METHODS TO PRODUCE ORGANOTIN COMPOSITIONS WITH CONVENIENT LIGAND PROVIDING REACTANTS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to copending U.S. provisional patent applications 63/070,098 filed August 25, 2020 to Edson et al., entitled "Methods to Produce Monoalkyl Tin Compositions Wit Low Concentration of Contaminants," and 63/191,646 filed on May 21, 2021 to Cardineau et al., entitled "High EUV Absorption Organotin Patterning Compositions and Coatings," both of which are incorporated herein by reference.

FIELD OF THE INVENTION

The invention relates to improved methods for the production of mono-organotin triamides and mono-organotin triacetylides, wherein the organo group is defined as a hydrocarbyl with or without one or more heteroatoms.

BACKGROUND OF THE INVENTION

Organometallic compounds provide metal ions in solution-processible and vapor-phase forms for deposition of thin films. Organotin compounds provide a radiation sensitive Sn-C bond that can be used to lithographically pattern thin films. The manufacture of semiconductor devices at ever shrinking dimensions requires new versatile materials to achieve required patterning resolutions; organotin compounds promise to deliver needed patterning advantages.

SUMMARY

In one aspect, the disclosure pertains to a solution comprising an organic solvent; and dissolved in the solvent, an organometallic composition comprising alkali metal ions, tin ions and organic ligands bonded to the tin as an SnL_3 moeity, wherein the organic ligands (L) are represented by -C≡CR' or -C≡CSiR"$_3$, or a mixture thereof, wherein the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms and wherein the three R" are independently H or R'. In some examples, the organometallic composition further comprises alkaline earth ions (Be (+2), Mg (+2), Ca (+2), Sr (+2), Ba (+2)) or pseudo-alkaline earth ions (Zn (+2), Cd (+2) or Hg (+2/+1)).

In another aspect, the disclosure pertains to a solution comprising an organic solvent; and dissolved in the solvent, an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition comprising alkali metal ions, tin ions having organic ligands (L) bonded to the tin as an SnL3 moiety, and alkaline earth ions (Be (+2), Mg (+2), Ca (+2), Sr (+2), Ba (+2)) or pseudo-alkaline earth ions (Zn (+2), Cd (+2), Hg (+2 / +1)), or combinations thereof, wherein the organic ligands (L) are represented by $–NR'_2$, -C≡CR', or $-C≡CSiR"_3$, or a mixture thereof, wherein the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the three R" are independently H or R'.

In another aspect, the disclosure pertains to a method for forming an alkali metal tin composition, the method comprising reacting ML, wherein M is Li and L is a dialkylamide represented by the formula $-NR'_2$ wherein R' is an organo group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds and optional hetero atoms, and tin (II) halide represented by the formula SnX_2, wherein X is a halide, in an organic solvent to form the alkali metal tin composition, wherein the alkali metal tin composition comprises M and a SnL_3 moeity, which is $Sn(NR'_2)_3$, wherein ML and tin(II) halide are provided in the reacting step in a molar ratio of ML to tin(II) halide of approximately 3:1, and wherein the reaction is initiated at a temperature of no more than 0°C. In some examples, the method further comprises reacting a (alkaline earth/pseudo-alkaline earth) metal halide ($M"'X_2$, X=F, Cl, B, I or a mixture thereof) with the alkali metal tin composition to form an alkali metal (alkaline earth/pseudo-alkaline earth) metal tin composition, where the alkaline earth/pseudo-alkaline earth metal is beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury or a combination thereof.

In yet another aspect, the disclosure pertains to a method for forming an alkali metal tin composition, the method comprising: reacting ML, wherein M is Li and L is a dialkylamide represented by the formula $-NR'_2$ wherein R' is an organo group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds and optional hetero atoms, tin (II) halide, represented by the formula SnX_2, wherein X is a halide, and $M'OR^0$, wherein M' is Na, K, Cs or a combination thereof and R^0 is a hydrocarbyl group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the associated metal cations further comprise M'.

In a further aspect, the disclosure pertains to a method for forming an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition, the method comprising: reacting (A) ML, wherein M is Li, Na, K, Cs or a combination thereof and L is a dialkylamide represented by the formula -NR'2 or an acetylide represented by the formula -C≡CR' or -C≡CSiR"$_3$, wherein the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the three R" are independently H or R', (B) tin (II) halide, represented by the formula SnX_2, wherein X is F, Cl, Br, I or a mixture thereof, in an organic solvent to form an alkali metal tin composition, wherein the alkali metal tin composition comprises a SnL3 moiety, which is $Sn(NR'_2)_3$, $Sn(C{\equiv}CR')_3$, or $Sn(C{\equiv}CSiR"_3)_3$, present with associated metal cations comprising M, and (C) wherein M"' is beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury or a combination thereof and X=F, Cl, Br, I or a mixture thereof, to form an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition.

In another aspect, the disclosure pertains to a method for forming an alkali metal tin composition, the method comprising: reacting ML, wherein M is Li, Na, K, Cs or a combination thereof and L is an acetylide represented by the formula -C≡CR' or -C≡CSiR"$_3$, the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the three R" are independently H or R', (B) tin (II) halide, represented by the formula SnX_2 and tin (II) halide, represented by the formula SnX_2, wherein X is F, Cl, Br, I or a mixture thereof, in an organic solvent to form an alkali metal tin composition, wherein the alkali metal tin composition comprises a SnL_3 moiety, which is $Sn(C{\equiv}CR')_3$ or $Sn(C{\equiv}CSiR"_3)_3$, present with associated metal cations comprising M.

In another aspect, the disclosure pertains to a method for forming an alkali metal tin composition, the method comprising: reacting ML, wherein M is Li and L is a dialkylamide represented by the formula -NR'$_2$ wherein R' is an organo group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds and optional hetero atoms, and tin (II) halide, represented by the formula SnX_2, wherein X is a halide, in an organic solvent wherein the reaction is initiated at a temperature of no more than about 0°C to form an alkali metal tin composition, wherein the alkali metal tin composition comprises M and a SnL_3 moiety, which is $Sn(NR'_2)_3$.

In some aspects, the disclosure pertains to an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition formed according to a method disclosed herein.

In another aspect, the disclosure pertains to an alkali metal tin composition formed according to a method disclosed herein.

In some examples, the disclosure pertains to a method for synthesizing a monohydrocarbyl tin compound, in which the method comprises reacting a primary halide hydrocarbyl compound (R-X, where X is a halide atom) with an organometallic composition comprising SnL_3 moieties associated with metal cations M, where M is an alkali metal, alkaline earth metal, and/or pseudo-alkali metal (Zn, Cd, or Hg), and L is either an amide ligand resulting in an alkali metal tin triamide compound or an acetylide ligand resulting in an alkali metal tin triacetylide, to form correspondingly a monohydrocarbyl tin triamide ($RSn(NR'_2)_3$) or a monohydrocarbyl tin triacetylide ($RSn(C{\equiv}CL^s)_3$), where the monohydrocarbyl ligand (R) is a hydrocarbyl group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, L^s is $SiR"_3$ or R', the three R" are independently H or R', and the R' are independently a hydrocarbyl group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, to form the alkali metal tin composition.

In additional examples, the invention pertains to a compound represented by the formula $RSn(C{\equiv}CSiR'_3)_3$, where R' and R are independently a hydrocarbyl group with from 1 to 31

carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms.

Moreover, the disclosure pertains to a halogenated hydrocarbyl tin compound represented by the formula R'R"ACSnL$_3$, where A is a halogen atom (F, Cl, Br or I) or an aromatic ring with at least one halogen substituent, where R' and R" are independently H, a halogen, or a hydrocarbyl group with from 1 to 15 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and L is L_H, where L_H is a hydrolysable ligand, or $O_x(OH)_{3-x}$, $0<x<3$.

Furthermore, the disclosure pertains to a hydrocarbyl tin compound represented by the formula R'R"(R'"O)CSnL$_3$ where R', R" and R'" are independently H or hydrocarbyl groups having from 1 to 15 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and L is L_H, where L_H is a hydrolysable ligand, or $O_x(OH)_{3-x}$, $0<x<3$.

In some examples, the disclosure pertains to a hydrocarbyl tin compound represented by the formula R'R"(N≡C)CSnL$_3$ where R' and R" are independently H or hydrocarbyl groups havingfrom 1 to 15 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and L is L_H, where L_H is a hydrolysable ligand, or $O_x(OH)_{3-x}$, $0<x<3$.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a ^{119}Sn NMR spectrum of LiSn(NEt$_2$)$_3$ in benzene-d$_6$.

Fig. 2 is a ^{119}Sn NMR spectrum of n-PrSn(NEt$_2$)$_3$ in benzene-d$_6$.

Fig. 3 is a ^{1}H NMR spectrum of n-PrSn(NEt$_2$)$_3$ in benzene-d$_6$.

Fig. 4 is a ^{119}Sn NMR spectrum of n-PrSn(O-tAm)$_3$ in benzene-d$_6$.

Fig. 5 is a ^{1}H NMR spectrum of n-PrSn(O-tAm)$_3$ in benzene-d$_6$.

Fig. 6 is a ^{119}Sn NMR spectrum of EtSn(NEt$_2$)$_3$ in benzene-d$_6$.

Fig. 7 is a ^{119}Sn NMR spectrum of EtSn(O-tAm)$_3$ in benzene-d$_6$.

Fig. 8 is a ^{119}Sn NMR spectrum of t-BuSn(NEt$_2$)$_3$ in benzene-d$_6$.

Fig. 9 is a ^{119}Sn NMR spectrum of t-BuSn(O-tAm)$_3$in benzene-d$_6$.

Fig. 10. is a ^{119}Sn NMR spectrum of (NC(CH$_3$)$_2$C)Sn(NEt$_2$)$_3$ in benzene-d$_6$.

Fig. 11 is a ^{119}Sn NMR spectrum of LiSn(CCSiMe$_3$)$_3$ in benzene-d$_6$.

Fig. 12 is a ^{119}Sn NMR spectrum of (CH$_3$OCH$_2$)Sn(CCSiMe$_3$)$_3$ in benzene-d$_6$.

Fig. 13 is a ^{119}Sn NMR spectrum of (NC(CH$_3$)$_2$C)Sn(CCSiMe$_3$)$_3$ in benzene-d$_6$.

Fig. 14 is a ^{119}Sn NMR spectra of 2-iodopropyltin tris(tert-butoxide) (2IP).

What is claimed is:

1. A solution comprising:

an organic solvent; and

dissolved in the solvent, an organometallic composition comprising alkali metal ions, tin ions and organic ligands bonded to the tin as an SnL_3 moiety, wherein the organic ligands (L) are represented by –-C≡CR' or -C≡CSiR"$_3$, or a mixture thereof, wherein the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms and wherein the three R" are independently H or R'.

2. A solution comprising:

an organic solvent; and

dissolved in the solvent, an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition comprising alkali metal ions, tin ions having organic ligands (L) bonded to the tin as an SnL_3 moiety, and alkaline earth ions (Be (+2), Mg (+2), Ca (+2), Sr (+2), Ba (+2)) or pseudo-alkaline earth ions (Zn (+2), Cd (+2), Hg (+2 / +1)), or combinations thereof, wherein the organic ligands (L) are represented by –NR'$_2$, -C≡CR', or -C≡CSiR"$_3$, or a mixture thereof, wherein the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the three R" are independently H or R'.

3. The solution of claim 1 or claim 2 wherein the solvent is an aprotic polar organic solvent.

4. The solution of any one of claims 1-3 wherein the alkali metal ions are Li, Na, K, Cs or a combination thereof.

5. The solution of any one of claims 1-3 wherein the alkali metal ions are lithium metal ions.

6. The solution of any one or claims 2-5 wherein L is $–NR'_2$, where R' is a linear or branched alkyl ($-C_nH_{2n+1}$, n is 1 to 5).

7. The solution of any one of claims 1-5 wherein L is –C≡C R', where R' is a linear or branched alkyl ($-C_nH_{2n+1}$, n is 1 to 5).

8. The solution of any one of claims 1-7 wherein R' is methyl (CH_3-), ethyl (CH_3CH_2-), isopropyl (CH_3CH_3HC-), t-butyl ($(CH_3)_3C$-), t-amyl ($CH_3CH_2(CH_3)_2C$-), sec-butyl ($CH_3(CH_3CH_2)CH$-), neopentyl ($(CH_3)_3CCH_2$-), cyclohexyl, cyclopentyl, cyclobutyl, or cyclopropyl.

9. The solution of any one of claims 1-8 wherein R' comprises hetero atoms, wherein the hetero atoms optionally comprise O, N, Si, Ge, Sn, and/or halogen atoms, and/or a phenyl or cyano group.

10. The solution of any one of claims 1-9 having a tin concentration from about 0.005M to about 2M.

11. The solution of claim 2 wherein the alkaline earth ions comprise zinc ions.

12. A method for forming an alkali metal tin composition, the method comprising:

reacting ML, wherein M is Li and L is a dialkylamide represented by the formula $-NR'_2$ wherein R' is an organo group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds and optional hetero atoms, and tin (II) halide represented by the formula SnX_2, wherein X is a halide, in an organic solvent to form the alkali metal tin composition, wherein the alkali metal tin composition comprises M, and a SnL_3 moiety, which is $Sn(NR'_2)_3$, wherein ML and tin(II) halide are provided in the reacting step in a molar ratio of ML to tin(II) halide of approximately 3:1, and wherein the reaction is initiated at a temperature of no more than 0°C.

13. A method for forming an alkali metal tin composition, the method comprising:

reacting ML, wherein M is Li and L is a dialkylamide represented by the formula $-NR'_2$ wherein R' is an organo group with from 1 to 31 carbon atoms and optional unsaturated carbon-

carbon bonds and optional hetero atoms, tin (II) halide, represented by the formula SnX_2, wherein X is a halide, and $M'OR^0$, wherein M' is Na, K, Cs or a combination thereof and R^0 is a hydrocarbyl group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the associated metal cations further comprise M'.

14. A method for forming an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition, the method comprising:

reacting (A) ML, wherein M is Li, Na, K, Cs or a combination thereof and L is a dialkylamide represented by the formula -NR'2 or an acetylide represented by the formula -C≡CR' or $-C\equiv CSiR''_3$, wherein the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the three R" are independently H or R', (B) tin (II) halide, represented by the formula SnX_2, wherein X is F, Cl, Br, I or a mixture thereof, in an organic solvent to form an alkali metal tin composition, wherein the alkali metal tin composition comprises a SnL3 moiety, which is $Sn(NR'_2)_3$, $Sn(C\equiv CR')_3$, or $Sn(C\equiv CSiR''_3)_3$, present with associated metal cations comprising M, and (C) wherein M'" is beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury or a combination thereof and X=F, Cl, Br, I or a mixture thereof, to form an alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition.

15. A method for forming an alkali metal tin composition, the method comprising:

reacting ML, wherein M is Li, Na, K, Cs or a combination thereof and L is an acetylide represented by the formula -C≡CR' or $-C\equiv CSiR''_3$, the R' are independently hydrocarbyl groups with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms, and wherein the three R" are independently H or R', (B) tin (II) halide, represented by the formula SnX_2 and tin (II) halide, represented by the formula SnX_2, wherein X is F, Cl, Br, I or a mixture thereof, in an organic solvent to form an alkali metal tin composition, wherein the alkali metal tin composition comprises a SnL_3 moiety, which is $Sn(C\equiv CR')_3$ or $Sn(C\equiv CSiR''_3)_3$, present with associated metal cations comprising M.

16. A method for forming an alkali metal tin composition, the method comprising:

reacting ML, wherein M is Li and L is a dialkylamide represented by the formula $-NR'_2$ wherein R' is an organo group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds and optional hetero atoms, and tin (II) halide, represented by the formula SnX_2, wherein X is a halide, in an organic solvent wherein the reaction is initiated at a temperature of no more than about 0°C to form an alkali metal tin composition, wherein the alkali metal tin composition comprises M and a SnL_3 moiety, which is $Sn(NR'_2)_3$.

17. The method of claim 14, wherein $M'''X_2$ is $ZnCl_2$.

18. The method of claim 14 wherein M is Li and/or L is an acetylide.

19. The method of claim 14 wherein ML and tin(II) halide are provided in the reacting step in a molar ratio of ML to tin (II) halide of approximately 3:1 and the molar ratio of M''' to Sn in the reacting step is approximately 1:1.

20. The method of claim 13 wherein M' is K.

21. The method of claim 15 wherein M is Li.

22. The method of any one of claims 12-21 wherein the reaction is performed under nitrogen atmosphere.

23. The method of any one of claims 12-22 wherein the organic solvent comprises an anhydrous organic solvent.

24. The method of any one of claims 12-23 wherein reacting ML and tin (II) halide in an organic solvent is initiated at a temperature of no more than about 0°C and/or the reaction is continued for a time of at least about two minutes.

25. The method of any one of claims 12-24 wherein R' is methyl (CH_3-), ethyl (CH_3CH_2-), isopropyl (CH_3CH_3HC-), t-butyl ($(CH_3)_3C$-), t-amyl ($CH_3CH_2(CH_3)_2C$-), sec-butyl

($CH_3(CH_3CH_2)CH$-), neopentyl ($(CH_3)_3CCH_2$-), cyclohexyl, cyclopentyl, cyclobutyl, or cyclopropyl.

26. The method of any one of claims 12-25 wherein R' comprises hetero atoms, wherein the hetero atoms optionally comprise O, N, Si, Ge, Sn, and/or halogen atoms, and/or a phenyl or cyano group.

27. An alkali metal alkaline earth metal/pseudo-alkaline earth metal tin composition formed according to the method of claim 14.

28. An alkali metal tin composition formed according to the method of any one of claims 12, 13, or 15, or 16.

29. The method of any one of claims 12-26 further comprising:

reacting the product of any one of claims 12-26 with a primary halide hydrocarbyl compound represented by the formula RX', wherein X' is a halide atom to form correspondingly a composition represented by the formula $RSn(NR'_2)_3$, ($R(Sn(C{\equiv}CR')_3$, or $R(SnC{\equiv}CSiR"_3)_3$ where ligand R is a hydrocarbyl group with from 1 to 31 carbon atoms and optional unsaturated carbon-carbon bonds, optional aromatic groups and optional hetero atoms.

30. The method of claim 29 wherein L is $-C{\equiv}CSiR"_3$, where R" is a linear or branched alkyl ($-C_nH_{2n+1}$, n is 1 to5).

31. The method of claim 29 wherein X' is an iodine atom.

32. The method of claim 29 wherein R comprises methyl (CH_3-), ethyl (CH_3CH_2-), isopropyl (CH_3CH_3HC-), t-butyl ($(CH_3)_3C$-), t-amyl ($CH_3CH_2(CH_3)_2C$-), sec-butyl ($CH_3(CH_3CH_2)CH$-), neopentyl ($(CH_3)_3CCH_2$-), cyclohexyl, cyclopentyl, cyclobutyl, or cyclopropyl.