

TITLE OF THE INVENTION

[0001] High Purity Alkyl Tin Compounds and Manufacturing Methods Thereof

CROSS-REFERENCE TO RELATED APPLICATION

- 5 [0002] This application claims priority to co-pending U.S. Provisional Application No. 63,348,173, filed June 2, 2022, the disclosure of which is herein incorporated by reference.

BACKGROUND OF THE INVENTION

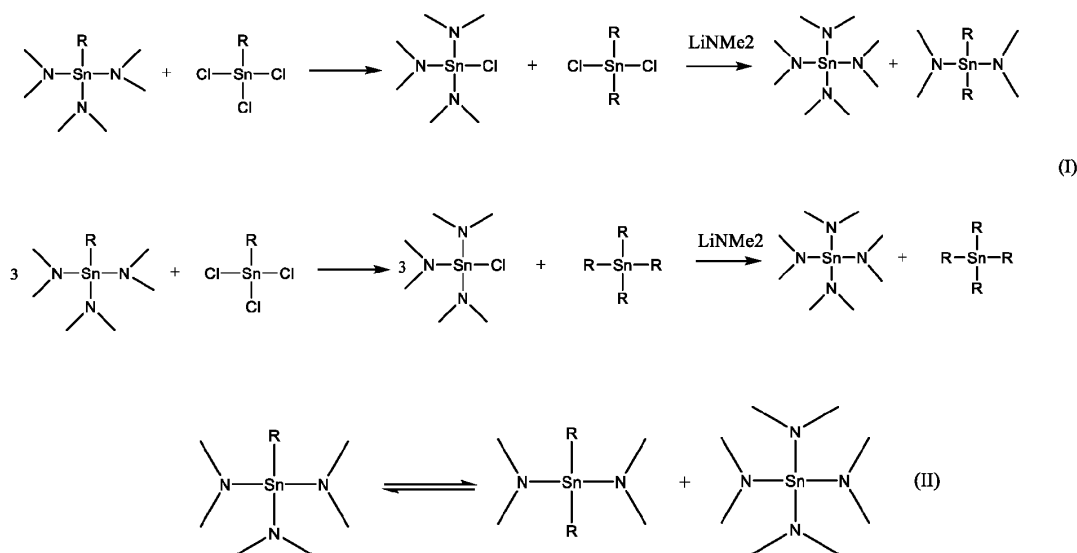
[0003] As semiconductor fabrication continues to advance, feature sizes continue to shrink, driving the need for new processing methods. Certain organotin compounds have been shown to
10 be useful in the deposition of tin oxide hydroxide coatings in applications such as extreme ultraviolet (EUV) lithography techniques. For example, alkyl tin compounds provide radiation sensitive Sn-C bonds that can be used to pattern structures lithographically.

[0004] Materials used in microelectronic fabrication are required to be extremely pure with tight limits placed on organic contamination (e.g., reaction by-products), metallic contamination,
15 and particulate contamination. Purity requirements are stringent in general, and particularly for lithography applications because the chemical is in contact with the semiconductor substrates and the organometallic impurities in compounds such as diisopropylbis(dimethylamino)tin, $3(iPr)_2Sn(NMe_2)_2$, can affect the properties of the resultant film. Exact targets for purities are determined by a variety of factors, including performance metrics, but typical minimum purity
20 targets are 3N+. Residual metals present in the chemicals can be deposited onto the semiconductor substrate and degrade the electrical performance of the device being fabricated. Typical specification for metals are less than 10 ppb for individual metals and total metal not to exceed ~100 ppb.

[0005] The processing and performance of semiconductor materials can also be sensitive to
25 dialkyl tin contaminants. Dialkyl tin impurities, $R_2Sn(NMe_2)_2$, where R is an alkyl group, are the source of off-gassing after vapor phase deposition or spin-on coating processes due to the oxostannate cluster films being less dense when the film contains dialkyl groups. To produce microelectronic products using EUV lithography, proper control of dialkyl tin contaminants is required. The high purity required from the mono-alkyl tin precursor manufacturing process

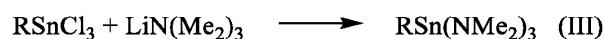
becomes a challenge. In general, the syntheses of monoalkyl tin triamides have previously employed lithium dimethylamide reagents reacted with alkyl tin trichloride, or followed by a lithium/Grignard reagent (alkylating agent) to convert the tin tetraamides to the desired triamides.

- 5 **[0006]** Kocheshkov-like comproportionation during scheme (I) and the disproportion scheme (II), shown below, during purification are the two main challenges when preparing primary alkyl tin triamides, such as methyl and longer alkyl tin triamides, which contain no more than 1% dialkyl tin after purification. Studies have shown that comproportionation occurs independent of the reaction temperature, down to -78 °C. In fact, lower temperatures have been found to slow the substitution reaction, which increases the risk of comproportionation.
- 10



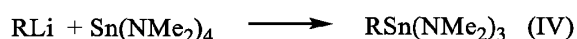
- [0007]** The preparation of monoalkyl tin triamide compounds may be accomplished by two different known synthetic pathways. When the alkyl group contains a primary and/or a secondary moiety, such as methyl tri(dimethylamino)tin (MeSn(NMe₂)₃) or isopropyl tri(dimethylamino)tin (iPrSn(NMe₂)₃), the synthesis may be performed using lithium dimethylamide and alkyl tin trichloride (amination) according to the method of Lorberth (*Journal of Organometallic*
- 15

Chemistry, 16(2), 235-48 (1969)); see also Jones and Lappert (*Organometal. Chem. Rev.*; 1, 67 (1966)), as shown in scheme (III). However, this reaction typically produces significant amounts of dialkyl tin and other tin impurities.



- 5 **[0008]** Alternatively, when the alkyl group contains a tertiary alkyl moiety, such as *tert*-butyl tris(dimethylamino)tin ($\text{t-BuSn}(\text{NMe}_2)_3$), the compounds must be synthesized using an alkylating reagent to convert tin tetraamides by controlling the stoichiometry according to the method reported by Hanssger *et al.* (*Journal of Organometallic Chemistry*, 293(2), 191-5 (1985)), as shown in scheme (IV).

10



- [0009]** The reaction of scheme (IV) using an alkylating reagent and tetraamides is not effective for the preparation of primary and secondary monoalkyl tin triamide compounds. Rather, the use of a primary alkylating reagent will convert tin tetraamides to trialkyltin amides and unreacted tetraamides, even when using the correct stoichiometry. Secondary alkylating reagents will also convert tin tetraamides to polyalkyl tin compounds.
- 15

- [0010]** When the alkyl group in the monoalkyltin triamide compound is a tertiary alkyl group such as t-BuSnCl_3 , Hanssger *et al.* also reports that this compound decomposes rapidly at room temperature, yielding SnCl_2 and t-BuCl . Therefore, tertiary monoalkyl tin triamide compounds cannot be prepared by synthesis with lithium dimethylamide and alkyl tin trichloride.
- 20

- [0011]** Distillation is a well-developed technology for separating materials in a mixture based on their relative volatility. The exact embodiment of the distillation process depends on the properties, the composition, and the amount of the mixture to be separated. Distillation can and has been used to reduce metallic contamination in multitudes of materials, including organometallic compounds.
- 25

[0012] For example, U.S. Patent Application Publication No. 2019/0337969 describes organometallic tin compounds which have low concentrations of metallic impurities as a result of a multistage distillation process which is compared to processes typically used for sea water desalination. U.S. Patent Application Publication No. 2020/0239498 describes the purification of
5 monoalkyl tin trialkoxides and monoalkyl tin triamides using fractional distillation and/or ultrafiltration for the removal of metal impurities and fine particulates. The removal of metallic impurities from similar compounds is also described in U.S. Patent Application Publication No. 2020/0241413.

[0013] U.S. Patent No. 10,787,466 and U.S. Patent No. 10,732,505 describe organotin
10 hydroxide, alkoxide, and amide compounds having low purity. However, extremely low levels of impurity have only been demonstrated for t-butyl analogs.

[0014] U.S. Patent No. 8,901,335 describes the purification of a long list of organometallic compounds using a stripping column and a gas stream; the more volatile impurities relative to the organometallic compound are removed and the metallic impurity contents are reduced to
15 specified levels. U.S. Patent No. 11,156,915 relates to the purification of actinic ray- or radiation-sensitive compounds, including tin compounds, using filtration to remove particulates. Finally, U.S. Patent No. 5,274,149 teaches a process for making alkyl arsine compounds which includes a distillation step, and which are taught to contain substantially no metallic or oxygenating impurities.

20 [0015] The ability to prepare and isolate alkyl-amino tin compounds having desired extremely high purity levels would be very attractive for use in the microelectronic industry.

BRIEF SUMMARY OF THE INVENTION

[0016] In one aspect of the disclosure, provided is a monoalkyl tin triamide compound
25 having formula (1) and having a purity of at least about 99 mol%:



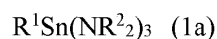
wherein R^1 is selected from R^A , R^B , and R^C ;

R^A is a primary alkyl group having about 1 to 10 carbon atoms, R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and R^C is a tertiary alkyl group having about 3 to 10 carbon atoms;

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; and

5 wherein a content of $R^1Sn(NR^2_2)_2(N(R^2)CH_2NR^2_2)$ is less than about 1 mol%.

[0017] In another aspect of the disclosure, provided is a method of synthesizing a monoalkyl tin triamide compound having formula (1a) and having a purity of at least about 85 mol%:



wherein R^1 is selected from R^A and R^B ;

10 R^A is a primary alkyl group having about 1 to 10 carbon atoms and R^B is a secondary alkyl group having about 3 to 10 carbon atoms; and

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; the method comprising:

(a) lithiating a solution comprising a dimethylamine and a first solvent to produce a
15 lithium dimethylamide solution having a concentration of up to about 10 wt %;

(b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the amount of alkyl trichlorotin;

(c) removing the LiCl salt product by filtration; and

20 (d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1a).

[0018] In a further aspect of the disclosure, provided is a method of storing a sample of a monoalkyl tin triamide compound having formula (1) and having a purity of at least about 99 mol%:



wherein R^1 is selected from R^A , R^B , and R^C ;

R^A is a primary alkyl group having about 1 to 10 carbon atoms, R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and R^C is a tertiary alkyl group having about 3 to 10 carbon atoms;

5 each R^2 is independently an alkyl group having about 1 to 10 carbon atoms;

the method comprising storing the sample of the monoalkyltin triamide compound having formula (1) without light exposure and at a temperature of less than about 30°C.

[0019] Advantageous refinements of the invention, which can be implemented alone or in combination, are specified in the dependent claims.

10 [0020] In summary, the following embodiments are proposed as particularly preferred in the scope of the present invention:

[0021] Embodiment 1: A monoalkyl tin triamide compound having formula (1) and having a purity of at least about 99 mol%:



15 wherein R^1 is selected from R^A , R^B , and R^C ;

R^A is a primary alkyl group having about 1 to 10 carbon atoms, R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and R^C is a tertiary alkyl group having about 3 to 10 carbon atoms;

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; and

20 wherein a content of $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)$ is less than about 1 mol%.

[0022] Embodiment 2: The monoalkyl tin triamide compound according to Embodiment 1, wherein a content of dialkyl bis(dialkylamino) tin having formula (2) is less than about 1 mol%.



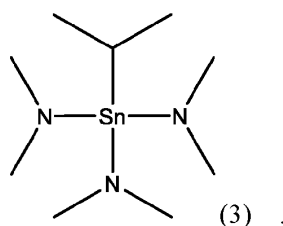
[0023] Embodiment 3: The monoalkyl tin triamide compound according to Embodiment 1 or 2, wherein a total content of tetrakis(dialkylamino)tin is less than about 1 mol%.

[0024] Embodiment 4: The monoalkyl tin triamide compound according to any of the preceding Embodiments, wherein a content of tetraalkyl tin is less than about 1 mol%.

5 [0025] Embodiment 5: The monoalkyl tin triamide compound according to any of the preceding Embodiments, wherein the color is substantially colorless.

[0026] Embodiment 6: The monoalkyl tin triamide compound according to Embodiment 5, wherein an APHA is less than about 20.

10 [0027] Embodiment 7: The monoalkyl tin triamide compound according to any of the preceding Embodiments, wherein R^1 is an isopropyl group, R^2 is a methyl group, and the compound has formula (3):

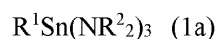


[0028] Embodiment 8: The monoalkyl tin triamide compound according to Embodiment 7, wherein a content of diisopropylbis(dimethylamino) tin is less than about 1 mol%.

15 [0029] Embodiment 9: The monoalkyl tin triamide compound according to Embodiment 8, wherein a total content of tetrakis(dimethylamino)tin is less than about 1 mol%.

[0030] Embodiment 10: The monoalkyl tin triamide compound according to any of the preceding Embodiments, wherein the content of $R^1Sn(NR^2_2)_2(N(R^2)CH_2NR^2_2)$ is less than about 0.05 mol%.

20 [0031] Embodiment 11: A method of synthesizing a monoalkyl tin triamide compound having formula (1a) and having a purity of at least about 85 mol%:



wherein R^1 is selected from R^A and R^B ;

R^A is a primary alkyl group having about 1 to 10 carbon atoms and R^B is a secondary alkyl group having about 3 to 10 carbon atoms; and

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; the method comprising:

5 (a) lithiating a solution comprising a dimethylamine and a first solvent to produce a lithium dimethylamide solution having a concentration of up to about 10 wt %;

(b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the amount of alkyl trichlorotin;

10 (c) removing the LiCl salt product by filtration; and

(d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1a).

[0032] Embodiment 12: The method according to Embodiment 11, wherein the compound having formula (1a) has a purity of at least about 99 mol%.

15 **[0033]** Embodiment 13: The method according to Embodiment 11 or 12, wherein the compound having formula (1a) contains less than about 1 mol% $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)$.

[0034] Embodiment 14: The method according to Embodiment 13, wherein the compound having formula (1a) contains less than about 0.05 mol% $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)$.

20 **[0035]** Embodiment 15: The method according to any of Embodiments 11-14, wherein step (b) is performed at about -78°C to 40°C .

[0036] Embodiment 16: The method according to Embodiment 15, wherein step (b) is performed at about 0°C to about 10°C .

25 **[0037]** Embodiment 17: The method according to any of Embodiments 11-16, wherein the first solvent and the second solvent are each independently selected from the group consisting of a hydrocarbon solvent, an aromatic solvent, and an ether solvent.

[0038] Embodiment 18: The method according to any of Embodiments 11-17, wherein steps (a) to (d) are performed substantially without light exposure.

[0039] Embodiment 19: The method according to any of Embodiments 11-18, wherein steps (a) and (b) are performed in a stainless steel vessel.

5 [0040] Embodiment 20: The method according to Embodiment 11, further comprising distilling the compound having formula (1a).

[0041] Embodiment 21: The method according to Embodiment 20, wherein the distillation comprises distilling the crude product having formula (1a) at about 1 torr, discarding any distillate before the boiling point of the monoalkyl triamide having formula (1a), and collecting
10 the distillate obtained at the boiling point of the monoalkyltin triamide having formula (1a) to yield a product containing at least about 99 mol% monoalkyl tin triamide having formula (1a).

[0042] Embodiment 22: The method according to Embodiment 20 or 21, comprising performing a fractional distillation using an operating pressure of about 0.1 to 50 torr and a pot temperature of about 50 to 120°C, wherein the purified monoalkyl tin triamide compound having
15 formula (1a) contains less than about 0.1 mol% of a dialkyl bis(dialkylamino)tin compound having formula (2).

[0043] Embodiment 23: The method according to any of Embodiments 20 to 22, comprising performing the distillation substantially without light exposure.

[0044] Embodiment 24: The method according to any of Embodiments 20 to 23, comprising
20 performing the distillation using a condenser temperature within about 1-10°C of the dew point of the monoalkyl tin triamide compound having formula (1a) at the operating pressure and at a reflux ratio of about 10 to 100.

[0045] Embodiment 25: The method according to any of Embodiments 20 to 24, wherein the distillation is performed using a stainless steel column packed with a stainless steel packing
25 material.

[0046] Embodiment 26: The method according to any of Embodiments 20 to 25, wherein the distillation is performed a light-shielded apparatus comprising glass.

[0047] Embodiments 27: A method of storing a sample of a monoalkyl tin triamide compound having formula (1) and having a purity of at least about 99 mol%:



wherein R^1 is selected from R^A , R^B , and R^C ;

5 R^A is a primary alkyl group having about 1 to 10 carbon atoms, R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and R^C is a tertiary alkyl group having about 3 to 10 carbon atoms;

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms;

10 the method comprising storing the sample of the monoalkyltin triamide compound having formula (1) substantively without light exposure and at a temperature of less than about 30°C.

[0048] Embodiment 28: The method according to Embodiment 27, wherein the sample of the monoalkyl tin triamide compound having formula (1) is stored for about three days to about one year.

15 [0049] Embodiment 29: The method according to Embodiment 27 or 28, wherein the sample of the monoalkyltin triamide undergoes substantively no decomposition after a storage time of about three days to about one year.

[0050] Embodiment 30: The method according to any of Embodiments 27 to 29, wherein a content of $R^1Sn(NR^2_2)_2(N(R^2)CH_2NR^2_2)$ in the sample of the monoalkyl tin triamide having formula (1) is less than about 1 mol%.

20 [0051] Embodiment 31: The method according to Embodiment 30, wherein the content of $R^1Sn(NR^2_2)_2(N(R^2)CH_2NR^2_2)$ in the sample of the monoalkyl tin triamide having formula (1) is less than about 0.05 mol%.

[0052] Embodiment 32: The monoalkyl tin triamide compound having formula (1) according to any of Embodiments 1 to 10, wherein R^1 is selected from R^A and R^B and the compound is
25 produced by a method comprising:

(a) lithiating a solution comprising a dimethylamine and a first solvent to produce a lithium dimethylamide solution having a concentration of up to about 10 wt %;

(b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the amount of alkyl trichlorotin;

(c) removing the LiCl salt product by filtration; and

(d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1).

[0053] Embodiment 33: The method according to Embodiment 32, wherein step (b) is performed at about -78°C to about 40°C.

[0054] Embodiment 34: The method according to Embodiment 33, wherein step (b) is performed at about 0°C to about 10°C.

[0055] Embodiment 35: The method according to any of Embodiments 32-34, wherein the first solvent and the second solvent are each independently selected from the group consisting of a hydrocarbon solvent, an aromatic solvent, and an ether solvent.

[0056] Embodiment 36: The method according to any of Embodiments 32-35, wherein steps (a) to (d) are performed substantially without light exposure.

[0057] Embodiment 37: The method according to any of Embodiments 32-36, wherein steps (a) and (b) are performed in a stainless steel vessel.

[0058] Embodiment 38: The method according to any of Embodiments 32-37, further comprising distilling the compound having formula (1).

BRIEF DESCRIPTION OF THE DRAWINGS

[0059] The foregoing summary, as well as the following detailed description of the invention, will be better understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred. It should be understood, however, that the invention is not limited to the precise arrangements and instrumentalities shown. In the drawings:

- [0060] Fig 1 is a graph depicting the boiling points of $i\text{PrSn}(\text{NMe}_2)_3$ (A) and $i\text{Pr}_2\text{Sn}(\text{NMe}_2)_2$ (B) at different pressures;
- [0061] Fig. 2 is a graph depicting the photodecomposition of $i\text{PrSn}(\text{NMe}_2)_3$ over time;
- [0062] Fig. 3 is a ^{119}Sn NMR (neat) spectrum depicting the formation of $i\text{PrSn}(\text{NMe}_2)_2(\text{NMeCH}_2\text{NMe}_2)$;
- [0063] Fig. 4 is a ^1H NMR (C_6D_6) spectrum of methyl tris(dimethylamino)tin;
- [0064] Fig. 5 is a ^{119}Sn NMR (neat) spectrum of methyl tris(dimethylamino)tin;
- [0065] Fig. 6 is a ^1H NMR (C_6D_6) spectrum of isopropyl tris(dimethylamino)tin;
- [0066] Fig. 7 is a ^{119}Sn NMR (neat) spectrum of isopropyl tris(dimethylamino)tin;
- [0067] Fig. 8 is a ^{119}Sn NMR (neat) spectrum of isopropyl tris(dimethylamino)tin synthesized in THF solution;
- [0068] Fig. 9 is a ^{119}Sn NMR (neat) spectrum of isopropyl tris(dimethylamino)tin synthesized at about 0°C ;
- [0069] Fig. 10 is a ^{119}Sn NMR (neat) spectrum of isopropyl tris(dimethylamino)tin synthesized at about -40°C ; and
- [0070] Fig. 11 is a ^{119}Sn NMR (neat) spectrum of isopropyl tris(dimethylamino)tin synthesized at about -78°C .

DETAILED DESCRIPTION OF THE INVENTION

- [0071] According to one aspect of the disclosure, provided are monoalkyl tin triamide compounds represented by formula (1) and having a purity of at least about 99 mol%. In a preferred embodiment, the compounds having formula (1) contain no more than about 1 mol% dialkyl bis(dialkylamino) tin compounds having formula (2) relative to the total amount of tin.



- [0072] In formulas (1) and (2), R^1 is selected from R^A , R^B , and R^C . R^A is a primary alkyl group having about 1 to 10 carbon atoms, preferably about 1 to about 5 carbon atoms, including

methyl, ethyl, n-propyl, n-butyl, n-pentyl, etc.; preferred are methyl or ethyl groups. R^B is a secondary alkyl (linear alkyl or cycloalkyl) group having about 3 to 10 carbon atoms, more preferably about 3 to about 5 carbon atoms, such as, without limitation, isopropyl, isobutyl, sec-butyl, cyclohexyl, cyclopentyl, cyclobutyl, cyclopropyl, isopentyl, sec-pentyl, etc.; presently
5 preferred are isopropyl and cyclopentyl groups. R^C is a tertiary alkyl group having about 3 to 10 carbon atoms such as tert-pentyl, 3-ethyl 3-pentyl, methyl 3-pentyl, methylcyclopentyl, methylcyclohexyl and the preferred t-butyl.

[0073] Each R^2 is independently an alkyl group having about 1 to 10 carbon atoms, preferably about 1 to 5 carbon atoms, including methyl, ethyl, propyl, butyl, pentyl, etc.;
10 preferred are methyl or ethyl groups.

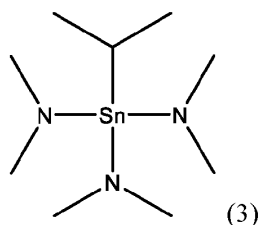
[0074] In the compound having formula (1), a total content of $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)_2$, also referred to herein as compound (4), is preferably less than about 1 mol%, preferably even lower as described below. Further, the content of the compound having formula (2) is preferably less than about 1 mol%, preferably even lower as described
15 below.

[0075] All numerical ranges expressed in this disclosure encompass all values within the range, including fractional and decimal amounts. Accordingly, the contents of the compounds having formulas (4) and (2) are each independently preferably less than about 0.9 mol%, less than about 0.8 mol %, less than about 0.7 mol %, less than about 0.6 mol %, less than about 0.5
20 mol %, less than about 0.4 mol %, less than about 0.3 mol %, less than about 0.2 mol %, less than about 0.1 mol %, less than about 0.05 mol %, less than about 0.04 mol %, less than about 0.03 mol %, less than about 0.02 mol %, less than about 0.01 mol %, or non-detectable by ^{119}Sn NMR, that is, the compounds having formulas (4) and (2) are in some embodiments undetectable in a sample of the compound having formula (1).

25 [0076] If the content of the compounds having formula (2) is too high, it reduces the cross-linking and toughness when the material is used for EUV lithography resists. Furthermore, the compound having formula (2) can cause outgassing when the photoresists are illuminated by extreme ultraviolet radiation which can lead to degradation of the very expensive multilayer-coated optics in extreme situations. As set forth below, it is possible to reduce the dialkyl tin

impurity level to as low as a level which is undetectable by ^{119}Sn NMR by employing carefully controlled reaction and distillation conditions. However, for industrial scale reactions such as more than 0.5 kg product scale, it is often sufficient and practical to control the impurity limit to less than about 0.3 mol%, more preferably less than about 0.1 mol% based on stable production and economic consideration.

[0077] In a preferred embodiment, R^1 is an isopropyl group, R^2 is a methyl group, and the compound having formula (1) is $(\text{iPr})\text{Sn}(\text{NMe}_2)_3$ (formula (3)), in which the dialkyl tin impurity is $(\text{iPr})_2\text{Sn}(\text{NMe}_2)_2$. In some embodiments, when the compound has formula (3), it has a purity of at least about 99 mol% and contains no more than about 1 mol% $(\text{iPr})_2\text{Sn}(\text{NMe}_2)_2$.

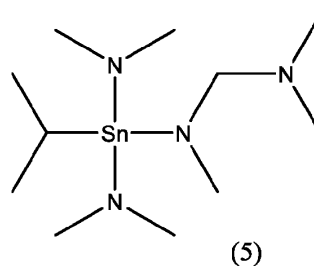
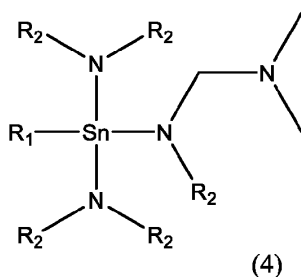


[0078] In some embodiments, the content of tetrakis(dialkylamino)tin (such as tetrakis(dimethylamino)tin) in the monoalkyl tin triamide compounds having formula (1) is less than about 1 mol%. In some embodiments, the content of tetraalkyl tin in the monoalkyl tin triamide compounds having formula (1) (such as tetrakis(isopropyl)tin in $(\text{iPr})\text{Sn}(\text{NMe}_2)_3$ as described above) is less than about 1 mol%. The contents of tetrakis(dialkylamino)tin and tetraalkyl tin (such as tetrakis(dimethylamino)tin and tetrakis(isopropyl)tin in $(\text{iPr})\text{Sn}(\text{NMe}_2)_3$) are each independently preferably less than about 0.9 mol%, less than about 0.8 mol %, less than about 0.7 mol %, less than about 0.6 mol %, less than about 0.5 mol %, less than about 0.4 mol %, less than about 0.3 mol %, less than about 0.2 mol %, less than about 0.1 mol %, less than about 0.05 mol %, less than about 0.04 mol %, less than about 0.03 mol %, less than about 0.02 mol %, less than about 0.01 mol %, or non-detectable by ^{119}Sn NMR, that is, these compounds are undetectable in the sample of the compound having formula (1).

[0079] If the content of tetrakis(dimethylamino)tin and tetraalkyl tin are too high, defects may be caused when the material is used for EUV lithography resists due to the boiling points and molecular weights of these compounds. As set forth below, it is possible to reduce the

impurity levels of these compounds to as low as a level which is undetectable by ^{119}Sn NMR by employing carefully controlled reaction and distillation conditions. However, for industrial scale reactions such as more than 0.5 kg product scale, it may be practical to control the impurity limit to less than about 0.3 mol%, more preferably less than about 0.1 mol% based on stable production and economic consideration.

[0080] In some embodiments, a total content of $\text{R}^1\text{Sn}(\text{NR}^2_2)_2(\text{N}(\text{R}^2)\text{CH}_2\text{NR}^2_2)$, also referred to herein as compound (4) is less than about 1 mol%, and may be a compound having formula $\text{R}^A\text{Sn}(\text{NMe}_2)_2(\text{NMeCH}_2\text{NMe}_2)$ or $\text{R}^B(\text{NMe}_2)_2(\text{NMeCH}_2\text{NMe}_2)$. When the compound having formula (4) is $\text{iPrSn}(\text{NMe}_2)_2(\text{NMeCH}_2\text{NMe}_2)$ (formula (5)), it has a chemical shift in the ^{119}Sn NMR spectrum of around -84 ppm: ^{119}Sn NMR(223.8 MHz; C_6D_6): δ -84ppm. ^1H NMR (600 MHz; C_6D_6): δ 3.37 (s, 2H, CH_2), 2.89 (s, 3H, Sn-NMe), 2.86 (s, 12H, Sn-(NMe_2)₂), 2.15 (s, 6H, NMe_2), 1.68 (m, 1H, iPr), 1.33 (s, 6H, iPr).



[0081] The content of the compounds having formula (4) or (5) is preferably less than about 1 mol%, less than about 0.9 mol %, less than about 0.8 mol%, less than about 0.7 mol%, less than about 0.6 mol %, less than about 0.5 mol%, less than about 0.4 mol %, more preferably less than about 0.3 mol%, even more preferably less than about 0.2 mol%, less than about 0.1 mol%, less than about 0.05 mol%, etc.

[0082] As set forth above, it is possible to reduce the level of the compound having formula (4) or (5) to as low as less than about 0.1 mol%, such as less than about 0.05 mol%, by employing carefully controlled reaction and distillation conditions. However, for industrial scale reactions such as more than 0.5 kg product scale, it is often practical to control the impurity limit to less than about 0.3 mol%, preferably less than about 0.1 mol%, based on stable production and economic considerations.

[0083] In some embodiments, the monoalkyl tin triamide compounds having formula (1) are substantially colorless. In some embodiments, the monoalkyl tin triamide compounds having formula (1) have APHA color of less than about 20. The APHA color of a composition containing tin compounds may be controlled (such as by minimizing the formation of colored impurities) during distillation such as by using light-shielding or appropriate distillation apparatuses, as described below.

[0084] APHA color, also referred to as the Hazen or Platinum/Cobalt (Pt/Co) scale, is commonly used in the chemical industry as a yellowness index to assess the color of liquids that appear colorless to yellow in color. Measured values of yellowness (APHA color) are compared to standard solutions containing potassium hexachloro-platinate(IV), cobalt(II) chloride (Pt/Co), and hydrochloric acid in water. The APHA color scale ranges from 0 to 500, where 1 APHA color is equal to 1 ppm of Pt/Co. APHA color can be assessed through visual comparison of standards or with a spectrophotometer, as described in ASTM D1209-05 (2019).

[0085] The organometallic tin compounds having formula (1) may be used for the formation of high-resolution EUV lithography patterning precursors and are attractive due to their high purity and minimized concentrations of dialkyl impurities having formula (2), as well as additional impurities as set forth above.

Methods of Synthesis

[0086] Aspects of the disclosure additionally relate to methods for synthesizing the high purity alkyl tin compounds having formula (1) described above which are suitable for use in the microelectronic industry. These high purity compounds may be substantially free of dialkyl tin compounds having formula (2) and/or impurities having formula (4) or (5), have desired color levels, and may be prepared without multi-stage distillation or, in some embodiments, without any purification.

[0087] For the purposes of this disclosure, the term “high purity” may be understood to mean a purity greater than about 99 mol%, more preferably greater than about 99.1 mol %, greater than about 99.2 mol%, greater than about 99.3 mol%, greater than about 99.4 mol %, greater than about 99.5 mol %, greater than about 99.6 mol %, greater than about 99.7 mol %, greater than

about 99.8 mol %, greater than about 99.9 mol %, greater than about 99.95 mol%, greater than about 99.98 mol%, greater than about 99.99 mol%, or even higher. The term “substantially free” may be understood to mean that the impurity is not detectable by ^{119}Sn NMR, which can have detection limits as low as 0.3 mol%, 0.1 mol%, 0.05 mol%, or 0.04 mol% (depending on the particular compound or impurity) when testing the sample using specific conditions without dilution in deuterated solvent, such as by using more than 2,000 scans. In the case of specific impurities described herein, the detection limit is 0.01 mol%.

[0088] ^{119}Sn NMR spectroscopy is ideally suited to the quantitative analysis of monoalkyl tin compounds due to its high sensitivity to small structural changes and large spectral range of 6500 ppm (see Davies et al., Eds.; Tin Chemistry: Fundamentals, Frontiers, and Applications; Wiley (2008)). This allows for easy identification and quantification of monoalkyl tin compounds and their impurities because ^{119}Sn resonances are highly resolved. ^{119}Sn NMR suffers from reduced sensitivity compared to other analytical methods such as GC, HPLC, or ^1H NMR. To improve sensitivity, monoalkyl tin compounds are analyzed without dilution, and a large number of spectral acquisitions (at least 2000, preferably more than 10,000 for unknown impurity detection) are acquired to measure the low levels of impurities described in this work. Using this approach, detection limits of 0.01 mol% dialkyl tin diamides and other Sn compounds such as compounds having formulas (2), (4), and (5) can be achieved. In the case of $\text{Sn}(\text{NMe}_2)_4$, the detection limit is 0.3 mol % because the peak is broad.

[0089] The ^{119}Sn NMR data described herein were obtained using a method similar to the relative purity method described in *J. Med. Chem.* (57, 22, 9220–9231 (2014)). ^{119}Sn NMR spectra were acquired using inverse-gated ^1H decoupling with a 45° pulse, one second relaxation delay, and sufficient scans to achieve the required sensitivity. Samples were prepared without dilution in deuterated solvent. Quantitation was performed by integrating all peaks in the spectrum and setting the total peak area to 100. Each peak in the spectrum represents a distinct tin compound and the area of each peak represents the concentration or purity of that compound in mol%.

[0090] In general, methods for preparing the monoalkyl tin triamide compounds according to aspects of the disclosure involves the following general steps, each of which is described below:

1. lithiating a solution of dimethylamine and a first solvent to produce lithium dimethylamide;
2. adding a solution containing an alkyl trichlorotin and a second solvent to the lithium dimethylamide solution with stirring;
- 5 3. removing the LiCl salt product by filtration;
4. removing the solvents under vacuum to produce a crude product; and optionally
5. distilling the crude product, to yield a product containing at least about 99 mol% monoalkyl tin triamide.

[0091] As previously explained, the reaction conditions and parameters such as solvent,
10 relative amounts of reactants, stirring conditions, temperature, and concentrations should be carefully controlled to ensure the production of the desired compound in high purity.

Solvent

[0092] The first and second solvents are not particularly limited, but preferred solvents
15 include hydrocarbons (such as, but not limited to, hexane, hexanes, heptane, and cyclohexane), aromatics (such as, but not limited to, toluene and xylene), and ethers (such as, but not limited to, THF and Et₂O), and mixtures thereof. Particularly presently preferred are hydrocarbons and aromatics as the main component of the solvent for removing LiCl by filtration. Toluene and hexane are presently the most preferred solvents for easy removal of the product under vacuum
20 at low temperature following the reaction. Additionally, ethers, such as the most preferred THF, are presently preferred solvents because of the high solubility of lithium dimethylamide in these types of solvents. It is also within the scope of the disclosure to use mixtures of these solvents. In some embodiments, the solvent used for the lithiation step and the solvent used for the amination step are the same.

25 Amount of Lithium Dimethylamide

[0093] The preferred amount of lithium dimethylamide relative to the alkyl trichlorotin is greater than about 3.0 equivalents, greater than about 3.05 equivalents, greater than about 3.09 equivalents, greater than about 3.10 equivalents, or greater than about 3.15 equivalents. If the

amount of lithium dimethylamide is too low, the reaction speed will be too low and the amount of impurities will increase due to side reactions such as redistribution.

Stirring Conditions during Addition of Alkyl Trichlorotin

5 [0094] The stirring speed during the addition of the alkyl trichlorotin is significant in determining the purity of the resulting product. A solution of lithium amide in hexane or toluene is in fact a heavy slurry, so stirring at a high speed is preferable for sufficient mixing. On the other hand, stirring at too high a speed can cause problems with the motor due to the heavy slurry. The preferred stirring speed is more than about 10 rpm, more than about 20 rpm, more
10 than about 40 rpm, more preferably more than about 60 rpm and most preferably more than about 100 rpm. On the other hand, the preferred stirring speed is less than about 500 rpm, less than about 400 rpm, less than about 300 rpm, more preferably less than about 250 rpm and most preferably less than about 200 rpm. To achieve good mixing, the selection of a suitable shape and size of the stirring blade is important. For example, appropriate stirring blades include
15 paddle blades, anchor blades, Twinstir blades, ribbon blades, 3-blade retreat impellers, and log bone blades. In the reaction between the lithium amide slurry and the alkyl trichlorotin (amination), it is important to have high blade peripheral speed because miniaturization and lithium amide slurry and high reactivity are high shear stress achieved in blade peripheral speed (blade tip speed, m/s). The preferred blade peripheral speed is about 0.1 rpm or more, preferably
20 0.3 rpm or more, most preferably 0.5 rpm or more and 1000 rpm or less, preferably 100 rpm or less, most preferably 50 rpm or less. The blade peripheral speed is calculated by the following formula (a):

$$\text{Blade peripheral speed (m/s)} = \pi \times D \times N/60 \quad (a)$$

In formula (a), D represents blade diameter (m) and N represents the number of rotations (rpm).

25

Temperatures

[0095] For the lithiation step, the lower preferred temperature is about -78°C, about -40°C, about -20°C, about -10°C, or the most preferred lower temperature of about 0°C, and the upper limit of the temperature is about 40°C, about 20°C, or the most preferred upper limit of about

10°C. Thus, the preferred temperature range is about 0°C to about 10°C. If the reaction temperature for the lithiation is too low, the reaction viscosity may be too high. Conversely, if the reaction temperature is too high, the HNMe₂ will evaporate.

[0096] For the step of adding the alkyl trichlorotin (amination), the lower preferred
5 temperatures are about -78°C, about -40°C, about -20°C, about -10°C, most preferably about 0°C and the upper limit of the temperature is about 40°C, about 25°C, about 20°C, or the most preferred upper limit of about 10°C. Thus, the preferred temperature range is about 0°C to about 10°C. In other embodiments, however, the reaction is preferably performed at room
10 temperature. If the temperature is too low, the reaction rate will be too slow, whereas if the temperature is too high, byproducts will be produced.

Lithium Dimethylamide Concentration

[0097] The lithium dimethylamine is presently present in the solution in an amount of up to about 30wt%, more preferably up to about 20 wt%, up to about 15 wt%, or up to about 10 wt %.
15 It has been found that this dilute concentration provides an effective slurry for solid and liquid reactions. On the other hand, the productivity is lower in dilute condition in industrial conditions.

[0098] A method for preparing a monoalkyl tin triamide compound having formula (1a)



20

according to aspects of the disclosure involves the following steps, each of which is described in further detail below:

- (a) lithiating a solution comprising a dimethylamine and a first solvent to produce a lithium dimethylamide solution having a concentration of up to about 10 wt %;
- 25 (b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the amount of alkyl trichlorotin;
- (c) removing the LiCl salt product by filtration; and

(d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1a).

[0099] In formula (1a), R^1 is selected from R^A and R^B ; R^A is a primary alkyl group having about 1 to 10 carbon atoms and R^B is a secondary alkyl group having about 3 to 10 carbon atoms; and each R^2 is independently an alkyl group having about 1 to 10 carbon atoms.

[0100] It is preferred if the method steps (a) to (d) are performed substantially without light exposure, such as performing at least steps (a) and (b) in an amber or stainless-steel reactor. Light exposure, as explained below, has detrimental effects on the monoalkyl tin triamide compounds.

10 [0101] In some embodiments, the first solvent and the second solvent are the same.

[0102] The first step in the method involves lithiating dimethylamine in a solution of a first solvent such as hexanes in an amount of up to (but not greater than) 10 wt %. It has been found that this dilute concentration provides an effective slurry for solid and liquid reactions. The lithiation is performed at a preferred temperature of about -10°C to about 10°C , and at about 0°C to about 10°C in some embodiments. The lithiation may be performed with n-BuLi or other common lithiating reagents commonly used in the art, such as t-BuLi or HexylLi. Such lithiating agents are commonly employed in a hexanes solution and additional hexanes may be added so that the lithium dimethylamide is present in the desired concentration range. Excess dimethylamine is required to ensure that the lithiating reagent is fully reacted. The reaction is performed under an inert atmosphere, such as nitrogen or argon, and the addition rate is controlled to limit the exothermic reaction. Following the completion of the addition, the reaction mixture is warmed to room temperature to vaporize the butane byproduct and excess dimethylamine, then cooled to about -10°C to about 10°C , or to at about 0°C to about 10°C in some embodiments.

25 [0103] In the second method step, an alkyl trichlorotin solution in a second solvent such as toluene is added to the reaction mixture which is maintained at a preferred temperature of about -10°C to about 10°C , or at about 0°C to about 10°C in some embodiments. The alkyl trichlorotin is added such that the amount of lithium dimethyl amide is in an amount of at least about 3.09 equivalents relative to the amount of alkyl trichlorotin. The alkyl trichlorotin solution is

preferably added in a dropwise fashion to control the exothermic reaction. The second method step is preferably performed in an inert atmosphere, such as nitrogen or argon.

[00104] After completing the addition of alkyl trichlorotin to the reaction mixture, the reaction mixture is allowed to slowly warm to room temperature, such as over a period of about four hours, and then stirred for an additional time period at room temperature, such as for about four hours. The reaction mixture is then filtered, such as through sparkler, to remove the LiCl byproduct. Other means of filtration which are known in the art may also be employed. The resulting salt is then rinsed, such as with anhydrous hexanes, and the solvents (such as hexanes and toluene) are removed under reduced pressure by means known in the art to produce a crude product containing at least about 85 mol% monoalkyl tin triamide.

[00105] Finally, in some embodiments, the crude product having formula (1a) is distilled such as at about 1 torr, such as by using a 300 mm Pro-Pak column, discarding any distillate before the boiling point of the monoalkyl tin triamide, and collecting only the distillate obtained at the boiling point of the monoalkyl tin triamide to yield a product containing at least about 99 mol% monoalkyl tin triamide having formula (1a). The boiling points of two representative monoalkyl tin triamides are shown in Table 1. As an example, if the desired product is methyl tin triamide, distillates obtained at lower than 34°C are discarded, and only distillates obtained at 34-35°C are collected.

Table 1: Boiling Points of Representative Monoalkyl Tin Triamide Compounds

Compound	B.p.(°C)
MeSn(NMe ₂) ₃	34-35/1 torr
EtSn(NMe ₂) ₃	38.0-38.5/0.6 torr

[00106] The distillate obtained at the boiling point, such as 34-35 °C for methyl tin triamide, contains the monoalkyl tin triamide compound having a purity of at least about 99 mol%. For example, when the desired compound having formula (1a) is methyl tin triamide, the ¹¹⁹Sn NMR (neat) spectrum showing peaks at δ -16.78 (99.5%) and δ 56.23 (0.5%) agrees with published data for methyl tin triamide and dimethyl tin diamide, respectively.

[00107] Following distillation, the compound having formula (1a) contains less than about 1 mol% $R^1\text{Sn}(\text{NR}^2_2)_2(\text{N}(\text{R}^2)\text{CH}_2\text{NR}^2_2)$ or less than about 0.05 mol% $R^1\text{Sn}(\text{NR}^2_2)_2(\text{N}(\text{R}^2)\text{CH}_2\text{NR}^2_2)$.

[00108] A further aspect of the disclosure relates to a method of synthesizing a monoalkyl tin triamide compound having formula (1) and having a purity of at least about 85 mol%:



wherein R^1 is selected from R^A and R^B ,

R^A is a primary alkyl group having about 1 to 10 carbon atoms, and R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; the method
10 comprising:

(a) lithiating a solution comprising a dimethylamine and a first solvent to produce a lithium dimethylamide solution having a concentration of up to about 10 wt %;

(b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the
15 amount of alkyl trichlorotin;

(c) removing the LiCl salt product by filtration; and

(d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1), wherein first solvent is the same as the second solvent; and

20 distilling the compound having formula (1).

[00109] One method for preparing an isopropyl tin triamide compound having formula (3) according to aspects of the disclosure involves the following steps:

(a) lithiating a dimethylamine in a solution of hexanes at about 0°C to 10°C to produce lithium dimethylamide having a concentration in the hexanes of up to about 10 wt %;

25 (b) adding an isopropyl trichlorotin solution in toluene at about 0 to 10°C; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the amount of isopropyl trichlorotin;

(c) removing the LiCl salt product by filtration; and

(d) removing the hexanes and toluene under vacuum to produce a product containing at least about 99 mol% isopropyl tin triamide having formula (3).

[00110] A second method for preparing an isopropyl tin triamide compound having formula
5 (3) according to aspects of the disclosure involves the following steps:

(a) lithiating a dimethylamine in a solution of THF at about 0°C to 10°C to produce lithium dimethylamide;

(b) adding an isopropyl trichlorotin solution in toluene at about 0 to 10°C; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the
10 amount of isopropyl trichlorotin;

(c) removing the LiCl salt product by filtration; and

(d) removing the THF and toluene under vacuum to produce a product containing at least about 99 mol% isopropyl tin triamide having formula (3).

[00111] The processes for producing the isopropyl tin triamide compound having formula (3)
15 are the same as that described above for producing a monoalkyl tin triamide compound having formula (1) except that no distillation step may be required, that is, the product obtained after step (b) is already at least about 99 mol% pure. The methods described above for synthesizing the isopropyl tin triamide compound having formula (3) may also be employed to synthesize other alkyl tin triamide compounds having formula (1) with only the alkyl trichlorotin reactant
20 varied.

[00112] Isopropyl tin triamide produced by the methods according to the disclosure are substantially colorless liquids with ^{119}Sn NMR (neat) spectra showing peaks at δ -64.85 (99.8%) and δ - 19.06 ppm (0.2%), agreeing with published and collected data for isopropyl tin triamide and diisopropyl tin diamide respectfully. However, if desired, the product may be further
25 distilled to remove any undesired organic impurities and/or byproducts, as well as to isolate any photo decomposed byproduct. It has been found that, contrary to literature reports of collecting distillation product at 50-52°C at 1.4 mTorr, the product obtained at 49-53°C and 0.5 torr has desired high purity and is desirably colorless.

[00113] While performing the amination reaction to form monoalkyl tin triamides, the Kocheshkov-like comproportionation shown in scheme (I) above also occurs, and even low temperature, such as from about -78°C to 10°C, does not prevent the comproportionation reaction from occurring. Instead, the low temperature has been found to slow the substitution
5 reaction, which increases the risk of comproportionation. Further, light or heat can accelerate the comproportionation and form up to 15 mol% dialkyl tin amides as determined by ^{119}Sn NMR. According to the method reported by Lorberth, the amination reaction is performed as a solid slurry in hexanes and is a liquid reaction.

[00114] The methods described herein solve the known problems in several ways. First, it has
10 been found as described herein that to prevent comproportionation from occurring during the reaction, the lithium dimethylamide must be prepared properly. Second, the concentration of reactants is diluted, such as by employing lithium dimethylamide in a hexane slurry at a concentration of not more than about 10 wt %. Third, comproportionation may be minimized by performing the reaction at preferred temperatures of around -10°C to 10°C or about 0°C to about
15 10°C rather than at a lower temperature. Finally, THF may be employed instead of hexanes to form a homogeneous solution of lithium dimethylamide. Using the methods described herein, $\text{iPrSn}(\text{NMe}_2)_3$ can be produced at very high purity (containing no more than about 0.05 mol% dialkyl tin compounds and other specified impurities) without purification in a pilot scale.

20 Purification

[00115] Further aspects of the disclosure additionally relate to methods of purifying monoalkyl tin triamide compounds having formula (1) described above.

[00116] Methods of purification encompassed by the disclosure include:

- single-stage flash to remove metal contamination;
- 25 • fractional distillation to remove di-alkyl tin impurities as a heavy fraction;
- fractional distillation to remove tetra-alkyl tin impurities as a light fraction;
- using fractional distillation to remove di- and tetra-alkyl tin impurities simultaneously in either a batch or a continuous mode;

- using microchannel distillation to remove close boiling di-alkyl and tetra-alkyl impurities;
 - fractional distillation to remove metal contaminants simultaneously with di- and tetra-alkyl tin impurities;
 - 5 • use of light-impervious materials to prevent the formation of photo decomposition products of organotin compounds;
 - distillation in which the bottoms temperature is limited (such as to less than 112°C) to limit the formation and tetra-alkyl tin compounds;
 - 10 • running a condenser at or near the dew point of the overhead product to increase operating efficiency;
 - processing the heel from an initial distillation process, with a concentrated di-alkyl tin impurity, through the same or a different purification process to recover more of the desired isopropyl trimethylamine tin product and/or a purified di-alkyl tin product;
 - 15 • re-equilibrating the di- and tetra-alkyl byproducts to generate the desired isopropyl trimethylamine tin product;
 - recycling the heel from the initial distillation process through the last step of the manufacturing process to take advantage of the equilibrium disproportionation of the desired product into di-alkyl and tetra-alkyl tin impurities;
 - 20 • maintaining a minimum di-alkyl tin impurity level in the feed to the distillation to take advantage of the same equilibrium disproportionation;
 - using adsorbents or ion exchange resins to reduce metallic impurities, chloride impurities, water, and oxygen; and/or
 - using adsorbents to reduce color without introducing isopropyl trimethylamine tin decomposition products.
- 25 **[00117]** The size of the alkyl group (and its similarity in size with the NMe₂ group) can affect the boiling point differences between monoalkyl tin triamides and dialkyl tin diamides, and fractional distillation is typically the superior method to isolate the contaminants. As an example,

the difference between the molecular weights of $^i\text{PrSn}(\text{NMe}_2)_3$ (**A**) and $^i\text{Pr}_2\text{Sn}(\text{NMe}_2)_2$ (**B**) is small (294 g/mol and 293 g/mol, respectively). For the t-butyl compounds, the triamido tin compound is lighter than the diamido tin compound by only 13 g/mol. Considering the isopropyl analog, with a difference of only 1 g/mol and very similar polarity between the isopropyl and dimethylamino group, the difference in the boiling points of compounds **A** and **B** can be extremely small. The boiling points of these two compounds having purities of > 97 mol% were measured over a wide range of pressures, as shown in Fig. 1. It may be seen that the boiling point difference between the two compounds is within 2 °C in the pressure range of 0.7-10 torr. In another example, the boiling points of $^t\text{BuSn}(\text{NMe}_2)_3$ and $^t\text{Bu}_2\text{Sn}(\text{NMe}_2)_2$ at 0.4 torr are 50 °C (measured) and 90 °C (reported in *Chemische Berichte*, 112(8), 2798-803 (1979)), respectively. Accordingly, purification by fractional distillation is challenging and requires specific distillation parameters which have been specifically developed. Employing such purification methods can provide $^i\text{PrSn}(\text{NMe}_2)_3$ or analogs with <0.5 mol % dialkyl, < 0.4 mol% dialkyl, < 0.3 mol% dialkyl, < 0.2 mol% dialkyl, < 0.1 mol% dialkyl, < 0.05 mol% dialkyl, or no detectable dialkyl tin compound contamination as explained below.

[00118] When the difference in mass between the alkyl group and the amido group is large, (for example, the tBu-NMe₂ pair has a difference of 13 amu), purification by fractional distillation is expected to be less difficult. When the difference is small, the purification is expected to be more difficult. For example, the iPr-NMe₂ pair has a difference of -1 amu (i.e., the iPr group is slightly lighter than the amido group). In other examples, the cyclohexyl - NMe₂ pair has a molecular weight difference of 39 amu and the cycloheptyl - NMe₂ pair has a molecular weight difference of 53 amu. Schwarzenbach et al. (*Environmental Organic Chemistry*; 56-75 (1993)) observes that increasing component molecular weight retards the vapor pressure over a range of molecular weights for an analogous series of compounds. Essentially, a compound having more electrons has stronger London forces. However, this does not address the non-ideal behavior often observed in multicomponent vapor liquid equilibrium.

[00119] A further aspect of the disclosure relates to a method of using fractional distillation to purify $^i\text{PrSn}(\text{NMe}_2)_3$ having an initial purity of at least about 85 mol%, and even a purity of at least about 97 mol% or at least about 99 mol%. The method comprises performing a fractional distillation using an operating pressure of about 0.1 to about 50 torr (such as greater than about

0.1 torr, greater than about 0.2 torr, greater than about 0.3 torr, preferably greater than about 0.5 torr, more preferably greater than about 1 torr, preferably less than about 50 torr, less than about 30 torr, less than about 20 torr, less than about 10 torr, most preferably about 1 torr). If the pressure is too high, the formation of decomposition and redistribution products is accelerated. If the pressure is too low, volatilization speed is too high and separation efficiency through the distillation column is too low.

[00120] The fractional distillation preferably employs a pot temperature of about 50°C to about 120°C (preferably greater than about 50°C, greater than about 60°C, preferably greater than about 70°C, preferably greater than about 80°C, preferably greater than about 90°C, preferably greater than about 100°C, most preferably greater than about 105°C and preferably less than about 120°C, preferably less than about 115°C, most preferably about 110°C). If the pot temperature is too low, the volatilization speed is too low and the distillation time is too long. Conversely, if the pot temperature is too high, decomposition of the product is accelerated.

[00121] The fraction distillation preferably employs a condenser temperature within about 10°C, more preferably within about 7°C, more preferably within about 5°C, more preferably within about 3°C, most preferably within about 1°C of the dew point of the desired compound having formula (1) such as $iPrSn(NMe_2)_3$ at the employed operating pressure and a reflux ratio of about 10 to 100 (preferably about 20 to 80, more preferably about 40 to 60, more preferably about 50), thereby obtaining a sample of $iPrSn(NMe_2)_3$ having a purity of greater than about 99.5 mol%. In one embodiment, the purified sample of $iPrSn(NMe_2)_3$ contains less than about 0.1 mol% $(iPr)_2Sn(NMe_2)_2$ as determined by known analytical methods, such as GC and HPLC or is even undetectable by ^{119}Sn NMR.

[00122] Thus, one method of purification of $iPrSn(NMe_2)_3$ according to the disclosure employs fractional distillation using a pot temperature below about 112°C to avoid the formation of the tetramethylamido tin compound $Sn(NMe_2)_4$ and the removal of substantial amounts of the dialkyl tin compound $(iPr)_2Sn(NMe_2)_2$.

[00123] For example, the following conditions may be employed in the fractional distillation purification method of $iPrSn(NMe_2)_3$ according to aspects of the disclosure: 10 torr pressure, 105°C pot temperature, 95°C condenser temperature, and a reflux ratio of 50. Starting with a feed purity of 97% $iPrSn(NMe_2)_3$, fractional distillation using these parameters produces a cut of

99.5% with a corresponding 95.7% in the bottoms product after removing 46 g from an initial charge of 8.6 kg. Purity is determined using ^{119}Sn NMR without diluting the sample with deuterated solvent.

- [00124]** Monoalkyl tin triamide compounds can undergo disproportionation to the dialkyl tin diamide and the tetraamide compounds. The degree of disproportionation is affected by the temperature in the distillation pot, with higher temperatures expected to lead to higher degrees of disproportionation. The disproportionation activation energy is related to the size of the alkyl group (R). For example, when R is a methyl group, disproportionation can be observed around 45 °C. As another example, when R is an isopropyl group, the disproportionation occurs around 110 °C. Disproportion of the tert-butyl group occurs at higher temperatures. The two impurities resulting from disproportionating the mono-alkyl tin tri-amide compounds differ in molecular weight from the starting mono-alkyl compound in accordance with the difference between the masses of the alkyl and amido groups. One product will be heavier than the starting mono-alkyl tin tri-amide and the other product will be lighter than the mono-alkyl tin tri-amide. Consequently, the lighter compound is expected to appear in the distillate fraction and the heavier compound to appear in the bottom fraction from the distillation, guaranteeing both a light and a heavy impurity and making the distillation more difficult. Thus, it has been found that limiting the pot temperature, and thus the degree of disproportionation, not only improves the yield by limiting loss of the desired mono-alkyl product, but also avoids the generation of additional impurity to be removed. As is well known in the art, determining the optimal conditions for separating similar components using distillation is not straightforward or predictable, and requires significant analysis and experimentation of the various inter-related parameters.

Light Sensitivity

- [00125]** It has been found that monoalkyl tin triamide compounds are light sensitive, so that proper light protection is necessary during reaction and purification. Freshly prepared $\text{iPrSn}(\text{NMe}_2)_3$ is a colorless liquid. However, when an NMR sample of $\text{iPrSn}(\text{NMe}_2)_3$ is allowed to sit in the lab under normal room lighting, the sample turns yellow. This change in color is highlighted by the shelf-life data shown in Fig. 2. After exposure to light, there is a new ^{119}Sn resonance at -84 ppm which indicates the formation of a light-induced decomposition by-product, the compound having formula (5), $\text{iPrSn}(\text{NMe}_2)_2(\text{NMeCH}_2\text{NMe}_2)$. The ^{119}Sn NMR

depicting the formation of the compound having formula (5) is shown in Fig. 3. The rate of photodecomposition is increased with increasing temperature. Accordingly, maintaining the purified samples of $iPrSn(NMe_2)_3$ in the dark (without light exposure) minimizes the formation of undesirable light-induced decomposition byproducts and making it possible to provide

5 $(iPr)Sn(NMe_2)_3$ in which a total content of substances having a chemical shift in the ^{119}Sn NMR spectrum of around -84 ppm in is less than 1% by mass. Light control during the reaction steps to produce the monoalkyl tin triamide compounds is also important and may be accomplished by employing amber or stainless-steel reactors or glass reactors which are shielded from light.

[00126] Similarly, the distillation may be performed using a stainless steel column packed

10 with a stainless steel packing material. Alternatively, the distillation may be performed in a light-shielded apparatus comprising glass such as glass equipment, glass-lined equipment, glass-coated equipment, etc. Shielding may be accomplished by any method known in the art such as, for example, employing light-shielded containers such as amber glass, metal (SUS) containers, wrapping the container with a light-shielding cover such as cloth, foil or film, using light-

15 shielding coatings, or performing the distillation in a dark room.

Storage

[00127] A method of storing a sample (such as, but not limited to a sample of more than about 0.5 kg) of a monoalkyl tin triamide compound having formula (1) and having a purity of at least about 99 mol% comprises storing the sample of the monoalkyltin triamide compound having

20 formula (1) substantially without light exposure and at a temperature of less than about 30°C. The sample of the compound having formula (1) may have a content of $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)_2$ of less than about 1 mol% or less than about 0.05 mol%.

[00128] The sample of the monoalkyl tin triamide compound having formula (1) may be stored for about three days to about one year, such as about a week or longer, not more than

25 about ten months, a period of about two to six weeks, and all intermediate times as desired. Preferably the sample is stored at a temperature of less than about 30°C, less than about 25°C, less than about 20°C, and preferably greater than about -10°C. "Substantively without light exposure" may be understood to mean that the sample is protected from light exposure to the greatest possible extent, such as by storage in an amber or stainless steel vessel. In embodiments,

the sample of the monoalkyltin triamide undergoes substantively no decomposition after a storage time of about three days to about one year as described above.

Reduction of Additional Impurities

- 5 [00129] It is reasonable to presume that metallic impurities in alkyl tin triamide compounds are present as metal chlorides. If so, removal may be affected over an adsorbent, such as BASF CL-750, a chloride adsorbent known in the industry. Additional chloride impurities may be present, such as amine hydrochlorides and lithium chlorides which may be carried forward in the production process and become impurities of concern. Removal over a chloride-scavenging adsorbent, e.g., CL-750, activated carbon, or activated alumina, may be effective for removal.
- 10 Finally, the desired tin compounds may contain water and oxygen impurities. Carbons promoted with metal halides and then activated have been used to remove water and oxygen from HCl gas, and a similar approach may be effective.

[00130] The invention will now be described in connection with the following, non-limiting examples.

15 Example 1: Column design and general operations

[00131] The following distillation parameters were employed in the Examples which follow:

- a. Glass-lined steel sump, nominal 16 liters
- b. 2" Schedule-40 316-SS heated column
- c. 0.24" 316L SS ProPak packing, 5 ft total column length
- 20 d. Off/On reflux splitter operating at apparent reflux ratios between 33 and 50
- e. Stainless steel shell-and-tube condenser operated as a total condenser
- f. 304SS receiver vessel
- g. 316SS product vessel

25 Example 2: Demonstration of Purification of (iPr)Sn(NMe₂)₃ by Distillation

[00132] A sample of (iPr)Sn(NMe₂)₃ having a purity of 97% was used as the feed, with a reflux ratio of 50, operating pressure of 10 Torr, pot temp 105-105.2 °C, and condenser

temperature of 95 °C. The product fraction purity was 99.5% and two inline distillate samples had purities of 99.8% and 99.7% (iPr)Sn(NMe₂)₃ using ¹¹⁹Sn NMR without diluting the sample with deuterated solvent.

5 Example 3: Effect of Condenser Temperature on Fractionation of (iPr)Sn(NMe₂)₃

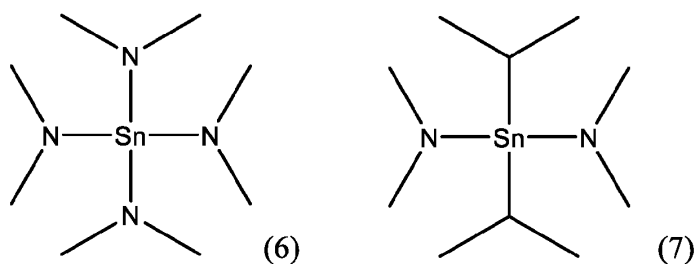
[00133] Three distillation runs of (iPr)Sn(NMe₂)₃ were performed with fractionating efficiency characterized using the Fenske equation (α^N) calculated analytically from samples collected from the pot and the receiver after running a period of time (2 to 8 hours). The reflux ratio was 50 and the pressure was 10 Torr. The results are tabulated below in Table 2 and
10 demonstrate that the condenser temperature has a significant effect on the overall performance of the distillation, as evaluated by higher fractionating efficiency. The dew point of iPrSn(NMe₂)₃ is observed to be 96 °C. Thus, operating the condenser at close approach to the dew point of the product stream is advantageous to effecting separation and maximizing the efficiency of the column.

15 **Table 2: Distillation Conditions of Example 3**

Run	Pot Jkt Temp (C)	Cndsr Temp (C)	Fractionating Efficiency
1	110	95	8.34
2	105	90	3.62
3	120	90	3.38

Example 4: Effect of Pot Temperature on Tetra-alkyl Sn(NMe₂)₄ Impurity Formation

[00134] The tetra-amido Sn(NMe₂)₄ impurity (6) is formed from the disproportionation of (iPr)Sn(NMe₂)₃, co-producing the already present di-alkyl (iPr)₂Sn(NMe₂)₂ impurity (7). The
20 effect becomes noticeable as the pot temperature increases from 110°C to 115°C.



[00135] The tetra-amido impurity (FW=295.0) is a light component in the distillation, and thus appears in the distillate. Conversely, the di-alkyl impurity (FW= 293) is a heavy component and appears in the bottoms product. This is counterintuitive based on the (admittedly slight) differences in formula weight. (iPr)Sn(NMe₂)₃ has a FW of 294.0. With both a light and a heavy impurity, the desired (iPr)Sn(NMe₂)₃ compound becomes a middle product. A batch distillation process would then require a forecut to remove the tetra- impurity. Continuous distillation would require two columns to recover the (iPr)Sn(NMe₂)₃.

[00136] The following conditions were employed:

- a. Condenser temp = 90°C
- b. Reflux ratio = 40 to 50
- c. Pressure = 10 Torr
- d. Pot temp = 111.1 to 111.9°C

[00137] Compositions measured in the system as shown in the following Tables 3 and 4 show the effect of increasing pot temperature on the degree of purification achieved. In Tables 3 and 4, the tin compounds (3), (6), and (7) have the structures shown above.

[00138] At 110 °C there was no tetra-amido tin (6) observed in the receiver nor in the samples collected from the reflux back to the column. At higher pot temperatures, the amount of tetra-amido tin in the receiver and reflux samples increased. None of the pot samples showed any tetra-amido tin, indicating that this compound is a light key, even though it is slightly heavier (by 1 amu) than the iPrSn(NMe₂)₃.

Table 3: Distillation Results of Example 4

Pot Temp (°C)	Pot Composition (mol%)			Receiver Composition (mol%)			Reflux Composition (mol%)		
	6	3	7	6	3	7	6	3	7
110	4.5	95.5	N.D.	1.1	98.9	N.D.	0.5	99.5	N.D.
112	3.6	96.4	N.D.	0.4	99.0	N.D.	0.0	98.9	1.1
115	4.2	95.8	N.D.	0.1	98.6	1.3	0.2	98.2	1.6

N.D.; Not detected by ^{119}Sn NMR

Table 4: Distillation Results Example 4

Compound	6	3	7
Mol weight	293	294	295
Mol% by NMR			
Pot	3.6	96.4	N.D.
Return 1	N.D.	98.8	1.2
Return 2	N.D.	99.1	0.9
Receiver	0.4	99.0	0.6

N.D.; Not detected by ^{119}Sn NMR

Example 5: Synthesis of Methyl tris(dimethylamino)tin

[00139] Anhydrous hexanes (970.5 g, 11.26 mol) and n-BuLi (429.8 g, 1.61 mol, 2.4 M solution in hexanes) were charged into a 5L reactor. Dimethylamine (145.1 g, 3.22 mol) was added subsurface at about 0~10°C. The reaction mixture was stirred for an additional four hours while warming to room temperature before methyl trichloro tin (125.0 g, 0.52 mol) in toluene (125g, 1.36 mol) was added dropwise at about 0~10°C. The resulting mixture was allowed to warm to room temperature over four hours and stirred for an additional four hours at room temperature. The reaction mixture was filtered through sparkler to remove the LiCl byproduct. The salt was rinsed with anhydrous hexanes (2 x 100 mL). The solvent was removed under reduced pressure, and the residue was distilled under reduced pressure (34-35 °C, 1 torr) with a 316 SS Pro-Pak column equipped with an amber distill head. The product was collected in an amber glass receiver as a clear colorless liquid. Yield: 74.0 g (53.4%), ^{119}Sn NMR (149.2 MHz; neat): δ -16.78. ^1H NMR (400 MHz; C_6D_6): δ 2.79 (s, 18H, NCH_3), δ 0.12 (s, 3H, CH_3). Purity

(^{119}Sn NMR): 99.5% product, 0.5% dimethyltin diamide. The ^{119}Sn and ^1H NMR spectra are shown in Figs. 4 and 5.

Example 6: Synthesis of Isopropyl tris(dimethylamino)tin

5 [00140] Anhydrous hexanes (6.3 kg, 73 mol) and n-BuLi (3.1 kg, 11.75 mol, 2.4 M solution in hexanes) were charged into a 22 L 316 stainless steel reactor equipped with a banana-shaped blade (CG-16). Dimethylamine (1.1 kg, 23.5 mol) was added subsurface at about 0~10°C with stirring at about 200 rpm. The reaction mixture was stirred for an additional four hours while
10 warming to room temperature before isopropyl trichloro tin (1.0 kg, 3.73 mol) was added dropwise at about 0~10°C. The resulting mixture was allowed to warm to room temperature over four hours and stirred for an additional four hours at room temperature. The reaction mixture was filtered through sparkler to remove the LiCl byproduct. The salt was rinsed with anhydrous hexanes (2 x 500 mL). The solvent was removed under reduced pressure. In order to further
15 purify the product, the residue was distilled under reduced pressure (49-53°C, 0.5 torr) with a 316 SS Pro-Pak column equipped with an amber distill head. The product was collected in an amber glass receiver as a clear colorless liquid. Yield: 803g (73.3%). ^{119}Sn NMR (149.2 MHz; neat): δ -64.85. ^1H NMR (400 MHz; C_6D_6): δ 2.85 (s, 18H, NCH_3), δ 1.61 (m, 1H, methine), δ 1.27 (d, 6H, CH_3). Purity (^{119}Sn NMR): 99.8% product, 0.2% diisopropyltin diamide (7), 0.0%
20 compound (5) (^{119}Sn NMR (149.2 MHz; neat): δ -84 ppm). The ^{119}Sn and ^1H NMR spectra are shown in Figs. 6 and 7. The product was stored in a 316 SS ampoule without light exposure at 25°C.

Example 7: Synthesis of Isopropyl tris(dimethylamino)tin

25 [00141] Anhydrous THF (1.0 kg, 13.86 mol) and n-BuLi (1.2 kg, 4.61 mol, 2.4 M solution in hexanes) were charged into an amber glass reactor. Dimethylamine (0.38 kg, 8.32 mol) was added subsurface at about 0~10°C. The reaction mixture was stirred for an additional four hours while warming to room temperature before isopropyl trichloro tin (0.4 kg, 1.49 mol) was added
30 dropwise at about 0~10°C. The resulting mixture was allowed to warm to room temperature over four hours and stirred for an additional four hours at room temperature. The reaction mixture was filtered through sparkler to remove the LiCl byproduct. The salt was rinsed with anhydrous

hexanes (2 x 200 mL). The solvent was removed under reduced pressure. In order to further purify the product, the residue was distilled under reduced pressure (49-53°C, 0.5 torr) with a 316 SS Pro-Pak column equipped with an amber distill head. The product was collected in an amber glass receiver as a clear colorless liquid. Yield: 305g (69.5%). ¹¹⁹Sn NMR (149.2 MHz; neat): δ -64.85. ¹H NMR (400 MHz; C₆D₆): δ 2.85 (s, 18H, NCH₃), δ 1.61 (m, 1H, methine), δ 1.27 (d, 6H, CH₃). Purity (¹¹⁹Sn NMR): 99.57% product, 0.43% diisopropyltin diamide. The ¹¹⁹Sn NMR spectrum is shown in Fig. 8.

Example 8: Effect of Temperature on Synthesis of Isopropyl tris(dimethylamino)tin

[00142] In three parallel experiments, anhydrous hexanes (217.1 g, 2.52 mol) and n-BuLi (186.6 g, 0.63 mol, 2.4 M solution in hexanes) were charged into a 5L reactor. Dimethylamine (56.8 g, 1.26 mol) was added subsurface at about 0~10°C. The reaction mixture was stirred for an additional four hours while warming to room temperature before isopropyl trichloro tin (53.6 g, 0.2 mol) was added dropwise at about -78°C, about -40°C, or about 0°C. The resulting mixture was allowed to warm to room temperature over four hours and stirred for an additional four hours at room temperature. The reaction mixture was filtered through sparkler to remove the LiCl byproduct. The salt was rinsed with anhydrous hexanes (2 x 100 mL). The solvent was removed under reduced pressure. The relative amounts of the desired product (3) and the biproduct (7) are shown in Table 5 and the ¹¹⁹Sn NMR spectra for the reactions at about 0°C, about -40°C, and about -78°C shown in Figs. 9, 10, and 11, respectively. It may be seen that the highest purities were obtained at about -78°C and about 0 °C and that the lowest purity was obtained at about -40 °C. Further, from among the three temperatures studied, the ideal temperature for the reaction is about 0 °C.

Table 5. Temperature Controlled Reaction Results

Pot Comp (mol%)	0 °C	-40°C	-78°C
7	0.87	2.03	1.08
3	99.13	97.97	98.92

Example 9: Effect of Photodecomposition on Synthesis of Isopropyl tris(dimethylamino)tin

[00143] Anhydrous hexanes (120.6 g, 1.40 mol) and n-BuLi (127 ml, 0.35 mol, 186.6 g, 2.76 M solution in hexanes) were charged into a 5L glass reactor with no shade to protect from light. Dimethylamine (48 ml, 0.70 mol) was added subsurface at about 0~10°C. The reaction mixture
5 was stirred for an additional four hours before isopropyl trichloro tin (30.4 g, 0.11 mol) was added dropwise at about 0°C. The resulting mixture was allowed to warm to room temperature over four hours and stirred for an additional sixteen hours at room temperature. The reaction mixture was filtered through a funnel to remove the LiCl byproduct. The salt was rinsed with anhydrous hexanes (100 mL). The solvent was removed under reduced pressure in a 1 L glass
10 flask with no shade. The relative amounts of the desired product (3) and biproducts (7) and (4) were determined by ^{119}Sn NMR to be: Product (3): 98.0 mol%, impurity (7): 0.4 mol%, compound (5): 1.6 mol%.

[00144] It will be appreciated by those skilled in the art that changes could be made to the
15 embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications within the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

I claim:

1. A monoalkyl tin triamide compound having formula (1) and having a purity of at least about 99 mol%:



wherein R^1 is selected from R^A , R^B , and R^C ;

R^A is a primary alkyl group having about 1 to 10 carbon atoms, R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and R^C is a tertiary alkyl group having about 3 to 10 carbon atoms;

10 each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; and

wherein a content of $\text{R}^1\text{Sn}(\text{NR}^2_2)_2(\text{N}(\text{R}^2)\text{CH}_2\text{NR}^2_2)$ is less than about 1 mol%.

2. The monoalkyl tin triamide compound according to claim 1, wherein a content of dialkyl bis(dialkylamino) tin having formula (2) is less than about 1 mol%.



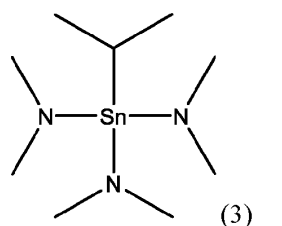
15 3. The monoalkyl tin triamide compound according to claim 1 or 2, wherein a total content of tetrakis(dialkylamino)tin is less than about 1 mol%.

4. The monoalkyl tin triamide compound according to any of the preceding claims, wherein a content of tetraalkyl tin is less than about 1 mol%.

20 5. The monoalkyl tin triamide compound according to any of the preceding claims, wherein the color is substantially colorless.

6. The monoalkyl tin triamide compound according to claim 5, wherein an APHA is less than about 20.

7. The monoalkyl tin triamide compound according to any of the preceding claims, wherein R^1 is an isopropyl group, R^2 is a methyl group, and the compound has formula (3):



8. The monoalkyl tin triamide compound according to claim 7, wherein the content of diisopropyl bis(dimethylamino) tin is less than about 1 mol%.

9. The monoalkyl tin triamide compound according to claim 5, wherein a total
5 content of tetrakis(dimethylamino)tin is less than about 1 mol%.

10. The monoalkyl tin triamide compound according to any of the preceding claims, wherein the content of $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)$ is less than about 0.05 mol%.

11. A method of synthesizing a monoalkyl tin triamide compound having formula (1a) and having a purity of at least about 85 mol%:



wherein R^1 is selected from R^A and R^B ,

R^A is a primary alkyl group having about 1 to 10 carbon atoms and R^B is a secondary alkyl group having about 3 to 10 carbon atoms; and

15 each R^2 is independently an alkyl group having about 1 to 10 carbon atoms; the method comprising:

(a) lithiating a solution comprising a dimethylamine and a first solvent to produce a lithium dimethylamide solution having a concentration of up to about 10 wt %;

(b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the
20 amount of alkyl trichlorotin;

(c) removing the LiCl salt product by filtration; and

(d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1a).

12. The method according to claim 11, wherein the compound having formula (1a) has a purity of at least about 99 mol%.

5 13. The method according to claim 11 or 12, wherein the compound having formula (1a) contains less than about 1 mol% $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2_2)$.

14. The method according to claim 13, wherein the compound having formula (1a) contains less than about 0.05 mol% $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2_2)$.

10 15. The method according to any of claims 11-14, wherein step (b) is performed at about -78°C to about 40°C .

16. The method according to claim 15, wherein step (b) is performed at about 0°C to about 10°C .

15 17. The method according to any of claims 11-16, wherein the first solvent and the second solvent are each independently selected from the group consisting of a hydrocarbon solvent, an aromatic solvent, and an ether solvent.

18. The method according to any of claims 11-17, wherein steps (a) to (d) are performed substantially without light exposure.

19. The method according to any of claims 11-18, wherein steps (a) and (b) are performed in a stainless steel vessel.

20 20. The method according to claim 11, further comprising distilling the compound having formula (1a).

25 21. The method according to claim 20, wherein the distillation comprises distilling the crude product having formula (1a) at about 1 torr, discarding any distillate before the boiling point of the monoalkyl triamide having formula (1a), and collecting the distillate obtained at the boiling point of the monoalkyltin triamide having formula (1a) to yield a product containing at least about 99 mol% monoalkyl tin triamide having formula (1a).

22. The method according to claim 20 or 21, comprising performing a fractional distillation using an operating pressure of about 0.1 to about 50 torr and a pot temperature of about 50 to about 120°C, wherein the purified monoalkyl tin triamide compound having formula (1a) contains less than about 0.1 mol% of a dialkyl bis(dialkylamino)tin compound having
5 formula (2).

23. The method according to any of claims 20 to 22, comprising performing the distillation substantially without light exposure.

24. The method according to any of claims 20 to 23, comprising performing the distillation using a condenser temperature within about 1 to about 10°C of the dew point of the
10 monoalkyl tin triamide compound having formula (1a) at the operating pressure and at a reflux ratio of about 10 to about 100.

25. The method according to any of claims 20 to 24, wherein the distillation is performed using a stainless steel column packed with a stainless steel packing material.

26. The method according to any of claims 20 to 25, wherein the distillation is performed
15 a light-shielded apparatus comprising glass.

27. A method of storing a sample of a monoalkyl tin triamide compound having formula (1) and having a purity of at least about 99 mol%:



wherein R^1 is selected from R^A , R^B , and R^C ;

20 R^A is a primary alkyl group having about 1 to 10 carbon atoms, R^B is a secondary alkyl group having about 3 to 10 carbon atoms, and R^C is a tertiary alkyl group having about 3 to 10 carbon atoms;

each R^2 is independently an alkyl group having about 1 to 10 carbon atoms;

the method comprising storing the sample of the monoalkyltin triamide compound having
25 formula (1) substantively without light exposure and at a temperature of less than about 30°C.

28. The method according to claim 27, wherein the sample of the monoalkyl tin triamide compound having formula (1) is stored for about three days to about one year.

29. The method according to claim 27 or 28, wherein the sample of the monoalkyltin triamide undergoes substantively no decomposition after a storage time of about three days to
5 about one year.

30. The method according to any of claims 27 to 29, wherein a content of $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)_2$ in the sample of the monoalkyl tin triamide having formula (1) is less than about 1 mol%.

31. The method according to claim 30, wherein the content of $R^1Sn(NR^2)_2(N(R^2)CH_2NR^2)_2$ in the sample of the monoalkyl tin triamide having formula (1) is
10 less than about 0.05 mol%.

32. The monoalkyl tin triamide compound having formula (1) according to any of claims 1 to 10, wherein R^1 is selected from R^A and R^B and the compound is produced by a method comprising:

15 (a) lithiating a solution comprising a dimethylamine and a first solvent to produce a lithium dimethylamide solution having a concentration of up to about 10 wt %;

(b) adding a solution comprising an alkyl trichlorotin and a second solvent; wherein the amount of lithium dimethylamide in the solution is at least about 3.09 equivalents relative to the amount of alkyl trichlorotin;

20 (c) removing the LiCl salt product by filtration; and

(d) removing the first solvent and the second solvent under vacuum to produce a crude product containing the monoalkyl tin triamide having formula (1).

33. The method according to claim 32, wherein step (b) is performed at about -78°C to about 40°C.

25 34. The method according to claim 33, wherein step (b) is performed at about 0°C to about 10°C.

35. The method according to any of claims 32-34, wherein the first solvent and the second solvent are each independently selected from the group consisting of a hydrocarbon solvent, an aromatic solvent, and an ether solvent.

36. The method according to any of claims 32-35, wherein steps (a) to (d) are
5 performed substantially without light exposure.

37. The method according to any of claims 32-36, wherein steps (a) and (b) are performed in a stainless steel vessel.

38. The method according to any of claims 32-37, further comprising distilling the compound having formula (1).