lithography process, the resist film is directly in contact with the refractive index liquid (immersion liquid) during the exposure, and hence the resist film is vulnerable to attack by the liquid. Resist compositions suitable for use in liquid immersion lithography processes must also be transparent to the exposure light. Further, conventional resist compositions may not be able to achieve a satisfactory resolution of pattern in liquid immersion lithography due to a change in their properties by the liquid, despite their utility in lithography employing the exposure through a layer of air.

[0011] Thus, there remains a need for improved transparent resist protection layers which can meet the increased requirements of the industry. Further, higher selectivity ALD films are needed for multi-patterning, as outlined above.

SUMMARY

[0012] Disclosed herein are compounds useful for the deposition of high purity tin oxide. Also disclosed are methods for the deposition of tin oxide films using such compounds. Such films demonstrate high conformality, high etch selectivity, high hardness and modulus, and are optically transparent.

~~[0012a] In an aspect, there is provided an organometallic compound of Formula 1:~~

~~R_x-Sn-A_{4-x} Formula I~~

~~wherein:~~

~~A is selected from the group consisting of ($Y_aR'_z$) and a 3- to 7-membered heterocyclic radical bound to Sn via nitrogen atom;~~

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

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

~~x is an integer from 0 to 4;~~

~~a is an integer from 0 to 1;~~

~~Y is selected from the group consisting of N, O, S, and P; and~~

~~z is 1 when Y is O, S or when Y is absent and z is 2 when Y is N or P.~~

~~[0012b] In another aspect, there is provided a composition comprising a combination of at least two organometallic compounds, wherein each of the organometallic compounds is represented by Formula I:~~

~~R_x-Sn-A_{4-x} Formula I~~

~~wherein:~~

A is selected from the group consisting of ($Y_aR'_z$) and a 3- to 7-membered N-containing heterocyclic group;

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

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

x is an integer from 0 to 4;

a is an integer from 0 to 1;

Y is selected from the group consisting of N and O; and

z is 1 when Y is O or when Y is absent and z is 2 when Y is N,

wherein at least one of the organometallic compounds is a compound represented by Formula 1 in which:

Y is N, a is 1, and x is 2; or

Y is N, a is 1, x is 0, 1, or 3, and R′ represents a combination of two different alkyl or aryl groups.

[0012ae] In another aspect, there is provided A a method comprising purifying an organometallic compound comprising

A) distilling in a first stage an organometallic compound of Formula 1:

R_x-Sn-$(NR'_2)_{4-x}$ Formula I

wherein:

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

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

x is an integer from 0 to 3;

wherein distilling in the first stage includes:

i) feeding feed material containing the first organometallic compound to a first distillation space at a reduced first pressure,

ii) heating the first distillation space to a first temperature to evaporate a portion of the feed material, and

iii) removing the evaporated portion of the feed material from the first distillation space such that a distillate is formed;

B) distilling, in at least one subsequent stage, the distillate from a previous stage, wherein distilling the distillate from a previous stage includes:

i) feeding distillate from a previous stage to a subsequent distillation space at a reduced subsequent pressure,

ii) heating the subsequent distillation space to a subsequent temperature to evaporate a portion of the distillate from a previous stage,

iii) removing the evaporated portion of the distillate from a previous stage from the subsequent distillation space such that a subsequent distillate is formed; and

C) removing a final distillate from last of the subsequent stages, wherein step B is repeated a number of times between 1 to and 19 sufficient to obtain the final distillate of the

organometallic compound having a purity greater than ~~95~~98% when measured by nuclear magnetic resonance (NMR) spectroscopy.

[0012~~b~~d] In another aspect, there is provided a high purity organometallic compound having a purity as measured by nuclear magnetic resonance (NMR) spectroscopy of greater than ~~95~~98% or having a metal contamination of less than 1 ppm, the high purity organometallic compound being a compound of Formula I:

R_x-Sn-$(NR'_2)_{4-x}$ Formula I

wherein:

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

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

x is an integer from 0 to 3.

[0013] Compounds include those of Formula I, below:

R_x-Sn-A_{4-x} Formula I

wherein:

A is selected from the group consisting of ($Y_aR'_z$) and a 3- to 7-membered N-containing heterocyclic group;

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

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

x is an integer from 0 to 4;

a is an integer from 0 to 1;

Y is selected from the group consisting of N, O, S, and P; and

z is 1 when Y is O, S or when Y is absent and z is 2 when Y is N or P

[0014] Also disclosed is the deposition of tin oxide using such compounds. The use of compounds of Formula I in the methods disclosed herein allows for chemical vapour deposition (CVD) and atomic layer deposition (ALD) of tin oxide at a low temperature, and produces films consisting of high purity tin oxide having low metallic impurities, low alpha

CLAIMS

What is claimed is:

1. An organometallic compound of Formula 1:

R_x-Sn-A_{4-x} Formula I

wherein:

A is selected from the group consisting of (YR'_z) and a saturated 3- to 7-membered heterocyclic radical bound to Sn via nitrogen atom;

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

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

x is an integer from 0 to 3;

Y is selected from the group consisting of N and O; and

z is 1 when Y is O and z is 2 when Y is N,

wherein when Y is N, x is 0 and R′ represents a combination of two different alkyl, or aryl groups, and wherein when Y is O, x is 2.

2. The organometallic compound of claim 1, wherein A is selected from the group consisting of (NR'_2) group and a saturated 3- to 7-membered heterocyclic radical bound to Sn via nitrogen atom.

3. The organometallic compound of claim 2, wherein A is an (NR'_2) group

4. The organometallic compound of claim 2, wherein A is a saturated 3- to 7-membered heterocyclic radical bound to Sn via nitrogen atom.

5. The organometallic compound of claim 4, wherein A is a pyrrolidinyl group.

6. The organometallic compound of claim 2, wherein A is (NEtMe).

7. The organometallic compound of claim 2, wherein each R and R′ group is an independently selected alkyl group having from 1 to 10 carbon atoms.

8. The organometallic compound of claim 7, wherein each R and R′ group is an independently selected alkyl group having from 1 to 6 carbon atoms.

9. The organometallic compound of claim 8, wherein each R and R′ group is an independently selected alkyl group having from 1 to 4 carbon atoms.

10. The organometallic compound of claim 2, wherein each R and R′ is independently selected from the group consisting of methyl, ethyl, propyl, iso-propyl, tert-butyl, iso-butyl and n-butyl.

11. The organometallic compound of claim 2, wherein the compound of Formula I is selected from the group consisting of Sn(Pyrrolidinyl)$_4$, and Bu_2Sn(Pyrrolidinyl)$_2$.

12. A composition comprising a combination of at least two organometallic compounds, wherein each of the organometallic compounds is represented by Formula I:

R_x-Sn-A_{4-x} Formula I

wherein:

A is selected from the group consisting of ($Y_aR'_z$) and a 3- to 7-membered N-containing heterocyclic group;

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

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

x is an integer from 0 to 4;

a is an integer from 0 to 1;

Y is selected from the group consisting of N and O; and

z is 1 when Y is O or when Y is absent and z is 2 when Y is N,

wherein at least one of the organometallic compounds is a compound represented by Formula 1 in which:

Y is N, a is 1, and x is 2; or

Y is N, a is 1, x is 0, 1, or 3, and R′ represents a combination of two different alkyl, or aryl groups.

~~13. The composition of claim 12, wherein at least one of the organometallic compounds is selected from the group consisting of $MeSn(NMe_2)_3$ and $Sn(NMe_2)_4$.~~

~~14.~~1. A method comprising purifying an organometallic compound comprising:

A) distilling in a first stage an organometallic compound of Formula 1:

R_x-Sn-$(NR'_2)_{4-x}$ Formula I

wherein:

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

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

x is an integer from 0 to 3;

wherein distilling in the first stage includes:

i) feeding feed material containing the first organometallic compound to a first distillation space at a reduced first pressure,

ii) heating the first distillation space to a first temperature to evaporate a portion of the feed material, and

iii) removing the evaporated portion of the feed material from the first distillation space such that a distillate is formed;

B) distilling, in at least one subsequent stage, the distillate from a previous stage, wherein distilling the distillate from a previous stage includes:

i) feeding distillate from a previous stage to a subsequent distillation space at a reduced subsequent pressure,

ii) heating the subsequent distillation space to a subsequent temperature to evaporate a portion of the distillate from a previous stage,

iii) removing the evaporated portion of the distillate from a previous stage from the subsequent distillation space such that a subsequent distillate is formed; and

C) removing a final distillate from last of the subsequent stages, wherein step B is repeated a number of times between 1 ~~to~~ and 19 sufficient to obtain the final distillate of the organometallic compound having a purity greater than ~~95%~~98% when measured by nuclear magnetic resonance (NMR) spectroscopy.

~~15.~~2. The method of claim ~~14~~1, wherein step B is repeated a number of times between 1 and 19 sufficient to reduce metal contamination to <1ppm.

~~16.~~3. The method of claim ~~14~~1, wherein step B is repeated a number of times between 1 and 19 sufficient to reduce metal contamination to <100ppb.

~~17.~~4. The method of claim ~~14~~1, wherein step B is repeated a number of times between 1 and 19 sufficient~~-~~ to reduce metal contamination to <10ppb.

~~18.~~5. The method of claim ~~14~~1, wherein step B is repeated a number of times between 1 and 19 sufficient to reduce metal contamination to 1ppb or less.

~~19.~~6. The method of claim ~~14~~1, wherein, in each subsequent stage, the distillation space has a subsequent pressure that is lower than a subsequent pressure in a previous stage.

~~20.~~7. The method of claim ~~19~~6, wherein, in each subsequent stage, a subsequent temperature is lower than a subsequent temperature in a previous stage.

~~21.~~8. The method of claim ~~14~~1, wherein, in each stage, the heating step is by steam in tubes and, in each subsequent stage, steam in the tubes is the evaporated portion of the feed material or distillate from a previous stage.

~~22.~~9. The method of claim ~~14~~1, wherein (NR'$_2$) is (NMe$_2$), (NEtMe), or (NEt$_2$).

~~23.~~10. The method of claim ~~14~~1, wherein the organometallic compound of Formula I is selected from the group consisting of Me$_2$Sn(NMe$_2$)$_2$, Me$_2$Sn(NEtMe)$_2$, t-BuSn(NEtMe)$_3$, t-BuSn(NMe$_2$)$_3$, t-BuSn(NEt$_2$)$_3$, i-PrSn(NEtMe)$_3$, i-PrSn(NMe$_2$)$_3$, n-PrSn(NEtMe)$_3$, n-PrSn(NMe$_2$)$_3$, EtSn(NEtMe)$_3$, i-BuSn(NEtMe)$_3$, i-BuSn(NMe$_2$)$_3$, n-BuSn(NMe$_2$)$_3$, sec-BuSn(NMe$_2$)$_3$, Et$_2$Sn(NEtMe)$_2$, Me$_2$Sn(NEtMe)$_2$, Sn(NMe$_2$)$_4$, Sn(NEt$_2$)$_4$, Sn(NEtMe)$_4$, Bu$_2$Sn(NEtMe)$_2$, Et$_2$Sn(NMe$_2$)$_2$, and Me$_2$Sn(NEt$_2$)$_2$.

~~24.~~11. The method of claim ~~23~~10, wherein the organometallic compound of Formula I is Sn(NMe$_2$)$_4$.

~~25.~~12. A high purity organometallic compound having a purity as measured by nuclear magnetic resonance (NMR) spectroscopy of greater than ~~95%~~98% or having a metal contamination of less than 1 ppm, the high purity organometallic compound being a compound of Formula I:

R_x-Sn-$(NR'_2)_{4-x}$ Formula I

wherein:

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

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

x is an integer from 0 to 3.

~~26. The high purity organometallic compound of claim 25, wherein the purity as measured by NMR spectroscopy is greater than 98%.~~

~~27.~~13. The high purity organometallic compound of claim ~~25~~12, wherein (NR'$_2$) is (NMe_2), (NEtMe), or (NEt_2).

~~28.~~14. The high purity organometallic compound of claim ~~25~~12, wherein each R group is an independently selected alkyl group having from 1 to 4 carbon atoms.

~~29.~~15. The high purity organometallic compound of claim ~~25~~12, wherein, each R' group represents different alkyl groups.

~~30.~~16. The high purity organometallic compound of claim ~~25~~12, wherein the organometallic compound of Formula I is selected from the group consisting of $Me_2Sn(NMe_2)_2$, $Me_2Sn(NEtMe)_2$, t-$BuSn(NEtMe)_3$, t-$BuSn(NMe_2)_3$, t-$BuSn(NEt_2)_3$, i-$PrSn(NEtMe)_3$, i-$PrSn(NMe_2)_3$, n-$PrSn(NEtMe)_3$, n-$PrSn(NMe_2)_3$, $EtSn(NEtMe)_3$, i-$BuSn(NEtMe)_3$, i-$BuSn(NMe_2)_3$, n-$BuSn(NMe_2)_3$, sec-$BuSn(NMe_2)_3$, $Et_2Sn(NEtMe)_2$, $Me_2Sn(NEtMe)_2$, $Sn(NMe_2)_4$, $Sn(NEt_2)_4$, $Sn(NEtMe)_4$, $Bu_2Sn(OMe)_2$, t-$BuSn(OtBu)_3$, t-$BuSn(OnBu)_3$, n-$BuSn(OtBu)_3$, i-$BuSn(OtBu)_3$, sec-$BuSn(OtBu)_3$, i-$PrSn(OtBu)_3$, n-$PrSn(OtBu)_3$, $Bu_2Sn(NEtMe)_2$, $Et_2Sn(NMe_2)_2$, and $Me_2Sn(NEt_2)_2$.

~~31.~~17. The high purity organometallic compound of claim ~~25~~12, wherein the organometallic compound of Formula I is $Sn(NMe_2)_4$.

~~32.~~18. The high purity organometallic compound of claim ~~25~~12, wherein the metal contamination is less than 100 ppb.

19. The high purity organometallic compound of claim ~~32~~12, wherein the metal contamination is 10 ppb or less.

~~33.~~20. The high purity organometallic compound of claim 12, wherein the metal contamination is 1 ppb or less