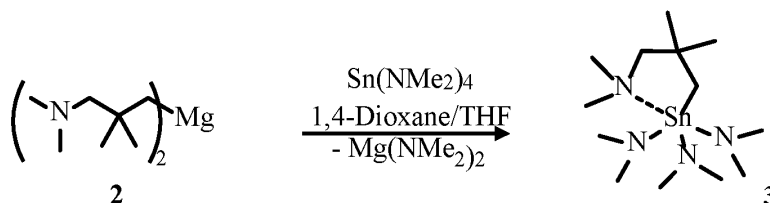
[0183] **Synthesis 1A:**

[0184] A solution of compound **1** in THF ($c = 0.731 \text{ m/L}$, 10 mL) was dissolved in dry dioxane (10 mL) and the mixture was stirred for 20 min to form the bis alkyl magnesium species **2**. While stirring, white solids precipitated. The suspension was filtered and the solution of bis alkyl magnesium species **2** was used without further characterization.



[0185] **Synthesis 1B:**

[0186] Compound **2** ($c = 0.366 \text{ m/L}$; dissolved in 20 mL of 1,4-dioxane/THF) was slowly added to a solution of $\text{Sn}(\text{NMe}_2)_4$ (2.16 g, 7.32 mmol) in THF (20 mL) at -78°C . The reaction mixture was allowed to warm to room temperature overnight. All volatiles were removed in vacuum, and the residue was extracted with *n*-pentane ($3 \times 5 \text{ mL}$). The *n*-pentane was removed in vacuum, and the residue was purified by distillation (70°C at $2.8 \times 10^{-2} \text{ mbar}$). The product ($(\text{DMDMP})\text{Sn}(\text{NMe}_2)_3$; compound “3”) was obtained as a colorless liquid. Yield: 1.9 g (71 %).

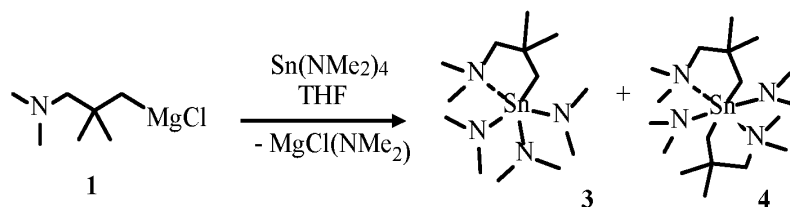


[0187] By using **2** as the starting material in 1,4-dioxane, the ratio of mono **3** and bis alkyl species **4** is 95:5, respectively. A simple distillation is sufficient to separate both products to produce compound **3** with a purity of >99%. See FIGs. 1-3.

[0188] Analysis

[0189] FIG. 1: ^1H NMR (500 MHz, C_6D_6) of **3**: δ 2.85 (t, $^3J_{\text{SnH}} = 20.6$ Hz, $\text{Sn-N}(\text{CH}_3)_2$, 18H), 2.19 (s, $\text{N}(\text{CH}_3)_2$, 6H), 1.97 (s, $\text{CH}_2\text{-N}(\text{CH}_3)_2$, 2H), 1.32 (t, $^2J_{\text{SnH}} = 35.6$ Hz, Sn-CH_2 , 2H), 0.99 (s, CH_3 , 6H) ppm. FIG. 2: ^{13}C NMR (125.8 MHz, C_6D_6) of **3**: δ 72.9 (t, $^1J_{\text{SnC}} = 30.8$ Hz, Sn-CH_2), 49.0 ($\text{N}(\text{CH}_3)_2$), 43.1 (t, $^2J_{\text{SnC}} = 4.2$ Hz, $\text{Sn-N}(\text{CH}_3)_2$), 35.7 (t, $^2J_{\text{SnC}} = 10.8$ Hz, $\text{C}_{\text{quat.}}$), 29.4 (t, $^3J_{\text{SnC}} = 22.4$ Hz, $\text{C}(\text{CH}_3)_2$), 27.5 (NCH_2) ppm. FIG. 3: ^{119}Sn NMR (186.6 MHz, C_6D_6) of **3**: δ -40.4 (s) ppm. FIGs. 1-3 show NMR spectra of compound **3** with a purity of >99%.

[0190] This level of purity is based on integrals of the Sn NMR signals of compounds made by the above synthetic route. In contrast, the same compound made by other traditional routes exhibit a much higher tendency of overalkylation. In the traditional/alternative synthesis, compound **3** directly is prepared directly from compound **1**:



[0191] The use of compound **1** in THF in the traditional synthesis of product **3** results in the formation of mono alkyl species **3** and bis alkyl species **4** in a ratio of 90:10 respectively, which makes the purification of the product more difficult. In order to separate both compounds, it was necessary to run a distillation twice. As shown in FIG. 4 and FIG. 5, when compounds **3** and **4** are made by the traditional route and the separated, there are significantly more impurities present (based on peak integration).

[0192] FIG. 6 shows the thermal gravimetric analysis (TGA) of compound **3** prepared by the disclosed and claimed process. In FIG. 6, it is demonstrated that compound **3** has a >99% vaporization behavior and further confirming that **3** is suitable for vapor deposition of organotin oxide films.

[0193] FIG. 7 shows the differential scanning calorimetry (DSC) of compound **3**; carried out in a gold coated crucible. The DSC shows an onset temperature of 196.6 °C which can be regarded as the decomposition temperature.

[0194] FIG. 8 shows the ^{119}Sn NMR spectra of compound **3** recorded at room temperature. No change was observed after 10 days based on integral values derived from ^{119}Sn NMR spectra, *i.e.*, a fresh sample (>99% NMR assay) was compared with a sample that had been exposure to lab light for 10 days (>99% NMR assay) and 24 days (99 % NMR assay), indicating a slow decomposition process upon light exposure. After 24 days of light exposure compound **3** shows a new decomposition

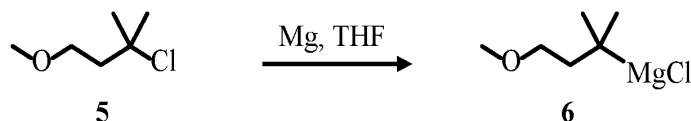
product (1% NMR assay) at -49 ppm. In comparison, $i\text{PrSn}(\text{NMe}_2)_3$ showed under the same conditions of light exposure of 24 days 45% decomposition (Figure 9). This data that this compound is significantly more stable towards light compared to the commonly used and known monoalkylated tin compounds such as $i\text{PrSn}(\text{NMe}_2)_3$ as disclosed in U.S. Patent No. 11,500,284 and the art cited therein.

[0195] Working Example 2: Synthesis of (MODMP)Sn(NMe)₃ (MODMP = 3-methoxy-1,1-dimethyl-propyl) (3-methoxy-1,1-dimethyl-propyl-tris-dimethylamidotin) in which the α -carbon is quaternary

[0196] All reactions were carried out with the strict exclusion of moisture and oxygen by using standard inert-atmosphere and Schlenk techniques. Solvents such as tetrahydrofuran (THF) and *n*-pentane were dried by standard methods before use. Commercially available $\text{Sn}(\text{NMe}_2)_4$ (Strem) was used without further purification. 3-methoxy-1,1-dimethyl-propylchlorid (**5**) was synthesized in a two-step process according to literature procedures. See *Chem. Eur. J.*, 8, 3773 (2002); *J. Am. Soc.*, 123, 10127(2001).

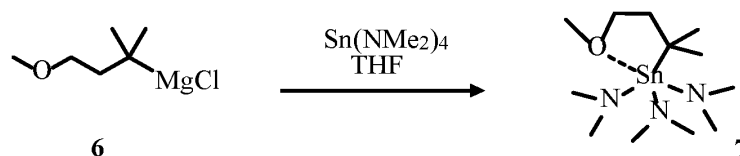
[0197] Synthesis 2A:

[0198] 3-methoxy-1,1-dimethylpropyl magnesiumchloride (**6**) was synthesized following a general synthetic procedure for Grignard reagents using 3-methoxy-1,1-dimethyl-propylchlorid (**5**) and magnesium turnings.



[0199] Synthesis 2B:

[0200] Compound **6** ($c = 0.207$ mL; dissolved in 21.3 mL of THF) was slowly added to a solution of $\text{Sn}(\text{NMe}_2)_4$ (1.30 g, 4.41 mmol) in THF (5 mL) at -78 °C. The reaction mixture was allowed to warm to room temperature overnight. All volatiles were removed in vacuum, and the residue was extracted with *n*-pentane (2 x 20 mL). The *n*-pentane was removed in vacuum, and the residual liquid was purified by distillation (40 °C at 1.4×10^{-2} mbar). The product ((MODMP)Sn(NMe)₃; compound “7”) was obtained as a colorless waxy solid. Yield: 1.4 g (88 %).



[0201] Analysis

[0202] FIG. 10: ¹H NMR (500 MHz, C₆D₆) of **7**: δ 3.17 (t, ³J_{HH} = 6.1 Hz, CH₂-OCH₃, 2H), 3.06 (s, OCH₃, 3H), 2.91 (t, ³J_{SnH} = 19.8 Hz, Sn-(N(CH₃)₂)₃, 18H), 1.64 (t, ³J_{HH} = 6.1 Hz, CH₂-CH₂-

OCH₃, 2H), 1.26 (t, $^3J_{\text{SnH}} = 47.6$ Hz, Sn-C-CH₃, 6H) ppm. FIG. 11: ^{119}Sn NMR (186.6 MHz, C₆D₆) of 7: $\delta = 109$ (s) ppm. FIGs. 10-11 show NMR spectra of compound 7 with a purity of 97%. The small impurity peaks in the ^1H and ^{119}Sn NMR spectra can be attributed to the bis alkylated species.

[0203] FIG. 6 shows the TGA of compound 7 prepared by the disclosed and claimed process. In FIG. 6, it is demonstrated that compound 7 has a >99% vaporization behavior and further confirming that 7 is suitable for vapor deposition of organotin oxide films.

[0204] FIG. 12 shows the DSC of compound 7; carried out in a gold coated crucible. The DSC shows an onset temperature of 188 °C which can be regarded as the decomposition temperature.

[0205] **Working Example 3: Deposition of Tin-Containing Films**

[0206] **Compound 3—(DMDMP)Sn(NMe)₃**

[0207] **Conditions:** Deposition temperature was 90 °C and 110 °C, respectively; reactor pressure was about 2 torr; (DMDMP)Sn(NMe)₃ (5 seconds) was employed as organotin precursor using pulse time ranging from 0.1 to 5 seconds and water pulse time of 0.1 second as an oxygen source.

[0208] As seen in FIGs. 13 and 14, linear growth behaviors were observed using an ALD-like process, demonstrating (DMDMP)Sn(NMe)₃ can be employed for vapor deposition of tin-containing films.

[0209] Although the invention has been described and illustrated with a certain degree of particularity, it is understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the invention.

Claims

What is claimed is

1. A compound of Formula (I): $(XR)M(NR^1R^2)_3$, wherein
 - (i) $M = \text{Sn or Ge}$;
 - (ii) R is a branched C_5 to C_{10} alkylene linker group wherein (i) three to eight main chain carbon moieties connect M and X and (ii) at least one of the first three main chain carbon moieties that connect M and X is a quaternary carbon moiety that is free of hydrogen;
 - (iii) R^1 and R^2 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_4 to C_6 alkyl group or a cyclic C_3 to C_6 alkyl group; and
 - (iv) X is selected is one of $-OR^3$ or $-NR^4R^5$ where R^3 , R^4 and R^5 are each independently selected from a linear C_1 to C_6 alkyl group, a branched C_4 to C_6 alkyl group or a cyclic C_3 to C_6 alkyl group.
2. The compound of claim 1, wherein $M = \text{Sn}$.
3. The compound of claim 1, wherein $M = \text{Ge}$.
4. The compound of claim 1, wherein R is a branched C_5 alkylene.
5. The compound of claim 1, wherein R is a branched C_6 alkylene.
6. The compound of claim 1, wherein R is a branched C_7 alkylene.
7. The compound of claim 1, wherein R is a branched C_8 alkylene.
8. The compound of claim 1, wherein R is a branched C_9 alkylene.
9. The compound of claim 1, wherein R is a branched C_{10} alkylene.
10. The compound of claim 1, wherein R the C_5 to C_{10} alkylene linker group consist of three main chain carbon moieties connecting M and X .
11. The compound of claim 1, wherein R the C_5 to C_{10} alkylene linker group consist of four main chain carbons moieties connecting M and X .
12. The compound of claim 1, wherein R the C_5 to C_{10} alkylene linker group consist of five main chain carbons moieties connecting M and X .
13. The compound of claim 1, wherein R the C_5 to C_{10} alkylene linker group consist of six main chain carbons moieties connecting M and X .
14. The compound of claim 1, wherein R the C_5 to C_{10} alkylene linker group consist of seven main chain carbons moieties connecting M and X .
15. The compound of claim 1, wherein R the C_5 to C_{10} alkylene linker group consist of eight main chain carbons moieties connecting M and X .

16. The compound of claim 1, wherein R the α -carbon moiety is a hydrogen-free quaternary carbon moiety.
17. The compound of claim 1, wherein R the β -carbon moiety is a hydrogen-free quaternary carbon moiety.
18. The compound of claim 1, wherein in R the γ -carbon moiety is a hydrogen-free quaternary carbon moiety.
19. The compound of claim 1, wherein R two or more of the α -carbon moiety, β -carbon moiety and γ -carbon moiety are hydrogen-free quaternary carbon moieties.
20. The compound of claim 1 having formula $(NR^1R^2)_3M-C(Me_2)CH_2CH_2-X$.
21. The compound of claim 1 having formula $(NR^1R^2)_3M-CH_2C(Me_2)CH_2-X$.
22. The compound of claim 1 having formula $(NR^1R^2)_3M-CH_2CH_2C(Me_2)-X$.
23. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_1 to C_6 alkyl group.
24. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_1 alkyl group.
25. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_2 alkyl group.
26. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_3 alkyl group.
27. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_4 alkyl group.
28. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_5 alkyl group.
29. The compound of claim 1, wherein one or both of R^1 and R^2 is a linear C_6 alkyl group.
30. The compound of claim 1, wherein one or both of R^1 and R^2 is a branched C_4 to C_6 alkyl group.
31. The compound of claim 1, wherein one or both of R^1 and R^2 is a branched C_4 alkyl group.
32. The compound of claim 1, wherein one or both of R^1 and R^2 is a branched C_5 alkyl group.
33. The compound of claim 1, wherein one or both of R^1 and R^2 is a branched C_6 alkyl group.
34. The compound of claim 1, wherein one or both of R^1 and R^2 is a cyclic C_3 to C_6 alkyl group.
35. The compound of claim 1, wherein one or both of R^1 and R^2 is a cyclic C_3 alkyl group.
36. The compound of claim 1, wherein one or both of R^1 and R^2 is a cyclic C_4 alkyl group.
37. The compound of claim 1, wherein one or both of R^1 and R^2 is a cyclic C_5 alkyl group.
38. The compound of claim 1, wherein one or both of R^1 and R^2 is a cyclic C_6 alkyl group.
39. The compound of claim 1, wherein X is a $-OR^3$ group.
40. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_1 to C_6 alkyl group.
41. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_1 alkyl group.
42. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_2 alkyl group.
43. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_3 alkyl group.

44. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_4 alkyl group.
45. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_5 alkyl group.
46. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a linear C_6 alkyl group.
47. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a branched C_4 to C_6 alkyl group.
48. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a branched C_4 alkyl group.
49. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a branched C_5 alkyl group.
50. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a branched C_6 alkyl group.
51. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a cyclic C_3 to C_6 alkyl group.
52. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a cyclic C_3 alkyl group.
53. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a cyclic C_4 alkyl group.
54. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a cyclic C_5 alkyl group.
55. The compound of claim 1, wherein X is a $-OR^3$ group and R^3 is a cyclic C_6 alkyl group.
56. The compound of claim 1, wherein X is a $-NR^4R^5$ group.
57. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_1 to C_6 alkyl group.
58. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_1 alkyl group.
59. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_2 alkyl group.
60. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_3 alkyl group.
61. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_4 alkyl group.
62. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_5 alkyl group.
63. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a linear C_6 alkyl group.
64. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a branched C_4 to C_6 alkyl group.
65. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a branched C_4 alkyl group.
66. The compound of claim 1, wherein X is a $-NR^4R^5$ group and one or both of R^4 and R^5 is a

branched C₅ alkyl group.

67. The compound of claim 1, wherein X is a -NR⁴R⁵ group and one or both of R⁴ and R⁵ is a branched C₆ alkyl group.

68. The compound of claim 1, wherein X is a -NR⁴R⁵ group and one or both of R⁴ and R⁵ is a cyclic C₃ to C₆ alkyl group.

69. The compound of claim 1, wherein X is a -NR⁴R⁵ group and one or both of R⁴ and R⁵ is a cyclic C₃ alkyl group.

70. The compound of claim 1, wherein X is a -NR⁴R⁵ group and one or both of R⁴ and R⁵ is a cyclic C₄ alkyl group.

71. The compound of claim 1, wherein X is a -NR⁴R⁵ group and one or both of R⁴ and R⁵ is a cyclic C₅ alkyl group.

72. The compound of claim 1, wherein X is a -NR⁴R⁵ group and one or both of R⁴ and R⁵ is a cyclic C₆ alkyl group.

73. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of (NMe₂CH₂CMe₂CH₂)Sn(NMe₂)₃.

74. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of (OMeCH₂CMe₂CH₂)Sn(NMe₂)₃.

75. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of (OMeCH₂CH₂CMe₂)Sn(NMe₂)₃.

76. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of (NMe₂CH₂CH₂CMe₂)Sn(NMe₂)₃.

77. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of one or more of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-ethylmethylamidotin, 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-diethylamidotin, 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-methyl-iso-propylamidotin, , 3-(N,N-dimethylamino)-1,1-dimethyl-propyl-tris-dimethylamidotin, 3-methoxy-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-ethoxy-2,2-dimethyl-propyl-tris-dimethylamidotin, 3-methoxy-2,2-dimethyl-propyl-tris-ethylmethylamidotin, 3-ethoxy-2,2-dimethyl-propyl-tris-ethylmethylamidotin, 3-methoxy-2,2-dimethyl-propyl-tris-diethylamidotin, 3-ethoxy-2,2-dimethyl-propyl-tris-methylisopropylamidotin, 3-methoxy-1,1-dimethyl-propyl-tris-dimethylamidotin, 3-ethoxy-1,1-dimethyl-propyl-tris-dimethylamidotin, 3-methoxy-1,1-dimethyl-propyl-tris-

ethylmethyamidotin and 3-ethoxy-1,1-dimethyl-propyl-tris-ethylmethyamidotin.

78. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin.

79. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-dimethylamidotin.

80. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-ethylmethyamidotin.

81. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-(N,N-diethylamino)-2,2-dimethyl-propyl-tris-diethylamidotin.

82. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-(N,N-dimethylamino)-2,2-dimethyl-propyl-tris-methyl-iso-propylamidotin.

83. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-(N,N-dimethylamino)-1,1-dimethyl-propyl-tris-dimethylamidotin.

84. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-methoxy-2,2-dimethyl-propyl-tris-dimethylamidotin.

85. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-ethoxy-2,2-dimethyl-propyl-tris-dimethylamidotin.

86. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-methoxy-2,2-dimethyl-propyl-tris-ethylmethyamidotin.

87. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-ethoxy-2,2-dimethyl-propyl-tris-ethylmethyamidotin.

88. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-methoxy-2,2-dimethyl-propyl-tris-diethylamidotin.

89. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-ethoxy-2,2-dimethyl-propyl-tris-methylisopropylamidotin.

90. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-methoxy-1,1-dimethyl-propyl-tris-dimethylamidotin.

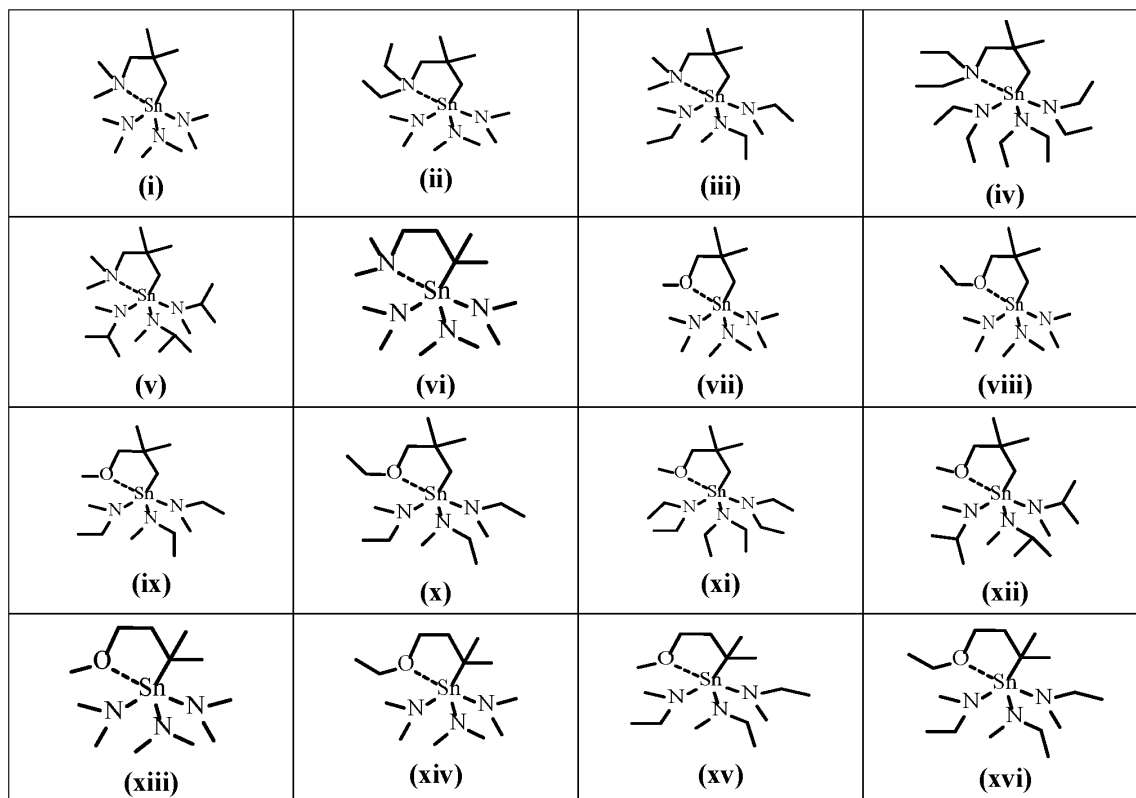
91. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-ethoxy-1,1-dimethyl-propyl-tris-dimethylamidotin.

92. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of 3-methoxy-1,1-dimethyl-propyl-tris-ethylmethyamidotin.

93. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially

of or consists of 3-ethoxy-1,1-dimethyl-propyl-tris-ethylmethamidotin.

94. The compound of claim 1, wherein the compound of Formula (I) comprises, consists essentially of or consists of one or more of:



95. A composition comprising (i) one or more compounds of any of claims 1-95 and (ii) one or more solvents.

96. A composition comprising (i) one or more compounds of any of claims 1-95 and (ii) one or more solvents selected from the group of toluene, mesitylene, cumene (isopropylbenzene), p-cymene (4-isopropyl toluene), 1,3-diisopropylbenzene, octane, dodecane, 1,2,4-trimethylcyclohexane, n-butylcyclohexane, decahydronaphthalene (decalin) and combinations thereof.

97. A method for depositing organotin oxide or tin oxide films comprising the steps of:

- a. providing one or more substrates in a reactor, where the reactor is heated to temperature of from about 25 °C to about 600 °C and optionally maintained at a pressure of about 100 torr or less;
- b. introducing into the reactor a vapor comprising one or more compounds or compositions of any of claims 1-96;

- c. purging the reactor with an inert gas;
 - d. introducing one or more oxygen source to convert the metal-containing layer to an organometal oxide or metal oxide layer; and
 - e. purging the reactor with an inert gas.
98. The method of claim 97, further comprising the steps of:
- f. introducing one or more carboxylic acid vapor having the formula R^3COOH where R^3 is selected from hydrogen, a linear C_1 to C_6 alkyl group, a branched C_3 to C_6 alkyl group, a C_3 to C_6 cyclic alkyl group, a C_2 to C_6 alkenyl group, a C_3 to C_6 alkynyl group, and a C_4 to C_{10} aryl group to react with the organometal oxide or metal oxide layer; and
 - g. purging the reactor with an inert gas.
99. The method of claim 97, wherein the one or more compounds or compositions comprises tin.
100. The method of claim 97, wherein the one or more compounds or compositions comprises germanium.
101. The method of claim 97, wherein step (b) comprises pulsing the vapor for about 0.1 seconds to about 3 seconds.
102. The method of claim 97, wherein the step (d) one or more oxygen source comprises one or more of oxygen (O_2), ozone (O_3), nitric oxide (NO), water (H_2O) vapor, hydrogen peroxide (H_2O_2), oxygen plasma (O^*), N_xO_y (wherein $x = 1$ or 2 and $y = 1, 2, 3$ or 4) and combinations thereof.
103. The method of claim 97, wherein the step (d) one or more oxygen source comprises water vapor.
104. The method of claim 97, wherein the step (d) one or more oxygen source comprises water vapor.
105. The method of claim 97, wherein step (d) comprises pulsing the one or more oxygen source for about 0.5 seconds to about 5 seconds.
106. The method of claim 98, wherein step (f) one or more carboxylic acid vapor comprises one or more of formic acid, acetic acid, propionic acid, butyric acid, iso-butyric acid, valeric acid, 2-methylbutyric acid, 3-methylbutyric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, fluoroacetic acid, chloroacetic acid, iodoacetic acid, dichloroacetic acid, 4,4,4-trifluorobutanoic acid, 3,3,3-trifluoropropanoic acid, cyclobutanecarboxylic acid, cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, 4,4-difluorocyclohexanecarboxylic acid and tetrahydro-3-furancarboxylic acid.
107. The method of claim 98, wherein step (f) one or more carboxylic acid vapor consists of a carboxylic acid has a boiling point of about $250^\circ C$ or lower.
108. The method of claim 98, wherein step (f) one or more carboxylic acid vapor consists of a carboxylic acid has a boiling point of about $200^\circ C$ or lower.

- 109. The method of claim 98, wherein step (f) one or more carboxylic acid vapor comprises acetic acid.
- 110. The method of claim 98, wherein step (f) one or more carboxylic acid vapor consists of acetic acid.
- 111. A tin-containing film deposited using one or more organotin compounds or compositions of any of claims 1-96.
- 112. A tin-containing film deposited by the method of any of claims 97-110.
- 113. An organotin oxide or tin oxide film deposited by the method of any of claims 97-110, wherein the film has an aspect ratio of about 1 to about 60.
- 114. An organotin oxide or tin oxide film deposited by the method of any of claims 97-110, wherein the film has a thickness of about 10 Å to about 5000 Å.
- 115. A germanium-containing film deposited using one or more organogermanium compounds or compositions of any of claims 1-96.
- 116. A germanium-containing film deposited by the method of any of claims 97-110.
- 117. An organogermanium oxide or germanium oxide film deposited by the method of any of claims 97-110, wherein the film has an aspect ratio of about 1 to about 60.
- 118. An organogermanium oxide or germanium oxide film deposited by the method of any of claims 97-110, wherein the film has a thickness of about 10 Å to about 5000 Å.