SUMMARY

[0012] The present disclosure provides compounds useful for the deposition of high purity tin oxide.

[0013] Organometallic compounds include those of Formula I, below:

Q_x-Sn-$(A^1R^{1\prime}_z)_{4-x}$ Formula I

wherein:

Q is OR^1 or Cp;

each R^1 group is independently selected from the group consisting of an alkyl or aryl group having from 1 to 10 carbon atoms;

each $R^{1\prime}$ group is independently selected from the group consisting of an alkyl, acyl or aryl group having from 1 to 10 carbon atoms;

x is an integer from 0 to 3;

A is O when x is 0 and A is N when x is an integer from 1 to 3; and

z is 1 when A is O and z is 2 when A is N.

[0013a] In one aspect, the present disclosure provides an organometallic compound of Formula I:

Q_x-Sn-$(NR^{1\prime}_2)_{4-x}$ Formula I

wherein:

Q is OR^1 or Cp;

each R^1 group is independently selected from the group consisting of an alkyl group having from 1 to 10 carbon atoms and an aryl group;

each $R^{1\prime}$ group is independently selected from the group consisting of an alkyl or acyl group having from 1 to 10 carbon atoms and an aryl group;

x is an integer from 1 to 4; and

Q is Cp when x is 4.

[0014] Also disclosed is the deposition of tin oxide using such compounds. The use of compounds of Formula I in the methods disclosed herein allows for chemical vapour deposition (CVD) and atomic layer deposition (ALD) of tin oxide.

[0015] In examples, Q is Cp, which is a cyclopentadienyl ligand. In some examples, x is 1 and compounds of Formula I are represented by the following formula: Cp-Sn-$(NR^{1\prime}_2)_3$, wherein each $R^{1\prime}$ group is independently selected from the group consisting of an alkyl, acyl or aryl group having from 1 to 10 carbon atoms.

[0016] In examples, x is an integer from 1 to 3. In such examples, compounds of Formula I are represented by the following formula: $(OR^1)_x$-Sn-$(NR^{1\prime}_2)_{4-x}$, wherein each $R^{1\prime}$ group is independently selected from the group consisting

of an alkyl, acyl or aryl group having from 1 to 10 carbon atoms and x is an integer from 1 to 3.

[0017] In other examples, each R^1 group and each $R^{1\prime}$ group is an independently selected alkyl group having from 1 to 10 carbon atoms. It is contemplated that each R^1 group and each $R^{1\prime}$ group may be an independently selected alkyl group having from 1 to 6 carbon atoms. In examples, each R^1 group and each $R^{1\prime}$ group is an independently selected alkyl group having from 1 to 4 carbon atoms. In examples, each R^1 group and each $R^{1\prime}$ group is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl. In examples, each R^1 group and each $R^{1\prime}$ group represent different alkyl, acyl, or aryl groups, in particular different alkyl groups.

[0018] In examples, x is 4. In such examples, Compounds of Formula I are represented by the following formula: $Sn(OR^1)_4$, wherein each R^1 group is independently selected from the group consisting of an alkyl, acyl, or aryl group having from 1 to 10 carbon atoms.

[0019] In other examples, each $R^{1\prime}$ group is an independently selected alkyl group having from 1 to 10 carbon atoms. It is contemplated that each $R^{1\prime}$ group may be an independently selected alkyl group having from 1 to 6 carbon atoms. In examples, each $R^{1\prime}$ group is an independently selected alkyl group having from 1 to 4 carbon atoms. In examples, each $R^{1\prime}$ group is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl. In examples, each $R^{1\prime}$ group represent different alkyl, acyl, or aryl groups, in particular different alkyl groups.

[0020] In examples, the organometallic compound is selected from the group consisting of $(MeO)_2Sn(NMe_2)_2$, $(MeO)_2Sn(NEtMe)_2$, $(MeO)_3Sn(NMe_2)$, $(MeO)_3Sn(NEtMe)$, $Sn(OMe)_4$, $CpSn(NMe_2)_3$, and $CpSn(NMeEt)_3$.

[0021] Other organometallic compounds include those of formula II, below:

$Sn(NR^2(CH_2)_nA^2)_2$ Formula II

wherein:

each A^2 is independently selected from $NR^{2\prime}$ or O;

each R^2 group is independently selected from the group consisting of hydrogen and an alkyl or aryl group having from 1 to 10 carbon atoms;

each $R^{2\prime}$ group is independently selected from the group consisting of hydrogen and an alkyl, acyl or aryl group having from 1 to 10 carbon atoms;

n is 2 or 3;

optionally $NR^2(CH_2)_nNR^{2\prime}$ forms a cyclic structure; and

optionally at least one of the (CH_2) has one or more substitutions with an alkyl group having from 1 to 10 carbon atoms.

[0021a] In another aspect, the present disclosure provides an organometallic compound of Formula II:

$Sn(NR^2(CH_2)_nA^2)_2$ Formula II

wherein:

each A^2 is independently selected from $NR^{2\prime}$ or O;

each R^2 group is independently selected from the group consisting of hydrogen, an alkyl having from 1 to 10 carbon atoms and an aryl group;

each $R^{2\prime}$ group is independently selected from the group consisting of hydrogen, an alkyl or acyl group having from 1 to 10 carbon atoms and an aryl group;

n is 2 or 3;

optionally $NR^2(CH_2)_nNR^{2\prime}$ forms a cyclic structure; and

optionally at least one of the (CH_2) has one or more substitutions with an alkyl group having from 1 to 10 carbon atoms.

[0022] Also disclosed is the deposition of tin oxide using such compounds. The use of compounds of Formula II in the methods disclosed herein allows for chemical vapour deposition (CVD) and atomic layer deposition (ALD) of tin oxide.

[0023] In examples, A^2 is O and Formula II is represented by Formula IIa: $Sn(NR^2(CH_2)_nO)_2$, wherein each R^2 group is independently selected from an alkyl or aryl group having from 1 to 10 carbon atoms, or selected from alkyl groups having from 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms. In examples, each R^2 group is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl.

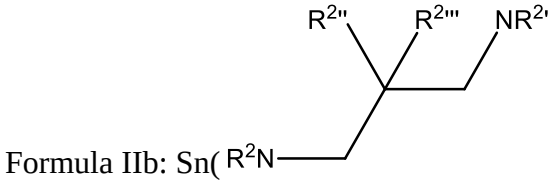
[0024] In examples, each R^2 group is independently selected from an alkyl group having from 1 to 10 carbon atoms. It is contemplated that each R^2 group may be an independently selected alkyl group having from 1 to 6 carbon atoms. In examples, each R^2 group is an independently selected alkyl group having from 1 to 4 carbon atoms. In examples, each R^2 group is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl. In examples, each R^2 group represents different alkyl, acyl, or aryl groups, in particular different alkyl groups.

[0025] In examples, each $R^{2\prime}$ group is independently selected from hydrogen or an alkyl group having from 1 to 10 carbon atoms. It is contemplated that each $R^{2\prime}$ group may be independently selected from hydrogen or an alkyl group having from 1 to 6 carbon atoms. In examples, each $R^{2\prime}$ group is independently selected from hydrogen or alkyl group having from 1 to 4 carbon atoms. In examples, each $R^{2\prime}$ group is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl. In examples each $R^{2\prime}$ group represents hydrogen or different alkyl, acyl, or aryl groups, in particular different alkyl groups.

[0026] In examples, n is 2. In other examples, n is 3.

[0027] In examples, at least one of the (CH_2) has one or more substitutions with an alkyl group having from 1 to 10 carbon atoms, or 1 to 6 carbon atoms, or 1 to 4 carbon atoms. Alternatively, the one or more substitutions are with methyl or ethyl. In particular examples, only one of the (CH_2) has one or more substitutions with an alkyl group, such as methyl or ethyl. In more particular examples, one of the (CH_2) is substituted with two methyl groups.

[0028] In examples, Formula II is represented by



Formula IIb: $Sn(\quad)_2$, wherein:

each R^2 group is independently selected from the group consisting of hydrogen and an alkyl or aryl group having from 1 to 10 carbon atoms;

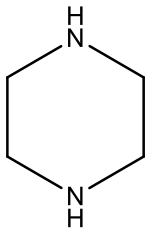
each $R^{2\prime}$ group is independently selected from the group consisting of hydrogen and an alkyl, acyl or aryl group having from 1 to 10 carbon atoms; and

each $R^{2\prime\prime}$ group and each $R^{2\prime\prime\prime}$ group is an independently selected alkyl group having 1 to 10 carbon atoms.

[0029] In examples, each R^2, $R^{2\prime}$, $R^{2\prime\prime}$, or $R^{2\prime\prime\prime}$ group of Formula IIb is independently selected from hydrogen or alkyl group having from 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms. In particular examples of Formula IIb, each R^2 and $R^{2\prime}$ is hydrogen and each $R^{2\prime\prime}$ and $R^{2\prime\prime\prime}$ group is an independently selected alkyl group having from 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms. In more particular examples of Formula IIb, each R^2 and $R^{2\prime}$ is hydrogen and each $R^{2\prime\prime}$ and $R^{2\prime\prime\prime}$ group is independently selected from ethyl or methyl.

[0030] In some examples where A^2 is $NR^{2\prime}$, $NR(CH_2)_nNR^{2\prime}$ forms a cyclic structure. In particular examples of the cyclic structure, R^2 and $R^{2\prime}$ groups are alkyl groups selected from methyl or ethyl. In examples, Formula II is

represented by Formula IIc:



Formula IIc: $Sn(\quad)_2$.

[0031] In examples, each ($NR^2(CH_2)_nA^2$) is selected from the group consisting of N,N′-dimethylethylenediamine ($NMe(CH_2)_2NMe$), piperazine ($N_2C_4H_8$), N,N′-diethylethylenediamine ($NEt(CH_2)_2NEt$), N,N′-diisopropylethylenediamine ($NiPr(CH_2)_2NiPr$), N,N′-di-tert-butylethylenediamine ($NtBu(CH_2)_2NtBu$), N,N′-dimethyl-1,3-propanediamine ($NMe(CH_2)_3NMe$), 2,2-dimethyl-1,3-propanediamine ($NH(CH_2)(C(CH_3))(CH_2)NH$), 2-(methylamino)ethanol ($NMe(CH_2)_2O$), and 2-(ethylamino)ethanol ($NEt(CH_2)_2O$).

[0032] The present disclosure provides compositions combining a second organometallic compound with a first organometallic compound to reduce disproportionation of the first organometallic compound so as to increase storage stability.

[0033] Compositions include:

a first organometallic compound represented by Formula III:

$R^3{}_2Sn(NR^{3\prime}{}_2)_2$ Formula III

wherein:

each R^3 group is independently selected from the group consisting of an alkyl or aryl group having from 1 to 10 carbon atoms;

each $R^{3\prime}$ group is independently selected from the group consisting of an alkyl or aryl group having from 1 to 10 carbon atoms; and

a second organometallic compound represented by Formula IV:

$Sn(NR^4_2)_4$ Formula IV

wherein each R^4 group is independently selected from the group consisting of an alkyl or aryl group having from 1 to 10 carbon atoms.

[0033a] In another aspect, the present disclosure provides a composition comprising:

a first organometallic compound represented by Formula I:

$R^3_2Sn(NR^{3\prime}_2)_2$ Formula I

wherein:

each R^3 group is independently selected from the group consisting of an alkyl group having from 1 to 10 carbon atoms and an aryl group;

each $R^{3\prime}$ group is independently selected from the group consisting of an alkyl group having from 1 to 10 carbon atoms and an aryl group; and

a second organometallic compound represented by Formula II:

$Sn(NR^4_2)_4$ Formula II

wherein each R^4 group is independently selected from the group consisting of an alkyl having from 1 to 10 carbon atoms and an aryl group.

[0034] In other examples, each R^3, $R^{3\prime}$, and R^4 group is an independently selected alkyl group having from 1 to 10 carbon atoms. It is contemplated that each R^3, $R^{3\prime}$, and R^4 group may be an independently selected alkyl group having from 1 to 6 carbon atoms. In examples, each R^3, $R^{3\prime}$, and R^4 group is an independently selected alkyl group having from 1 to 4 carbon atoms. In examples, each R^3, $R^{3\prime}$, and R^4 group is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl. In examples, each R^3, $R^{3\prime}$, and R^4 group represent different alkyl, acyl, or aryl groups, in particular different alkyl groups.

[0035] In examples, the second organometallic compound is selected from the group consisting of $Sn(NMe_2)_4$, $Sn(NEt_2)_4$, and $Sn(NMeEt)_4$.

[0036] The present disclosure provides a new etching process that solves the problems discussed above with previous methods of etching and cleaning ALD reactors, and in particular, ALD reactors in tin oxide fabrication.

[0037] One process that solves the problems discussed above includes: a process for removing tin oxide deposits from interior surfaces of a reactor chamber or from a substrate within said reactor chamber, including:

[0038] introducing an etchant gas into said reactor chamber, said etchant gas being of the general formula $A^3O_mX_n$, wherein: A^3 is selected from the group consisting of C, N, and S; O is oxygen; each X is independently selected from a group consisting of halogens; and the subscripts $_m$ and $_n$ are greater than zero;

[0039] activating said etchant gas either before or after said introduction;

[0040] allowing an etching reaction to proceed between said activated etchant gas and said tin oxide deposits; and

[0041] evacuating the etchant gas together with gaseous products of the etching reaction.

[0041a] In another aspect, the present disclosure provides a process for removing tin oxide deposits from interior surfaces of a reactor chamber or from a substrate within said reactor chamber, comprising:

introducing an etchant gas into said reactor chamber comprising tin oxide deposits, said etchant gas being of the general formula $A^3O_mX_n$, wherein:

A^3 is selected from the group consisting of C, N, and S,

O is oxygen,

each X is independently selected from a group consisting of halogens, and

the subscripts $_m$ and $_n$ are greater than zero;

activating said etchant gas either before or after said introduction;

allowing an etching reaction to proceed between said activated etchant gas and said tin oxide deposits; and

evacuating the etchant gas together with gaseous products of the etching reaction.

[0042] Another process that solves the problems discussed above includes: a process for removing deposits from interior surfaces of a reactor chamber or from a substrate within said reactor chamber, including:

[0043] introducing an etchant gas and additive into said reactor chamber, said etchant gas being of the general formula $A^3O_mX_n$, wherein: A^3 is selected from the group consisting of C, N, and S; O is oxygen; each X is independently selected from a group consisting of halogens; the subscripts $_m$ and $_n$ are greater than zero; and said additive

being of the general formula $C_xH_yO_z$, wherein the subscripts $_x$ and $_z$ are greater than zero;

[0044] activating said etchant gas either before or after said introduction;

[0045] allowing an etching reaction to proceed between said activated etchant gas and said deposits; and

[0046] evacuating the etchant gas together with gaseous products of the etching reaction.

[0046a] In another aspect, the present disclosure provides a process for removing deposits from interior surfaces of a reactor chamber or from a substrate within said reactor chamber, comprising:

introducing an etchant gas and additive into said reactor chamber, said etchant gas being of the general formula $A^3O_mX_n$, wherein:

A^3 is selected from the group consisting of N and S,

O is oxygen,

each X is independently selected from a group consisting of halogens,

the subscripts $_m$ and $_n$ are greater than zero, and

said additive being of the general formula $C_xH_yO_z$, wherein the subscripts $_x$ and $_z$ are greater than zero;

activating said etchant gas either before or after said introduction;

allowing an etching reaction to proceed between said activated etchant gas and said deposits; and

evacuating the etchant gas together with gaseous products of the etching reaction.

[0047] In an example according to any of the above processes, X represents a combination of two different halogens.

[0048] In an example according to any of the above processes, generating said etchant gas occurs prior to said introduction into said chamber.

[0049] In an example according to any of the above processes, bubbling a carrier gas through a liquid chemical constituent to volatilize said liquid chemical constituent

into said etchant, occurs prior to said introduction of said etchant gas into said chamber.

[0050] In an example according to any of the above processes, said etchant gas is generated by bubbling a carrier gas through a plurality of liquid chemical constituents and then combining the resulting gases.

[0051] In an example according to any of the above processes, said etchant gas is generated by mixing two or more chemical constituent gases.

[0052] In an example according to any of the above processes, said etchant gas is activated by exposing it to an activation mechanism in a gas activation chamber prior to introduction into said chamber; said gas activation mechanism being selected from the group consisting of heat, ultraviolet light and plasma discharge.

[0053] In an example according to any of the above processes, said etchant gas is activated by exposing it to a thermal activation mechanism after introduction into said chamber; said thermal activation mechanism being selected from the group consisting of: the overall temperature within said chamber and a local heat source within said chamber.

[0054] In an example according to any of the above processes, said etchant gas is selected from the group consisting of $COCl_2$, $COBr_2$, COI_2, SOI_2, $SOCl_2$, $SOBr_2$, SO_2Cl_2, SO_2Br_2, NOCl, NOBr, NOI, SOClBr, SOClF, and SOFBr. In particular examples, thionyl chloride ($SOCl_2$) is used.

[0055] In an example according to any of the above processes, said additive is CO or CO_2.

[0056] In an example according to any of the above processes, a halogen containing additive is added to a gaseous mixture with said etchant gas.

[0057] In an example according to any of the above processes, the halogen containing additive is an active halogen or a compound of the general formula R^5X^1, wherein R^5 is selected from the group consisting of H and Me; and X^1 is a halogen selected from the group consisting of F, Cl, Br, and I.

[0058] In an example according to any of the above processes, the active halogen includes Cl or Br.

[0059] In an example according to any of the above processes, a dilution additive is added to a gaseous mixture with said etchant gas.

[0060] In an example according to any of the above processes, the dilution additive includes N, Ar, He, or Ne.

[0061] In an example according to any of the above processes, said reactor chamber is heated to a temperature of at least 100°C, between 100°C and 900°C, or between 100°C and 400°C.

[0062] In an example according to any of the above processes, said reactor chamber is provided with a pressure of between 0.1 mBar and 1500 mBar, preferably between 0.1 mBar and 1000 mBar.

[0063] The foregoing and other features of the disclosure and advantages of the present disclosure will become more apparent in light of the following detailed description of the preferred examples, as illustrated in the accompanying figures. As will be realized, the disclosure is capable of modifications in various respects, all without departing from the disclosure. Accordingly, the drawings and the description are to be regarded as illustrative in nature, and not as restrictive.