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 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.

[0012b] In another aspect, there is provided a composition comprising the organometallic compound of any one of the compounds as defined above and another organometallic compound containing Sn.

[0012c] In another aspect, there is provided a method for the deposition of a tin oxide layer on a substrate by a vapour deposition process, the method comprising the steps of:

a. providing at least one substrate having functional O-H groups covering the surface;

b. delivering to said substrate the organometallic compound as defined above in the gaseous phase;

c. delivering to said substrate an oxygen source in the gaseous phase, forming the tin oxide layer; and

d. repeating steps a to c to generate the desired thickness of the tin oxide layer,

wherein steps b and c are carried out under activating conditions.

[0012d] In another aspect, there is provided a method for spacer-defined double patterning deposition, the method comprising the steps of:

(a) depositing a layer of (photo)resist onto a substrate having functional O-H groups covering the surface, forming a pattern in the resist with electron-beam (e-beam) lithography, and developing the photoresist to give the pattern;

(b) depositing a spacer layer onto the resist using energy-enhanced ALD in the presence of the organometallic compound as defined above;

(c) performing an anisotropic etch to remove the tops of the features, using reactive ion etching (RIE) or ion milling (IM);

(d) removing the photoresist, either by a wet or plasma etch;

(e) anisotropically etching into the target layer; and

(f) removing the spacer, leaving the patterned substrate.

[0012e] In another aspect, there is provided a method of using multistage distillation to purify the organometallic compound as defined above.

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

$$R_x\text{-}Sn\text{-}A_{4-x} \qquad \text{Formula I}$$

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

[0021] In embodiments, the compound of Formula I is selected from the group consisting of $Me_2Sn(NEtMe)_2$ and $Me_2Sn(NMe_2)_2$.

[0022] In embodiments, the compound of Formula I is $Me_2Sn(NMe_2)_2$.

[0023] In embodiments, a composition is provided that comprises the organometallic compound of any of the disclosed compounds and another organometallic compound containing Sn. The another organometallic compound may be a compound of Formula I.

[0024] In various embodiments, another organometallic compound is selected from the group consisting of $MeSn(NMe_2)_3$ and $Sn(NMe_2)_4$.

[0025] A method id disclosed for the deposition of a tin oxide layer on a substrate by a vapour deposition process. The method comprises the steps of:

(a) providing at least one substrate having functional O-H groups covering the surface;

(b) delivering to said substrate the organometallic compound as defined herein in the gaseous phase;

(c) delivering to said substrate an oxygen source in the gaseous phase, forming the tin oxide layer; and

(d) repeating steps a to c to generate the desired thickness of the tin oxide layer,

(e) wherein steps b and c are carried out under activating conditions.

[0026] In certain embodiments, the activation condition is plasma generation.

[0027] A method is also disclosed for spacer-defined double patterning deposition. The method comprises the steps of:

(a) depositing a layer of (photo)resist onto a substrate having functional O-H groups covering the surface, forming a pattern in the resist with electron-beam (e-beam) lithography, and developing the photoresist to give the pattern;

(b) depositing a spacer layer onto the resist using energy-enhanced ALD in the presence of the organometallic compound as defined herein;

(c) performing an anisotropic etch to remove the tops of the features, using reactive ion etching (RIE) or ion milling (IM);

(d) removing the photoresist, either by a wet or plasma etch;

(e) anisotropically etching into the target layer; and

(f) removing the spacer, leaving the patterned substrate.

[0028] In an embodiment, a method of using multistage distillation to purify the organometallic compounds disclosed. In an embodiment, 2 to 20 stages are required to reduce metal contamination to <1ppm. In an embodiment, 2 to 20 stages are required to

reduce metal contamination to <100ppb. In an embodiment, 2 to 20 stages are required to reduce metal contamination to <10ppb. In an embodiment, 2 to 20 stages are required to reduce metal contamination to 1ppb or less.

[0029] The foregoing and other features of the disclosure and advantages of the present disclosure will become more apparent in light of the following detailed description of the preferred embodiments, as illustrated in the accompanying figures. As will be realized, the disclosure is capable of modifications in various respects, all without departing from the disclosure. Accordingly, the drawings and the description are to be regarded as illustrative in nature, and not as restrictive

BRIEF DESCRIPTION OF THE DRAWINGS

[0030] Figure 1 shows a sectional view of one embodiment of a processing chamber useful for the processes disclosed herein.

[0031] Figure 2 illustrates schematically cross-sectional views of a substrate at different stages of an integrated circuit fabrication sequence.

[0032] Figure 3 is a process flow diagram depicting a method for depositing a tin oxide film

[0033] Figure 4 is a schematic representation of a spacer-defined double-patterning technique.

[0034] Figure 5 shows the NMR spectrum of Me_3SnNMe_2.

[0035] Figure 6 shows the NMR spectrum of $Sn(NMe_2)_4$.

[0036] Figure 7 shows the NMR spectrum of $Me_2Sn(NEtMe)_2$.

[0037] Figure 8 shows the NMR spectrum of $Bu_2Sn(NMe_2)_2$.

[0038] Figure 9 shows the NMR spectrum of Me_2SnEt_2.

[0039] Figure 10 shows the NMR spectrum of Me_4Sn.

[0040] Figure 11 shows the NMR spectrum of $Bu_2Sn(OMe)_2$.

[0041] Figure 12 shows the NMR spectrum of $Bu_2Sn(OAc)_2$.

[0042] Figure 13 shows the NMR spectrum of $Et_2Sn(NMe_2)_2$.

[0043] Figure 14 shows the NMR spectrum of $Me_2Sn(NEt_2)_2$.

[0044] Figure 15 shows the NMR spectrum of $Sn(Pyrrolodinyl)_4$.

[0045] Figure 16 shows the NMR spectrum of $Bu_2Sn(Pyrrolodinyl)_2$.

[0046] Figure 17 shows the NMR spectrum of $Et_2Sn(Pyrrolodinyl)_2$.

[0047] Figure 18 shows the NMR spectrum of $Me_2Sn(NMe_2)_2$.

[0048] Figure 19 shows the NMR spectrum of $tBuSn(NMe_2)_3$

[0049] Figure 20 shows the NMR of the reaction of $(NMe_2)_4Sn$ with ethanol.