(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
15 March 2018 (15.03.2018)

WIPO | PCT

(10) **International Publication Number**
WO 2018/048481 A1

(51) **International Patent Classification:**
C23C 16/455 (2006.01) *C23C 16/50* (2006.01)
C23C 16/18 (2006.01) *C07F 7/28* (2006.01)

(21) **International Application Number:**
PCT/US2017/026817

(22) **International Filing Date:**
10 April 2017 (10.04.2017)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
62/385,689 09 September 2016 (09.09.2016) US

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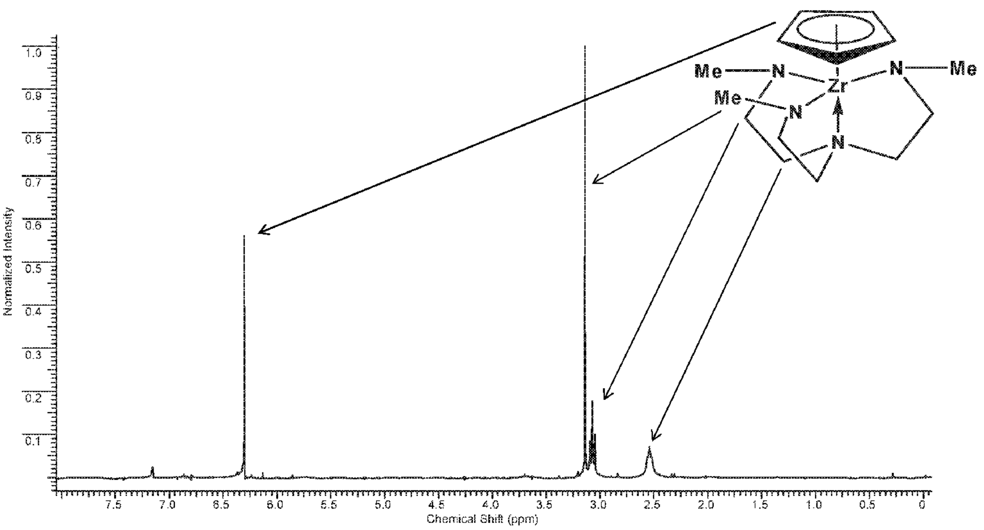
(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

(54) Title: GROUP 4 TRANSITION METAL-CONTAINING FILM FORMING COMPOSITIONS FOR VAPOR DEPOSITION OF GROUP 4 TRANSITION METAL-CONTAINING FILMS



NMR Spectrum of Recrystallized Product in C_6D_6

FIG 4

(57) **Abstract:** Group 4 transition metal-containing film forming compositions comprising Group 4 transition metal azatrane precursors are disclosed. Also disclosed are methods of synthesizing and using the disclosed precursors to deposit Group 4 transition metal-containing films on one or more substrates via vapor deposition processes.

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GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

GROUP 4 TRANSITION METAL-CONTAINING FILM FORMING COMPOSITIONS FOR VAPOR DEPOSITION OF GROUP 4 TRANSITION METAL-CONTAINING FILMS

Cross Reference to Related Applications

The present application claims the benefit of U.S. Provisional Application Serial No. 62/385,689 filed September 9, 2016, herein incorporated by reference in its entirety for all purposes.

Technical Field

Disclosed are Group 4 transition metal-containing film forming compositions comprising Group 4 transition metal azatrane precursors. Also disclosed are methods of synthesizing and using the disclosed precursors to deposit Group 4 transition metal-containing films on one or more substrates via vapor deposition processes.

Background

With the scaling down of semiconductor devices, new materials with high dielectric constant are required. Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) have become the main deposition techniques for such thin films. CVD and ALD may provide different films (metal, oxide, nitride, etc.) having a finely defined thickness and high step coverage. In CVD and ALD, the precursor molecule plays a critical role to obtain high quality films with high conformality and low impurities.

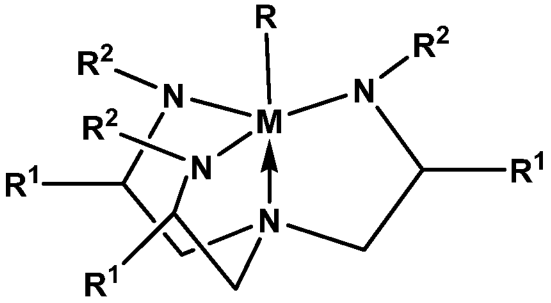
Among high-k dielectrics, Group 4 based materials, such as TiO_2, HfO_2 or ZrO_2, are very promising, whether used as pure or mixed oxides or in laminates. Group 4-containing films, such as TiN, may also be used for electrode and/or Cu diffusion barrier applications. The Group 4 oxides may also be used for their etch resistance properties in lithography applications, such as for hard masks or spacer-defined multiple patterning applications.

U.S. Pat. Nos. 5,344,948 and 5,464,656 to Verkade disclose neutral single-source molecular organic precursors containing tetradentate tripodal chelating ligands, including Me_2N-Ti((-N(Me)-CH_2CH_2-)$_3$N-) and tBuO-Ti((-N(Me)-CH_2CH_2-)$_3$N-).

A need remains for thermally stable, Group 4 precursor molecules capable of providing controlled film thickness during vapor phase deposition at high temperature.

Summary

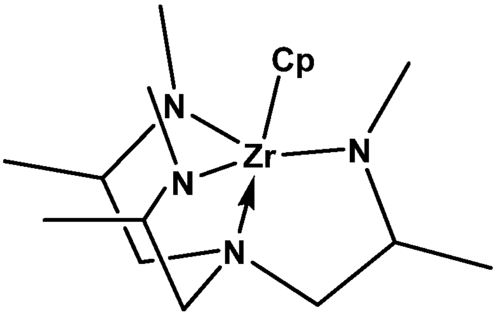
Group 4 transition metal-containing film forming compositions are disclosed comprising Group 4 transition metal azatrane precursors having the following formula:



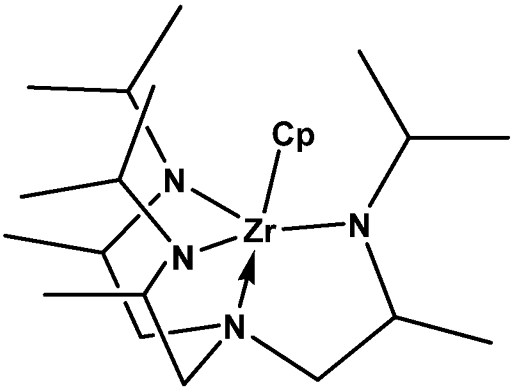
wherein M is selected from Group 4 transition metals consisting of Ti, Zr, or Hf; R is a halide, Cp, alkyl or silyl substituted Cp, alkoxy, alkyl, dialkylamino, disilylamino, trialkylsiloxy, amidinate, or DAD; each R^1 is independently selected from H or a C1 to C6 hydrocarbyl group; and each R^2 is independently selected from a C1 to C6 hydrocarbyl group. The disclosed Group 4 transition metal-containing film forming compositions may further include one or more of the following aspects:

- M being Ti;
- M being Zr;
- M being Hf;
- R being Cp;
- R being MeCp;
- R being EtCp;
- R being iPrCp;
- R being tBuCp;
- R being nBuCp;
- R being iPr_2Cp;
- R being Me_5Cp;

- R being Me_3SiCp;
- R being NR'_2, with each R' being independently selected from a C1-C6 hydrocarbyl group or a silyl group;
- R being NMe_2;
- R being NEt_2;
- R being NMeEt;
- R being $NiPr_2$;
- R being $NtBu_2$;
- Each R^1 independently being H, Me, Et, nPr, iPr, nBu, sBu, iBu, tBu, or tAmyl;
- Each R^1 being H;
- Each R^1 being Me;
- Each R^1 being iPr;
- Each R^2 independently being Me, Et, nPr, iPr, nBu, sBu, iBu, tBu, or tAmyl;
- Each R^2 being Me;
- Each R^2 being iPr;
- the Group 4 transition metal azatrane precursor being



- the Group 4 transition metal azatrane precursor being



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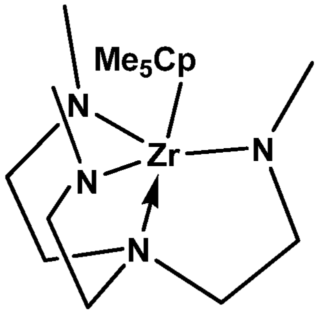

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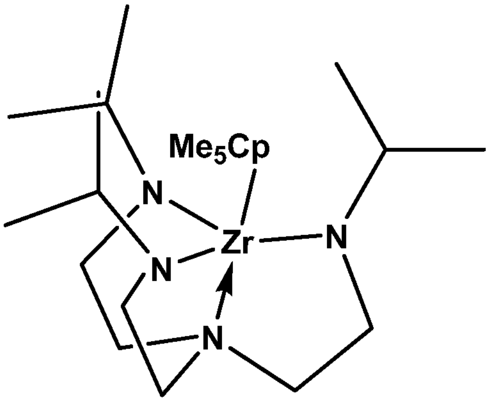

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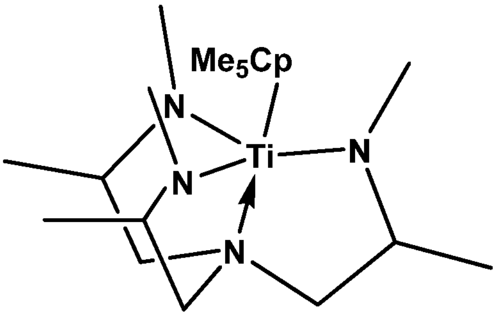

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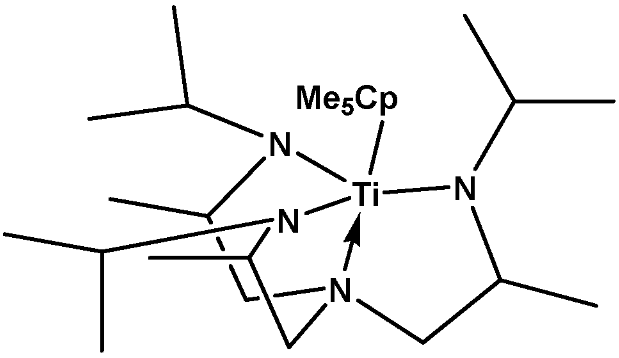

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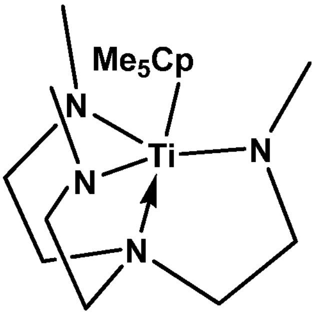

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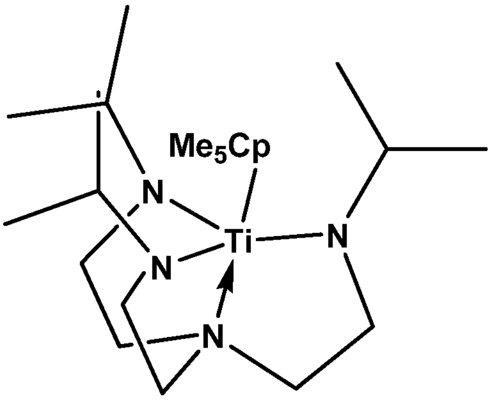

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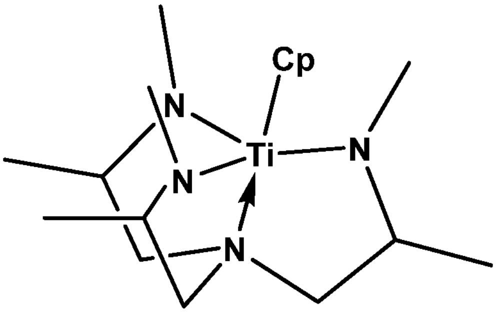
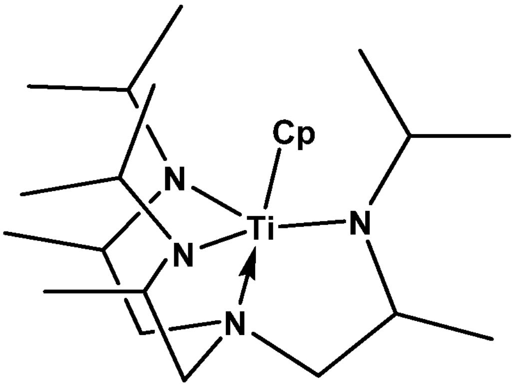
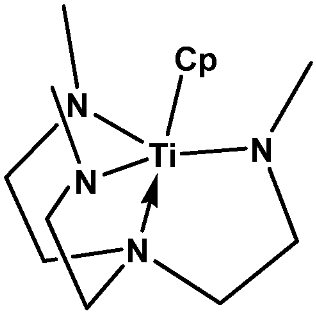


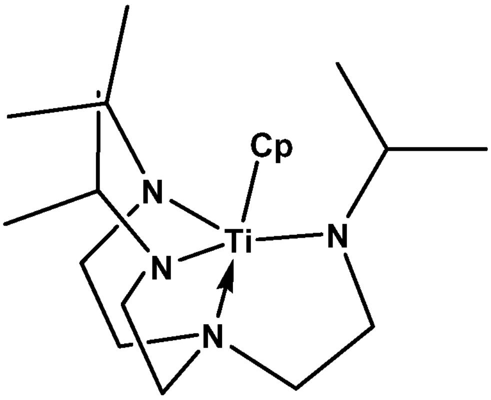
- the Group 4 transition metal azatrane precursor being



- the Group 4 transition metal azatrane precursor being



- the Group 4 transition metal azatrane precursor being



- the Group 4 transition metal-containing film forming composition comprising between approximately 0.1 molar % and approximately 50 molar % of the Group 4 transition metal azatrane precursor;
- the Group 4 transition metal-containing film forming composition having a viscosity between approximately 1 and approximately 20 cps, preferably between approximately 1 and approximately 5 cps, preferably around 3 cps;
- the Group 4 transition metal-containing film forming composition comprising between approximately 95% w/w to approximately 100% w/w of the Group 4 transition metal azatrane precursors;
- the Group 4 transition metal-containing film forming composition comprising between approximately 99% w/w to approximately 100% w/w of the Group 4 transition metal azatrane precursor;
- the Group 4 transition metal-containing film forming composition further comprising a solvent;
- the Group 4 transition metal-containing film forming composition comprising between approximately 0 % w/w and 5 % w/w of a hydrocarbon solvent;
- the solvent being selected from the group consisting of C1-C16 hydrocarbons, whether saturated or unsaturated, ketones, ethers, glymes,

esters, tetrahydrofuran (THF), dimethyl oxalate (DMO), and combinations thereof;

- the solvent being a C1-C16 hydrocarbon;
- the solvent being tetrahydrofuran (THF);
- the solvent being DMO;
- the solvent being an ether;
- the solvent being a glyme; and
- the difference between the boiling point of the Group 4 transition metal azatrane precursor and the solvent being less than 100°C.

Also disclosed are Group 4 transition metal-containing film forming composition delivery devices comprising a canister having an inlet conduit and an outlet conduit and containing any of the Group 4 transition metal-containing film forming compositions disclosed above. The disclosed delivery devices may include one or more of the following aspects:

- the Group 4 transition metal-containing film forming composition having a total concentration of non Group 4 metal contaminants of less than 10 ppmw;
- an end of the inlet conduit located above a surface of the Group 4 transition metal-containing film forming composition and an end of the outlet conduit located above the surface of the Group 4 transition metal-containing film forming composition;
- an end of the inlet conduit end located above a surface of the Group 4 transition metal-containing film forming composition and an end of the outlet conduit located below the surface of the Group 4 transition metal-containing film forming composition;
- an end of the inlet conduit end located below a surface of the Group 4 transition metal-containing film forming composition and an end of the outlet conduit located above the surface of the Group 4 transition metal-containing film forming composition;
- the Group 4 transition metal azatrane precursor being $CpZr((-N(Me)-CH_2-CH_2-)_3N-)$;
- the Group 4 transition metal azatrane precursor being $CpZr((-N(iPr)-CH_2-CH_2-)_3N-)$;

- the Group 4 transition metal azatrane precursor being $(Me_5Cp)Zr((-N(Me)-CH_2-CH_2-)_3N-)$;
- the Group 4 transition metal azatrane precursor being $(Me_5Cp)Zr((-N(iPr)-CH_2-CH_2-)_3N-)$;
- the Group 4 transition metal azatrane precursor being $CpTi((-N(Me)-CH_2-CH_2-)_3N-)$;
- the Group 4 transition metal azatrane precursor being $CpTi((-N(iPr)-CH_2-CH_2-)_3N-)$;
- the Group 4 transition metal azatrane precursor being $(Me_5Cp)Ti((-N(Me)-CH_2-CH_2-)_3N-)$; and
- the Group 4 transition metal azatrane precursor being $(Me_5Cp)Ti((-N(iPr)-CH_2-CH_2-)_3N-)$.

Also disclosed are processes for the deposition of Group 4 transition metal-containing films on one or more substrates. At least one Group 4 transition metal-containing film forming compositions disclosed above is introduced into a reactor having at least one substrate disposed therein. At least part of the Group 4 transition metal azatrane precursor is deposited onto the substrate(s) to form the Group 4 transition metal-containing film. The disclosed processes may further include one or more of the following aspects:

- introducing at least one reactant into the reactor;
- the reactant being plasma-treated;
- the reactant being remote plasma-treated;
- the reactant not being plasma-treated;
- the reactant being selected from the group consisting of H_2, NH_3, hydrazines (such as N_2H_4, $MeHNNH_2$, $MeHNNHMe$), organic amines (such as $NMeH_2$, $NEtH_2$, NMe_2H, NEt_2H, NMe_3, NEt_3, cyclic amines like pyrrolidine or pyrimidine), diamines (such as ethylene diamine, dimethylethylene diamine, tetramethylethylene diamine), aminoalcohols (such as ethanolamine $[HO-CH_2-CH_2-NH_2]$, bis ethanolamine $[HN(C_2H_5OH)_2]$ or tris ethanolamine$[N(C_2H_5OH)_3]$), pyrazoline, and pyridine;
- the reactant being selected from the group consisting of $(SiH_3)_3N$, hydridosilanes (such as SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{10}, Si_6H_{12}), chlorosilanes and chloropolysilanes (such as $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, Si_2Cl_6,

Si_2HCl_5, Si_3Cl_8), alkylsilanes (such as Me_2SiH_2, Et_2SiH_2, $MeSiH_3$, $EtSiH_3$), and aminosilanes (such as tris-dimethylaminosilane, bis-diethylaminosilane, di-isopropylaminosilane and other mono, dis or tris aminosilanes);

- the reactant being selected from the group consisting of NH_3, $N(SiH_{3)3}$, aminosilanes, and mixtures thereof;
- the reactant being selected from trialkylaluminum, dialkylaluminum halide, alkylamino and alkoxy derivatives of aluminum, and mixtures thereof;
- the reactant being NH_3;
- the reactant being selected from the group consisting of: O_2, O_3, H_2O, H_2O_2, NO, N_2O, NO_2, an alcohol, a diol (such as ethylene glycol), oxygen radicals thereof, and mixtures thereof;
- the reactant being H_2O;
- the reactant being O_2;
- the reactant being plasma treated O_2;
- the reactant being O_3;
- the Group 4 transition metal-containing film forming composition and the reactant being introduced into the reactor simultaneously;
- the reactor being configured for chemical vapor deposition;
- the reactor being configured for plasma enhanced chemical vapor deposition;
- the Group 4 transition metal-containing film forming composition and the reactant being introduced into the chamber sequentially;
- the reactor being configured for atomic layer deposition;
- the reactor being configured for plasma enhanced atomic layer deposition;
- the reactor being configured for spatial atomic layer deposition;
- the Group 4 transition metal-containing film being a Group 4 transition metal oxide (M_nO_m, wherein M is the Group 4 transition metal and each of n and m is an integer which inclusively range from 1 to 6);
- the Group 4 transition metal-containing film being TiO_2, ZrO_2 or HfO_2;
- the Group 4 transition metal-containing film being MM'_iO_x, wherein i ranges from 0 to 1; x ranges from 1 to 6; and M' is selected from a Group 3 element, a different Group 4 element (*i.e.*, M≠M'), a Group 5 element, a lanthanide, Si, Al, B, P or Ge; and

- the Group 4 transition metal-containing film being $MM'_iN_yO_x$, wherein i ranges from 0 to 1; x and y range from 1 to 6; and M' is selected from a Group 3 element, a different Group 4 element (*i.e.*, M≠M'), a Group 5 element, a lanthanide, Si, Al, B, P or Ge.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the following description and claims, and include:

As used herein, the indefinite article “a” or “an” means one or more.

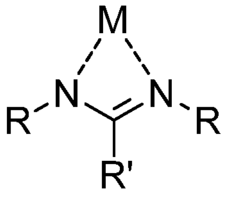
As used herein, the terms “approximately” or “about” mean ± 10% of the value stated.

As used herein, the term “independently” when used in the context of describing R groups should be understood to denote that the subject R group is not only independently selected relative to other R groups bearing the same or different subscripts or superscripts, but is also independently selected relative to any additional species of that same R group. For example in the formula $MR^1_x(NR^2R^3)_{(4-x)}$, where x is 2 or 3, the two or three R^1 groups may, but need not be identical to each other or to R^2 or to R^3. Further, it should be understood that unless specifically stated otherwise, values of R groups are independent of each other when used in different formulas.

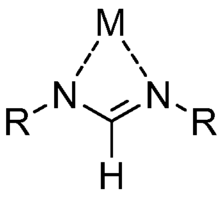
As used herein, the term “hydrocarbyl group” refers to a functional group containing carbon and hydrogen; the term “alkyl group” refers to saturated functional groups containing exclusively carbon and hydrogen atoms. The hydrocarbyl group may be saturated or unsaturated. Either term refers to linear, branched, or cyclic groups. Examples of linear alkyl groups include without limitation, methyl groups, ethyl groups, propyl groups, butyl groups, etc. Examples of branched alkyls groups include without limitation, t-butyl. Examples of cyclic alkyl groups include without limitation, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, etc.

As used herein, the abbreviation “Me” refers to a methyl group; the abbreviation “Et” refers to an ethyl group; the abbreviation “Pr” refers to a propyl group; the abbreviation “nPr” refers to a “normal” or linear propyl group; the abbreviation “iPr” refers to an isopropyl group; the abbreviation “Bu” refers to a butyl group; the abbreviation “nBu” refers to a “normal” or linear butyl group; the abbreviation “tBu” refers to a tert-butyl group, also known as 1,1-dimethylethyl; the abbreviation “sBu” refers to a sec-butyl group, also known as 1-methylpropyl; the abbreviation “iBu” refers to an iso-butyl group, also known as 2-methylpropyl; the term “amyl” refers to an amyl or pentyl group (i.e., a C5 alkyl group); the term “tAmyl” refers to a tert-amyl group, also known as 1,1-dimethylpropyl; the abbreviation “Cp” refers to cyclopentadienyl; the abbreviation “Cp*” refers to pentamethylcyclopentadienyl; the term “halide” refers to the halogen anions F^-, Cl^-, Br^-, and I^-; the term “silyl” refers to a R_3Si- ligand, wherein each R is independently H or a C1-C4 alkyl group; and the abbreviation “DAD” refers to diazadiene and more specifically “tBuDAD” refers to N,N-bis(tert-butyl)ethene-1,2-diaminato.

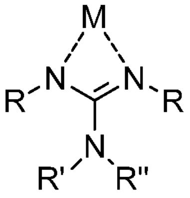
As used herein, the abbreviation “$N^{R, R'}$ R”-amd” or N^R R”-amd when R=R’ refers to the amidinate ligand [R-N-C(R”)=N-R’], wherein R, R’ and R” are H or defined alkyl groups, such as Me, Et, nPr, iPr, nBu, iBi, sBu or tBu; the abbreviation “$N^{R, R'}$-fmd” or N^R-fmd when R=R’ refers to the formidinate ligand [R-N-C(H)=N-R’], wherein R and R’ are defined alkyl groups, such as Me, Et, nPr, iPr, nBu, iBi, sBu or tBu; the abbreviation “$N^{R, R'}$, $N^{R'', R'''}$-gnd” or N^R, $N^{R''}$-gnd when R=R’ and R”=R’” refers to the guanidinate ligand [R-N-C(NR”R’”)=NR’], wherein R, R’, R” and R’” are defined alkyl group such as Me, Et, nPr, iPr, nBu, iBi, sBu or tBu. Although depicted here as having a double bond between the C and N of the ligand backbone, one of ordinary skill in the art will recognize that the amidinate, formidinate and guanidinate ligands do not contain a fixed double bond. Instead, one electron is delocalized amongst the N-C-N chain.



i) Amidinate ligand

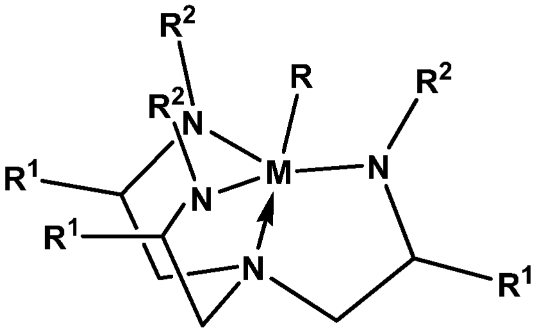


ii) Formamidinate ligand



iii) Guanidinate ligand

As used herein, the chemical formula $RM((-N(R^2)-CHR^1-CH_2-)_3N)$ refers to:



wherein M is selected from Group 4 transition metals consisting of Ti, Zr, or Hf; R is a halide, Cp, alkyl or silyl substituted Cp, alkoxy, alkyl, dialkylamino, disilylamino, trialkylsiloxy, amidine, or DAD; each R^1 is independently H or a C1 to C6 hydrocarbyl group; and each R^2 is independently a C1 to C6 hydrocarbyl group.

The standard abbreviations of the elements from the periodic table of elements are used herein. It should be understood that elements may be referred to by these abbreviations (e.g., Mn refers to manganese, Si refers to silicon, C refers to carbon, etc.). Additionally, Group 3 refers to Group 3 of the Periodic Table (i.e., Sc, Y, La, or Ac). Similarly, Group 4 refers to Group 4 of the Periodic Table (i.e., Ti, Zr, or Hf) and Group 5 refers to Group 5 of the Periodic Table (i.e., V, Nb, or Ta).

Any and all ranges recited herein are inclusive of their endpoints (i.e., x=1 to 4 or x ranges from 1 to 4 includes x=1, x=4, and x=any number in between), irrespective of whether the term “inclusively” is used.

Please note that the films or layers deposited, such as silicon oxide or silicon nitride, may be listed throughout the specification and claims without reference to their proper stoichiometry (i.e., SiO_2, Si_3N_4). The layers may include pure (Si) layers, carbide (Si_oC_p) layers, nitride (Si_kN_l) layers, oxide (Si_nO_m) layers, or mixtures thereof, wherein k, l, m, n, o, and p inclusively range from 1 to 6. For instance, silicon oxide is Si_nO_m, wherein n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, the silicon oxide layer is SiO_2 or SiO_3. These films may also contain Hydrogen, typically from 0 at% to 15 at%. However, since not routinely measured, any film compositions given ignore their H content, unless explicitly stated otherwise.

Brief Description of the Figures

For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying figures wherein:

FIG. 1 is a side view of one embodiment of a liquid Group 4 transition metal-containing film forming composition delivery device **1**;

FIG. 2 is a side view of a second embodiment of the Group 4 transition metal-containing film forming composition delivery device **1**;

FIG 3 is an exemplary embodiment of a solid precursor sublimator **100** for subliming solid Group 4 transition metal-containing film forming compositions;

FIG 4 is the ^{1}H NMR spectrum of $CpZr((-N(Me)-CH_2-CH_2-)_3N)$;

FIG 5 is a ThermoGravimetric Analysis/Differential Thermal Analysis (TGA/DTA) graph illustrating the percentage of weight loss (TGA) or the differential temperature (DTA) of $CpZr((-N(Me)-CH_2-CH_2-)_3N)$ with increasing temperature;

FIG 6 is the ^{1}H NMR spectrum of $CpZr((-N(iPr)-CH_2-CH_2-)_3N)$;

FIG 7 is a TGA/DTA graph illustrating the percentage of weight loss (TGA) or the differential temperature (DTA) of $CpZr((-N(iPr)-CH_2-CH_2-)_3N)$ upon temperature increase;

FIG 8 is the ^{1}H NMR spectrum of $MeCpZr((-N(Me)-CH_2-CH_2-)_3N)$;

FIG 9 is a TGA/DTA graph illustrating the percentage of weight loss (TGA) or the differential temperature (DTA) of $MeCpZr((-N(Me)-CH_2-CH_2-)_3N)$ upon temperature increase;

FIG 10 is the ^{1}H NMR spectrum of $Me_2N-Zr((-N(Me)-CH_2-CH_2-)_3N)$;

FIG 11 is a TGA/DTA graph illustrating the percentage of weight loss (TGA) or the differential temperature (DTA) of $Me_2N-Zr((-N(Me)-CH_2-CH_2-)_3N)$ upon temperature increase;

FIG 12 is the ^{1}H NMR spectrum of $Et_2N-Zr((-N(Me)-CH_2-CH_2-)_3N)$;

FIG 13 is a TGA/DTA graph illustrating the percentage of weight loss (TGA) or the differential temperature (DTA) of $Et_2N-Zr((-N(Me)-CH_2-CH_2-)_3N)$ upon temperature increase;

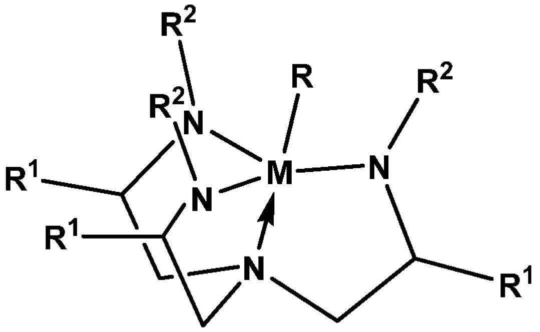
FIG 14 is the ^{1}H NMR spectrum of $Me_2N-Zr((-N(iPr)-CH_2-CH_2-)_3N)$;

FIG 15 is a TGA/DTA graph illustrating the percentage of weight loss (TGA) or the differential temperature (DTA) of $Me_2N\text{-}Zr((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$ upon temperature increase; and

FIG 16 is the ^1H NMR spectrum of $Me_2N\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$.

Description of Preferred Embodiments

Group 4 transition metal-containing film forming compositions are disclosed. The Group 4 transition metal-containing film forming compositions comprise Group 4 transition metal azatrane precursors having the following formula:



wherein M is selected from Group 4 transition metals consisting of Ti, Zr, or Hf; R is a halide, Cp, alkyl or silyl substituted Cp, alkoxy, alkyl, dialkylamino, disilylamino, amidinate, trialkylsiloxy, or DAD; each R^1 is independently H or a C1 to C6 hydrocarbyl group; and each R^2 is independently a C1 to C6 hydrocarbyl group.

Exemplary Ti-containing azatrane precursors include but are not limited to $Cl\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Cl\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Cl\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Cl\text{-}Ti((\text{-}N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Cp\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Cp\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Cp\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Cp\text{-}Ti((\text{-}N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $MeCp\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $MeCp\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $MeCp\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $MeCp\text{-}Ti((\text{-}N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $EtCp\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $EtCp\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $EtCp\text{-}Ti((N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $EtCp\text{-}Ti((N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $iPrCp\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $iPrCp\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $iPrCp\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $iPrCp\text{-}Ti((\text{-}N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Me_5Cp\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Me_5Cp\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Me_5Cp\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Me_5Cp\text{-}Ti((\text{-}N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Me_3SiCp\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Me_3SiCp\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $Me_3SiCp\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $Me_3SiCp\text{-}Ti((\text{-}N(iPr)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, $MeO\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $MeO\text{-}Ti((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$, $MeO\text{-}Ti((\text{-}N(Me)\text{-}CHMe\text{-}CH_2\text{-})_3N)$, MeO-Ti((-N(iPr)-CHMe-

CH$_2$-)$_3$N), tBuO-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBuO-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBuO-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), tBuO-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), Me-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBu-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBu-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBu-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), tBu-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), Et$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Et$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Et$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), Et$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeEtN-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeEtN-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeEtN-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), MeEtN-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), iPr$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), iPr$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), iPr$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), iPr$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBu$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBu$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBu$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), tBu$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBuDAD-Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBuDAD-Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBuDAD-Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), tBuDAD-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$SiO-)Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), or (Me$_3$SiO-)Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N).

Exemplary Zr-containing azatrane precursors include but are not limited to Cl-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cl-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cl-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Cl-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Cp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Cp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeCp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), MeCp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), EtCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), EtCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), EtCp-Zr((N(Me)-CHMe-CH$_2$-)$_3$N), EtCp-

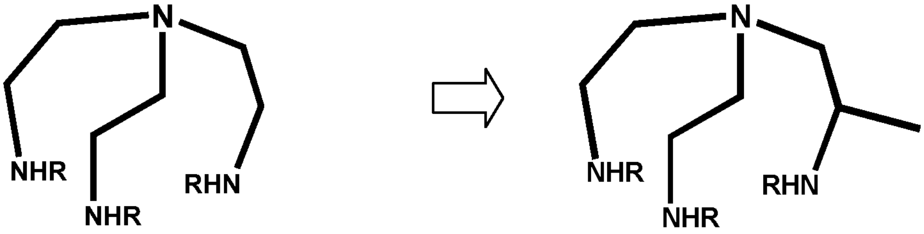
Zr((N(iPr)-CHMe-CH$_2$-)$_3$N), iPrCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), iPrCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), iPrCp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), iPrCp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeO-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeO-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeO-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), MeO-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBuO-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBuO-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBuO-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), tBuO-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Me-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBu-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBu-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBu-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), tBu-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Et$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Et$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Et$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Et$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeEtN-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeEtN-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeEtN-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), MeEtN-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), iPr$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), iPr$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), iPr$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), iPr$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBu$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBu$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBu$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), tBu$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), (Me$_2$HSi)$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), (Et$_3$Si)$_2$N-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBuDAD-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBuDAD-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBuDAD-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), tBuDAD-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$SiO-)Zr((-N(Me)-CH$_2$-

CH$_2$-)$_3$N), (Me$_3$SiO-)Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), or (Me$_3$SiO-)Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N).

Exemplary Hf-containing azatrane precursors include but are not limited to Cl-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cl-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cl-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Cl-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Cp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Cp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeCp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeCp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeCp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), MeCp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), EtCp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), EtCp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), EtCp-Hf((N(Me)-CHMe-CH$_2$-)$_3$N), EtCp-Hf((N(iPr)-CHMe-CH$_2$-)$_3$N), iPrCp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), iPrCp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), iPrCp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), iPrCp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_5$Cp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_5$Cp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_5$Cp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_5$Cp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_3$SiCp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_3$SiCp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_3$SiCp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_3$SiCp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeO-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeO-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeO-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), MeO-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBuO-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBuO-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBuO-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), tBuO-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Me-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBu-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBu-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBu-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), tBu-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_2$N-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_2$N-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_2$N-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_2$N-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Et$_2$N-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Et$_2$N-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Et$_2$N-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Et$_2$N-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeEtN-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeEtN-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeEtN-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), MeEtN-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), iPr$_2$N-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), iPr$_2$N-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), iPr$_2$N-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), iPr$_2$N-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBu$_2$N-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBu$_2$N-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBu$_2$N-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), tBu$_2$N-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), (H$_3$Si)$_2$N-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), (Me$_3$Si)$_2$N-Hf((-N(iPr)-CHMe-CH$_2$-

$)_3N)$, $(Me_2HSi)_2N-Hf((-N(Me)-CH_2-CH_2-)_3N)$, $(Me_2HSi)_2N-Hf((-N(iPr)-CH_2-CH_2-)_3N)$, $(Me_2HSi)_2N-Hf((-N(Me)-CHMe-CH_2-)_3N)$, $(Me_2HSi)_2N-Hf((-N(iPr)-CHMe-CH_2-)_3N)$, $(Et_3Si)_2N-Hf((-N(Me)-CH_2-CH_2-)_3N)$, $(Et_3Si)_2N-Hf((-N(iPr)-CH_2-CH_2-)_3N)$, $(Et_3Si)_2N-Hf((-N(Me)-CHMe-CH_2-)_3N)$, $(Et_3Si)_2N-Hf((-N(iPr)-CHMe-CH_2-)_3N)$, $N^{iPr}Me-Amd-Hf((-N(Me)-CH_2-CH_2-)_3N)$, $N^{iPr}Me-Amd-Hf((-N(iPr)-CH_2-CH_2-)_3N)$, $N^{iPr}Me-Amd-Hf((-N(Me)-CHMe-CH_2-)_3N)$, $N^{iPr}Me-Amd-Hf((-N(iPr)-CHMe-CH_2-)_3N)$, $tBuDAD-Hf((-N(Me)-CH_2-CH_2-)_3N)$, $tBuDAD-Hf((-N(iPr)-CH_2-CH_2-)_3N)$, $tBuDAD-Hf((-N(Me)-CHMe-CH_2-)_3N)$, $tBuDAD-Hf((-N(iPr)-CHMe-CH_2-)_3N)$, $(Me_3SiO-)Hf((-N(Me)-CH_2-CH_2-)_3N)$, $(Me_3SiO-)Hf((-N(iPr)-CH_2-CH_2-)_3N)$, $(Me_3SiO-)Hf((-N(Me)-CHMe-CH_2-)_3N)$, or $(Me_3SiO-)Hf((-N(iPr)-CHMe-CH_2-)_3N)$.

For sake of simplicity, structures with asymmetric substituted tris[(alkylamino)alkyl]amine ligands have not been listed above, but are included in the scope of the disclosure and the examples that follow.



The inventors recognize that using these asymmetric substituted triethanolamine ligands may help reduce the melting points of the Group 4 transition metal azatrane precursors obtained from them, in the same way as metallocene having substituted Cp rings tend to have lower melting points.

The Group 4 transition metal azatrane precursors may exhibit (i) sufficient volatility to provide a rapid and reproducible delivery into the reaction chamber from the vessel in which they are stored, (ii) high thermal stability to avoid decomposition during the storage in the canister and to enable self limiting growth in ALD mode at high temperature, typically > 275°C, (iii) appropriate reactivity toward the substrate terminal functions and with the reacting gas to an easy conversion into the desired film, and (iv) high purity to obtain a film with low impurities.

While precursors are ideally liquids and vaporized in bubblers or direct liquid injection systems, the use of solid precursors for ALD and CVD precursor vaporization is also possible using sublimators such as ones disclosed in PCT Publication WO2009/087609 to Xu et al. Alternatively, solid precursors may be mixed or dissolved in a solvent to reach a usable melting point and viscosity for usage by Direct Liquid Injection systems.

Preferably, the R in the Group 4 transition metal-containing azatrane precursors is Cp* and R^1 is H or Me because of their excellent vaporization results in atmospheric thermogravimetric analysis, leaving a small amount of final residue.

The disclosed Group 4 transition metal-containing azatrane precursors may be synthesized by reacting at low temperature the corresponding Group 4 transition metal-containing amino and R group compound (i.e., $M(NR_2)_4$), wherein R and M are defined above) with the corresponding tris[(alkylamino)alkyl]amine in a suitable solvent, such as heptanes, dichloromethane, THF or ether. The $M(NR_2)_4$ and tris[(alkylamino)alkyl]amine are commercially available. After completion of the addition, the mixture warms to room temperature with stirring. The solvent is removed under vacuum to produce the crude Group 4 transition metal-containing azatrane precursor. Exemplary synthesis methods containing further details are provided in the Examples that follow.

Alternatively, the disclosed Group 4 transition metal-containing azatrane precursors may be synthesized by reacting at low temperature the corresponding Group 4 transition metal-containing amide and R group compound (i.e., $RM(NR'''_2)_3$), wherein R and M are defined above and R''' is a C1-C6 alkyl group) with the corresponding tris[(alkylamino)alkyl]amine in a suitable solvent, such as heptanes, dichloromethane, THF or ether. The $RM(NR'''_2)_3$ and tris[(alkylamino)alkyl]amine are commercially available. After completion of the addition, the mixture warms to room temperature with stirring. The solvent is removed under vacuum to produce the crude Group 4 transition metal-containing azatrane precursor. Exemplary synthesis methods containing further details are provided in the Examples that follow.

In another alternative, the disclosed Group 4 transition metal-containing azatrane precursors may be synthesized by reacting at low temperature the corresponding Group 4 transition metal-containing halide and R group compound (i.e., RMX_3), wherein R and M are defined above and X is Cl, Br, or I) with the corresponding tris[(alkylamino)alkyl]amino alkali (Li, Na, or K) in a suitable solvent, such as heptanes, dichloromethane, THF or ether. The RMX_3 and tris[(alkylamino)alkyl]amine are commercially available. The tris[(alkylamino)alkyl]amine is treated with three molar equivalents of nBuLi, NaH, or KH at low temperature to produce the tris[(alkylamino)alkyl]amino alkali reactant. After completion of the addition, the mixture warms to room temperature with stirring. The solid by-product is removed by filtration. The solvent in filtrate is removed under vacuum to produce the crude Group 4 transition metal-containing azatrane precursor.

To ensure process reliability, the Group 4 transition metal-containing film forming compositions may be purified by continuous or fractional batch distillation or sublimation prior to use to a purity ranging from approximately 93% w/w to approximately 100% w/w, preferably ranging from approximately 99% w/w to approximately 100% w/w. The Group 4 transition metal-containing film forming compositions may contain any of the following impurities: undesired congeneric species; solvents; chlorinated metal compounds; or other reaction products. In one alternative, the total quantity of these impurities is below 0.1% w/w.

The concentration of each of hexane, pentane, dimethyl ether, or anisole in the purified Group 4 transition metal-containing film forming compositions may range from approximately 0% w/w to approximately 5% w/w, preferably from approximately 0% w/w to approximately 0.1% w/w. Solvents may be used in the composition’s synthesis. Separation of the solvents from the precursor may be difficult if both have similar boiling points. Cooling the mixture may produce solid precursor in liquid solvent, which may be separated by filtration. Vacuum distillation may also be used, provided the precursor product is not heated above approximately its decomposition point.

In one alternative, the disclosed Group 4 transition metal-containing film forming compositions contain less than 5% v/v, preferably less than 1% v/v, more preferably less than 0.1% v/v, and even more preferably less than 0.01% v/v of any of its undesired congeneric species, reactants, or other reaction products. This alternative may provide better process repeatability. This alternative may be produced by distillation of the Group 4 transition metal-containing azatrane precursors.

In another alternative, the disclosed Group 4 transition metal-containing film forming compositions may contain between 5% v/v and 50% v/v of one or more of cogeneric Group 4 transition metal-containing azatrane precursors, reactants, or other reaction products, particularly when the mixture provides improved process parameters or isolation of the target compound is too difficult or expensive. For example, a mixture of two Group 4 transition metal azatrane precursors may produce a stable, liquid mixture suitable for vapor deposition.

The concentration of trace metals and metalloids in the purified Group 4 transition metal-containing film forming compositions may each range from approximately 0 ppb to approximately 100 ppb, and more preferably from approximately 0 ppb to approximately 10 ppb. These metal impurities include, but are not limited to, Aluminum (Al), Arsenic (As), Barium (Ba), Beryllium (Be), Bismuth (Bi), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Gallium (Ga), Germanium (Ge), Hafnium (Hf), Zirconium (Zr), Indium (In), Iron (Fe), Lead (Pb), Lithium (Li), Magnesium (Mg), Manganese (Mn), Tungsten (W), Nickel (Ni), Potassium (K), Sodium (Na), Strontium (Sr), Thorium (Th), Tin (Sn), Titanium (Ti), Uranium (U), Vanadium (V) and Zinc (Zn).

Also disclosed are methods for forming Group 4 transition metal-containing layers on a substrate using a vapor deposition process. The method may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The disclosed Group 4 transition metal-containing film forming compositions may be used to deposit thin Group 4 transition metal-containing films using any deposition methods known to those of skill in the art. Examples of suitable vapor deposition methods include chemical vapor deposition (CVD) or atomic layer deposition (ALD). Exemplary CVD methods include thermal CVD, plasma enhanced CVD (PECVD), pulsed CVD (PCVD), low pressure CVD (LPCVD), sub-atmospheric CVD (SACVD) or atmospheric pressure CVD (APCVD), hot-wire CVD (HWCVD, also known as cat-CVD, in which a hot wire serves as an energy source for the deposition process), radicals incorporated CVD, and combinations thereof. Exemplary ALD methods include thermal ALD, plasma enhanced ALD (PEALD), spatial isolation ALD, hot-wire ALD (HWALD), radicals incorporated ALD, and combinations thereof. Super critical fluid deposition may also be used. The deposition method is preferably ALD, spatial ALD, or PE-ALD to provide suitable step coverage and film thickness control. Additionally, the disclosed Group 4 transition metal-containing film forming compositions are particularly suitable for ALD processes because their thermal stability enables perfect self-limited growth.

Applicants believe the one N-M bond may stabilize the precursor making it thermally robust, which may help during conformal ALD deposition in high aspect ratio structures. The second N-M bond may provide good reactivity to any hydroxyl groups on the substrate surface, permitting the required physi- or chemi-sorption desired in ALD deposition. Finally, when R is Cp (substituted or not), Applicants believe that the Cp may remain like an umbrella over the M atom on the surface and ensure perfect self-limited ALD growth.

The disclosed Group 4 transition metal-containing film forming composition may be supplied either neat or may further comprise a suitable solvent, such as ethyl benzene, xylene, mesitylene, decane, and/or dodecane. The disclosed Group 4 transition metal azatrane precursors may be present in varying concentrations in the solvent.

The neat or blended Group 4 transition metal-containing film forming compositions are introduced into a reactor in vapor form by conventional means, such as tubing and/or flow meters. The vapor form may be produced by vaporizing the neat or blended composition through a conventional vaporization step such as direct vaporization, distillation, or by bubbling, or by using a sublimator such as the one disclosed in PCT Publication WO2009/087609 to Xu et al. The composition may be fed in a liquid state to a vaporizer where it is vaporized before it is introduced into the reactor. Alternatively, the composition may be vaporized by passing a carrier gas into a container containing the compound or by bubbling the carrier gas into the compound. The carrier gas may include, but is not limited to, Ar, He, N_2,and mixtures thereof. Bubbling with a carrier gas may also remove any dissolved oxygen present in the neat or blended compound solution. The carrier gas and vapor form of the composition are then introduced into the reactor as a vapor.

If necessary, the container may be heated to a temperature that permits the composition to be in its liquid phase and to have a sufficient vapor pressure. The container may be maintained at temperatures in the range of, for example, approximately 50°C to approximately 180°C. Those skilled in the art recognize that the temperature of the container may be adjusted in a known manner to control the amount of composition vaporized.

The Group 4 transition metal-containing film forming compositions may be delivered to a semiconductor processing tool by the disclosed Group 4 transition metal-containing film forming composition delivery devices. **FIGS. 1 and 2** show two embodiments of the disclosed delivery devices **1**.

FIG. 1 is a side view of one embodiment of the Group 4 transition metal-containing film forming composition delivery device **1**. In **FIG. 1**, the disclosed Group 4 transition metal-containing film forming composition **11** is contained within a container **2** having at least two conduits, an inlet conduit **3** and an outlet conduit **4**. One of ordinary skill in the precursor art will recognize that the container **2**, inlet conduit **3**, and outlet conduit **4** are manufactured to prevent the escape of the gaseous form of the Group 4 transition metal-containing film forming composition **11**, even at elevated temperature and pressure.

Suitable valves include spring-loaded or tied diaphragm valves. The valve may further comprise a restrictive flow orifice (RFO). The delivery device **1** should be connected to a gas manifold and in an enclosure. The gas manifold should permit the safe evacuation and purging of the piping that may be exposed to air when the delivery device **1** is replaced so that any residual amount of the material does not react.

The delivery device **1** must be leak tight and be equipped with valves that do not permit escape of even minute amounts of the material when closed. The delivery device **1** fluidly connects to other components of the semiconductor processing tool, such as the gas cabinet disclosed above, via valves **6** and **7**. Preferably, the container **2**, inlet conduit **3**, valve **6**, outlet conduit **4**, and valve **7** are typically made of 316L EP stainless steel.

In **FIG. 1**, the end **8** of inlet conduit **3** is located above the surface of the Group 4 transition metal-containing film forming composition **11**, whereas the end **9** of the outlet conduit **4** is located below the surface of the Group 4 transition metal-containing film forming composition **11**. In this embodiment, the Group 4 transition metal-containing film forming composition **11** is preferably in liquid form. An inert gas, including but not limited to nitrogen, argon, helium, and mixtures thereof, may be introduced into the inlet conduit **3**. The inert gas pressurizes the container **2** so that the liquid Group 4 transition metal-containing film forming composition **11** is forced through the outlet conduit **4** and to components in the semiconductor processing tool (not shown). The semiconductor processing tool may include a vaporizer which transforms the liquid Group 4 transition metal-containing film forming composition **11** into a vapor, with or without the use of a carrier gas such as helium, argon, nitrogen or mixtures thereof, in order to deliver the vapor to a chamber where a wafer to be repaired is located and treatment occurs in the vapor phase. Alternatively, the liquid Group 4 transition metal-containing film forming composition **11** may be delivered directly to the wafer surface as a jet or aerosol.

FIG. 2 is a side view of a second embodiment of the Group 4 transition metal-containing film forming composition delivery device **1**. In **FIG. 2**, the end **8** of inlet conduit **3** is located below the surface of the Group 4 transition metal-containing film forming composition **11**, whereas the end **9** of the outlet conduit **4** is located above the surface of the Group 4 transition metal-containing film forming composition **11**. **FIG. 2** also includes an optional heating element **14**, which may increase the temperature of the Group 4 transition metal-containing film forming composition **11**. The Group 4 transition metal-containing film forming composition **11** may be in solid or liquid form. An inert gas, including but not limited to nitrogen, argon, helium, and mixtures thereof, is introduced into the inlet conduit **3**. The inert gas flows through the Group 4 transition metal-containing film forming composition **11** and carries a mixture of the inert gas and vaporized Group 4 transition metal-containing film forming composition **11** to the outlet conduit **4** and to the components in the semiconductor processing tool.

Both **FIGS 1 and 2** include valves **6** and **7**. One of ordinary skill in the art will recognize that valves **6** and **7** may be placed in an open or closed position to allow flow through conduits **3** and **4**, respectively. Either delivery device **1** in **FIGS. 1 or 2**, or a simpler delivery device having a single conduit terminating above the surface of any solid or liquid present, may be used if the Group 4 transition metal-containing film forming composition **11** is in vapor form or if sufficient vapor pressure is present above the solid/liquid phase. In this case, the Group 4 transition metal-containing film forming composition **11** is delivered in vapor form through the conduit **3** or **4** simply by opening the valve **6** in **FIG. 1** or **7** in **FIG. 2**, respectively. The delivery device **1** may be maintained at a suitable temperature to provide sufficient vapor pressure for the Group 4 transition metal-containing film forming composition **11** to be delivered in vapor form, for example by the use of an optional heating element **14**.

While **FIGS. 1 and 2** disclose two embodiments of the Group 4 transition metal-containing film forming composition delivery device **1**, one of ordinary skill in the art will recognize that the inlet conduit **3** and outlet conduit **4** may both be located above the surface of the Group 4 transition metal-containing film forming composition **11** without departing from the disclosure herein. Furthermore, inlet conduit **3** may be a filling port.

When the Group 4 transition metal-containing film forming compositions are solids, their vapors may be delivered to the reactor using a sublimator. **FIG 3** shows one embodiment of a suitable sublimator **100**. The sublimator **100** comprises a container **33**. Container **33** may be a cylindrical container, or alternatively, may be any shape, without limitation. The container **33** is constructed of materials such as stainless steel, nickel and its alloys, quartz, glass, and other chemically compatible materials, without limitation. In certain instances, the container **33** is constructed of another metal or metal alloy, without limitation. In certain instances, the container **33** has an internal diameter from about 8 centimeters to about 55 centimeters and, alternatively, an internal diameter from about 8 centimeters to about 30 centimeters. As understood by one skilled in the art, alternate configurations may have different dimensions.

Container **33** comprises a sealable top **15**, sealing member **18**, and gasket **20**. Sealable top **15** is configured to seal container **33** from the outer environment. Sealable top **15** is configured to allow access to the container **33**. Additionally, sealable top **15** is configured for passage of conduits into container **33**. Alternatively, sealable top **15** is configured to permit fluid flow into container **33**. Sealable top **15** is configured to receive and pass through a conduit comprising a dip tube **92** to remain in fluid contact with container **33**. Dip tube **92** having a control valve **90** and a fitting **95** is configured for flowing carrier gas into container **33**. In certain instances, dip tube **92** extends down the center axis of container **33**. Further, sealable top **15** is configured to receive and pass through a conduit comprising outlet tube **12**. The carrier gas and vapor of the Group 4 transition metal-containing film forming composition is removed from container **33** through the outlet tube **12**. Outlet tube **12** comprises a control valve **10** and fitting **5**. In certain instances, outlet tube **12** is fluidly coupled to a gas delivery manifold, for conducting carrier gas from the sublimator **100** to a film deposition chamber.

Container **33** and sealable top **15** are sealed by at least two sealing members **18**; alternatively, by at least about four sealing members. In certain instance, sealable top **15** is sealed to container **33** by at least about eight sealing members **18**. As understood by one skilled in the art, sealing member **18** releasably couples sealable top **15** to container **33**, and forms a gas resistant seal with gasket **20**. Sealing member **18** may comprise any suitable means known to one skilled in the art for sealing container **33**. In certain instances, sealing member **18** comprises a thumbscrew.

As illustrated in **FIG 3**, container **33** further comprises at least one disk disposed therein. The disk comprises a shelf, or horizontal support, for solid material. In certain embodiments, an interior disk **30** is disposed annularly within the container **33**, such that the disk **30** includes an outer diameter or circumference that is less than the inner diameter or circumference of the container **33**, forming an opening **31**. An exterior disk **86** is disposed circumferentially within the container **33**, such that the disk **86** comprises an outer diameter or circumference that is the same, about the same, or generally coincides with the inner diameter of the container **33**. Exterior disk **86** forms an opening **87** disposed at the center of the disk. A plurality of disks is disposed within container **33**. The disks are stacked in an alternating fashion, wherein interior disks **30**, **34**, **36**, **44** are vertically stacked within the container with alternating exterior disks **62**, **78**, **82**, **86**. In embodiments, interior disks **30**, **34**, **36**, **44** extend annularly outward, and exterior disks **62**, **78**, **82**, **86** extend annularly toward the center of container **33**. As illustrated in the embodiment of **FIG 3**, interior disks **30**, **34**, **36**, **44** are not in physical contact with exterior disks **62**, **78**, **82**, **86**.

The assembled sublimator **100** comprises interior disks **30**, **34**, **36**, **44** comprising aligned and coupled support legs **50**, interior passage **51**, concentric walls **40**, **41**, **42**, and concentric slots **47**, **48**, **49**. The interior disks **30**, **34**, **36**, **44** are vertically stacked, and annularly oriented about the dip tube **92**. Additionally, the sublimator comprises exterior disks **62**, **78**, **82**, **86**. As illustrated in **FIG 3**, the exterior disks **62**, **78**, **82**, **86** should be tightly fit into the container **33** for a good contact for conducting heat from the container **33** to the disks **62**, **78**, **82**, **86**.

Preferably, the exterior disks **62**, **78**, **82**, **86** are coupled to, or in physical contact with, the inner wall of the container **33**.

As illustrated, exterior disks **62**, **78**, **82**, **86** and interior disks **30**, **34**, **36**, **44** are stacked inside the container **33**. When assembled in container **33** to form sublimator **100**, the interior disks **30**, **34**, **36**, **44** form outer gas passages **31**, **35**, **37**, **45** between the assembled exterior disks **62**, **78**, **82**, **86**. Further, exterior disks **62**, **78**, **82**, **86** form inner gas passages **56**, **79**, **83**, **87** with the support legs of the interior disks **30**, **34**, **36**, **44**. The walls **40**, **41**, **42** of interior disks **30**, **34**, **36**, **44** form the grooved slots for holding solid precursors. Exterior disks **62**, **78**, **82**, **86** comprise walls **68**, **69**, **70** for holding solid precursors. During assembly, the solid precursors are loaded into the annular slots **47**, **48**, **49** of interior disks **30**, **34**, **36**, **44** and annular slots **64**, **65**, **66** of exterior disks **62**, **78**, **82**, **86**.

While **FIG 3** discloses one embodiment of a sublimator capable of delivering the vapor of any solid Group 4 transition metal-containing film forming composition to the reactor, one of ordinary skill in the art will recognize that other sublimator designs may also be suitable, without departing from the teachings herein. Finally, one of ordinary skill in the art will recognize that the disclosed Group 4 transition metal-containing film forming composition **11** may be delivered to semiconductor processing tools using other delivery devices, such as the ampoules disclosed in WO 2006/059187 to Jurcik *et al.*, without departing from the teachings herein.

The reaction chamber may be any enclosure or chamber of a device in which deposition methods take place, such as, without limitation, a parallel-plate type reactor, a cold-wall type reactor, a hot-wall type reactor, a single-wafer reactor, a multi-wafer reactor, or other such types of deposition systems. All of these exemplary reaction chambers are capable of serving as an ALD reaction chamber. The reaction chamber may be maintained at a pressure ranging from about 0.5 mTorr to about 20 Torr, preferably between about 0.1 Torr and about 5 Torr. In addition, the temperature within the reaction chamber may range from about 50°C to about 600°C. One of ordinary skill in the art will recognize that the optimal deposition temperature range for each Group IV transition metal-containing azatrane precursors may be determined experimentally to achieve the desired result.

The reactor contains one or more substrates onto which the thin films will be deposited. A substrate is generally defined as the material on which a process is conducted. The substrates may be any suitable substrate used in semiconductor, photovoltaic, flat panel, or LCD-TFT device manufacturing. Examples of suitable substrates include wafers, such as silicon, SiGe, silica, glass, or Ge. Plastic substrates, such as poly(3,4-ethylenedioxythiophene)poly (styrenesulfonte) [PEDOT:PSS], may also be used. The substrate may also have one or more layers of differing materials already deposited upon it from a previous manufacturing step. For example, the wafers may include silicon layers (crystalline, amorphous, porous, etc.), silicon oxide layers, silicon nitride layers, silicon oxy nitride layers, carbon doped silicon oxide (SiCOH) layers, or combinations thereof. Additionally, the wafers may include copper, cobalt, ruthenium, tungsten and/or other metal layers (*e.g.* platinum, palladium, nickel, ruthenium, or gold). The wafers may include barrier layers or electrodes, such as tantalum, tantalum nitride, etc. Plastic layers, such as poly(3,4-ethylenedioxythiophene)poly (styrenesulfonate) [PEDOT:PSS] may also be used. The layers may be planar or patterned. The substrate may be an organic patterened photoresist film. The substrate may include layers of oxides which are used as dielectric materials in MIM, DRAM, or FeRam technologies (for example, ZrO_2 based materials, HfO_2 based materials, TiO_2 based materials, rare earth oxide based materials, ternary oxide based materials, etc.) or from nitride-based films (for example, TaN, TiN, NbN) that are used as electrodes. The disclosed processes may deposit the Group IV-containing layer directly on the wafer or directly on one or more than one (when patterned layers form the substrate) of the layers on top of the wafer. Furthermore, one of ordinary skill in the art will recognize that the terms “film” or “layer” used herein refer to a thickness of some material laid on or spread over a surface and that the surface may be a trench or a line. Throughout the specification and claims, the wafer and any associated layers thereon are referred to as substrates. The actual substrate utilized may also depend upon the specific precursor embodiment utilized. In many instances though, the preferred substrate utilized will be selected from TiN, NbN, Ru, Si, and SiGe type substrates, such as polysilicon or crystalline silicon substrates. For example, a Group 4 metal oxide film may be deposited onto a TiN substrate. In subsequent processing, a TiN layer may be deposited on the Group 4 metal oxide layer, forming a TiN/Group 4 metal oxide/TiN stack used as DRAM capacitor. The Metal Oxide layer itself may be made of a stack of several layers of various metal oxides, generally selected from Group 4 metal oxide, Group 5 metal oxide, Al_2O_3, SiO_2, and MoO_2.

The temperature and the pressure within the reactor are held at conditions suitable for vapor depositions. In other words, after introduction of the vaporized composition into the chamber, conditions within the chamber are such that at least part of the vaporized Group IV transition metal-containing azatrane precursor is deposited onto the substrate to form a Group 4 transition metal-containing film. For instance, the pressure in the reactor may be held between about 1 Pa and about 10^5 Pa, more preferably between about 25 Pa and about 10^3 Pa, as required per the deposition parameters. Likewise, the temperature in the reactor may be held between about 100°C and about 500°C, preferably between about 200°C and about 450°C. One of ordinary skill in the art will recognize that "at least part of the vaporized Group IV transition metal-containing azatrane precursor is deposited" means that some or all of the precursor reacts with or adheres to the substrate.

The temperature of the reactor may be controlled by either controlling the temperature of the substrate holder or controlling the temperature of the reactor wall. Devices used to heat the substrate are known in the art. The reactor wall is heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the reactor wall may be heated includes from approximately 100°C to approximately 500°C. When a plasma deposition process is utilized, the deposition temperature may range from approximately 50°C to approximately 400°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 200°C to approximately 450°C.

In addition to the disclosed Group IV transition metal-containing film forming composition, a reactant may also be introduced into the reactor. The reactant may be an oxidizing gas such as one of O_2, O_3, H_2O, H_2O_2, NO, N_2O, NO_2, a diol (such as ethylene glycol or hydrated hexafluoroacetone), oxygen containing radicals such as $O^\cdot$ or $OH^\cdot$, NO, NO_2, carboxylic acids, formic acid, acetic acid, propionic acid, and mixtures thereof. Preferably, the oxidizing gas is selected from the group consisting of O_2, O_3, H_2O, H_2O_2, oxygen containing radicals thereof such as $O^{\cdot}$ or $OH^{\cdot}$, and mixtures thereof.

Alternatively, the reactant may be H_2, NH_3, hydrazines (such as N_2H_4, $MeHNNH_2$, Me_2NNH_2, MeHNNHMe, phenyl hydrazine), organic amines (such as $NMeH_2$, $NEtH_2$, NMe_2H, NEt_2H, NMe_3, NEt_3, $(SiMe_3)_2NH$, cyclic amines like pyrrolidine or pyrimidine), diamines (such as ethylene diamine, dimethylethylene diamine, tetramethylethylene diamine), aminoalcohols (such as ethanolamine [HO-CH_2-CH_2-NH_2], bis ethanolamine [$HN(C_2H_5OH)_2$] or tris ethanolamine[$N(C_2H_5OH)_3$]), pyrazoline, pyridine, radicals thereof, or mixtures thereof. Preferably the reactant is H_2, NH_3, radicals thereof, or mixtures thereof.

In another alternative, the reactant may be $(SiH_3)_3N$, hydridosilanes (such as SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10}, Si_5H_{10}, or Si_6H_{12}), chlorosilanes and chloropolysilanes (such as $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, Si_2Cl_6, Si_2HCl_5, or Si_3Cl_8), alkylsilanes (such as Me_2SiH_2, Et_2SiH_2, $MeSiH_3$, $EtSiH_3$, or phenyl silane), and aminosilanes (such as tris-dimethylaminosilane, bis-diethylaminosilane, di-isopropylaminosilane or other mono, dis or tris aminosilanes), radicals thereof, or mixtures thereof. Preferably, the reactant is $(SiH_3)_3N$ or an aminosilane.

The reactant may be treated by a plasma, in order to decompose the reactant into its radical form. N_2 may also be utilized as a reducing gas when treated with plasma. For instance, the plasma may be generated with a power ranging from about 50 W to about 2500 W, preferably from about 100 W to about 400 W. The plasma may be generated or present within the reactor itself. Alternatively, the plasma may generally be at a location removed from the reactor, for instance, in a remotely located plasma system. One of skill in the art will recognize methods and apparatus suitable for such plasma treatment.

For example, the reactant may be introduced into a direct plasma reactor, which generates plasma in the reaction chamber, to produce the plasma-treated reactant in the reaction chamber. Exemplary direct plasma reactors include the Titan™ PECVD System produced by Trion Technologies. The reactant may be introduced and held in the reaction chamber prior to plasma processing. Alternatively, the plasma processing may occur simultaneously with the introduction of the reactant. In-situ plasma is typically a 13.56 MHz RF inductively coupled plasma that is generated between the showerhead and the substrate holder. The substrate or the showerhead may be the powered electrode depending on whether positive ion impact occurs. Typical applied powers in in-situ plasma generators are from approximately 30 W to approximately 1000 W. Preferably, powers from approximately 30 W to approximately 600 W are used in the disclosed methods. More preferably, the powers range from approximately 100 W to approximately 500 W. The disassociation of the reactant using in-situ plasma is typically less than achieved using a remote plasma source for the same power input and is therefore not as efficient in reactant disassociation as a remote plasma system, which may be beneficial for the deposition of Group 4 transition metal-containing films on substrates easily damaged by plasma.

Alternatively, the plasma-treated reactant may be produced outside of the reaction chamber. The MKS Instruments' ASTRONi® reactive gas generator may be used to treat the reactant prior to passage into the reaction chamber. Operated at 2.45 GHz, 7kW plasma power, and a pressure ranging from approximately 0.5 Torr to approximately 10 Torr, the reactant O_2 may be decomposed into two $O^{\cdot}$ radicals. Preferably, the remote plasma may be generated with a power ranging from about 1 kW to about 10 kW, more preferably from about 2.5 kW to about 7.5 kW.

The vapor deposition conditions within the chamber allow the disclosed Group IV transition metal-containing film forming composition and the reactant to react and form a Group 4 transition metal-containing film on the substrate. In some embodiments, Applicants believe that plasma-treating the reactant may provide the reactant with the energy needed to react with the disclosed composition.

Depending on what type of film is desired to be deposited, an additional precursor compound may be introduced into the reactor. The precursor may be used to provide additional elements to the Group 4 transition metal-containing film. The additional elements may include lanthanides (e.g., Ytterbium, Erbium, Dysprosium, Gadolinium, Praseodymium, Cerium, Lanthanum, Yttrium), germanium, silicon, aluminum, boron, phosphorous, a Group 3 element (i.e., Sc, Y, La, or Ac), a different Group 4 element, or a Group 5 element (i.e., V, Nb, or Ta), or mixtures of these. When an additional precursor compound is utilized, the resultant film deposited on the substrate contains the Group 4 transition metal in combination with at least one additional element.

The Group 4 transition metal-containing film forming compositions and reactants may be introduced into the reactor either simultaneously (chemical vapor deposition), sequentially (atomic layer deposition) or different combinations thereof. The reactor may be purged with an inert gas between the introduction of the composition and the introduction of the reactant. Alternatively, the reactant and the composition may be mixed together to form a reactant/compound mixture, and then introduced to the reactor in mixture form. Another example is to introduce the reactant continuously and to introduce the Group 4 transition metal-containing film forming composition by pulse (pulsed chemical vapor deposition).

The vaporized composition and the reactant may be pulsed sequentially or simultaneously (*e.g.* pulsed CVD) into the reactor. Each pulse of composition may last for a time period ranging from about 0.01 seconds to about 100 seconds, alternatively from about 0.3 seconds to about 30 seconds, alternatively from about 0.5 seconds to about 10 seconds. The reactant may also be pulsed into the reactor. In such embodiments, the pulse of each gas may last from about 0.01 seconds to about 100 seconds, alternatively from about 0.3 seconds to about 30 seconds, alternatively from about 0.5 seconds to about 10 seconds. In another alternative, the vaporized composition and one or more reactants may be simultaneously sprayed from a shower head under which a susceptor holding several wafers is spun (spatial ALD).

Depending on the particular process parameters, deposition may take place for a varying length of time. Generally, deposition may be allowed to continue as long as desired or necessary to produce a film with the necessary properties. Typical film thicknesses may vary from several angstroms to several hundreds of microns, depending on the specific deposition process. The deposition process may also be performed as many times as necessary to obtain the desired film.

In one non-limiting exemplary CVD type process, the vapor phase of the disclosed Group 4 transition metal-containing film forming composition and a reactant are simultaneously introduced into the reactor. The two react to form the resulting Group 4 transition metal-containing thin film. When the reactant in this exemplary CVD process is treated with a plasma, the exemplary CVD process becomes an exemplary PECVD process. The reactant may be treated with plasma prior or subsequent to introduction into the chamber.

In one non-limiting exemplary ALD type process, the vapor phase of the disclosed Group 4 transition metal-containing film forming composition is introduced into the reactor, where the Group 4 transition metal-containing azatrane precursor physi- or chemisorbs on the substrate. Excess composition may then be removed from the reactor by purging and/or evacuating the reactor. A desired gas (for example, O_3) is introduced into the reactor where it reacts with the physi- or chemisorped precursor in a self-limiting manner. Any excess reducing gas is removed from the reactor by purging and/or evacuating the reactor. If the desired film is a Group 4 transition metal film, this two-step process may provide the desired film thickness or may be repeated until a film having the necessary thickness has been obtained.

Alternatively, if the desired film contains Group 4 transition metal and a second element, the two-step process above may be followed by introduction of the vapor of an additional precursor compound into the reactor. The additional precursor compound will be selected based on the nature of the Group 4 transition metal film being deposited. After introduction into the reactor, the additional precursor compound is contacted with the substrate. Any excess precursor compound is removed from the reactor by purging and/or evacuating the reactor. Once again, a desired gas may be introduced into the reactor to react with the precursor compound. Excess gas is removed from the reactor by purging and/or evacuating the reactor. If a desired film thickness has been achieved, the process may be terminated. However, if a thicker film is desired, the entire four-step process may be repeated. By alternating the provision of the Group 4 transition metal-containing compound, additional precursor compound, and reactant, a film of desired composition and thickness can be deposited.

When the reactant in this exemplary ALD process is treated with a plasma, the exemplary ALD process becomes an exemplary PEALD process. The reactant may be treated with plasma prior or subsequent to introduction into the chamber.

In a second non-limiting exemplary ALD type process, the vapor phase of one of the disclosed Zr -containing azatrane precursors, for example $CpZr((-N(Me)-CH_2-CH_2-)_3N)$, is introduced into the reactor, where it is contacted with a TiN substrate. Excess Zr-containing azatrane precursor may then be removed from the reactor by purging and/or evacuating the reactor. A desired gas (for example, O_3)

is introduced into the reactor where it reacts with the absorbed Zr-containing precursor in a self-limiting manner to form a ZrO_2 film. Any excess oxidizing gas is removed from the reactor by purging and/or evacuating the reactor. These two steps may be repeated until the ZrO_2 film obtains a desired thickness. The resulting $TiN/ZrO_2/TiN$ stack may be used in DRAM capacitors. The ZrO_2 metal oxide film may be included within a more complex stack containing a laminate of various metal oxides. Typically, $ZrO_2/Al_2O_3/ZrO_2$ stacks are used, but also $TiO_2/ZrO_2/Al_2O_3/ZrO_2$, $ZrO_2/Nb_2O_3/ZrO_2$, $ZrO_2/HfO_2/TiO_2/ZrO_2$, etc.

The Group 4 transition metal-containing films resulting from the processes discussed above may include a Group 4 transition metal oxide (MM'_iO_x, wherein i ranges from 0 to 1; x ranges from 1 to 6; and M' is selected from a Group 3 element, a different Group 4 element (*i.e.*, M≠M'), a Group 5 element, a lanthanide, Si, Al, B, P or Ge) or a Group 4 transition metal oxynitride ($MM'_iN_yO_x$, wherein i ranges from 0 to 1; x and y range from 1 to 6; and M' is selected from a Group 3 element, a different Group 4 element (*i.e.*, M≠M'), a Group 5 element, a lanthanide, Si, Al, B, P or Ge) wherein m, n, and p are numbers which inclusively range from 1 to 6. One of ordinary skill in the art will recognize that by judicial selection of the appropriate disclosed compound, optional precursor compounds, and reactant species, the desired film composition may be obtained.

Upon obtaining a desired film thickness, the film may be subject to further processing, such as thermal annealing, furnace-annealing, rapid thermal annealing, UV or e-beam curing, and/or plasma gas exposure. Those skilled in the art recognize the systems and methods utilized to perform these additional processing steps. For example, the Group 4 transition metal-containing film may be exposed to a temperature ranging from approximately 200°C and approximately 1000°C for a time ranging from approximately 0.1 second to approximately 7200 seconds under an inert atmosphere, a H-containing atmosphere, a N-containing atmosphere, an O-containing atmosphere, or combinations thereof. Most preferably, the temperature is 400°C for 3600 seconds under a H-containing atmosphere or an O-containing atmosphere. The resulting film may contain fewer impurities and therefore may have an improved density resulting in improved leakage current. The annealing step may be performed in the same reaction chamber in which the deposition process is performed. Alternatively, the substrate may be removed from the reaction chamber, with the annealing/flash annealing process being performed in a separate apparatus. Any of the above post-treatment methods, but especially thermal annealing, has been found effective to reduce carbon and nitrogen contamination of the Group 4 transition metal-containing film. This in turn tends to improve the resistivity of the film.

Examples

The following examples illustrate experiments performed in conjunction with the disclosure herein. The examples are not intended to be all inclusive and are not intended to limit the scope of disclosure described herein.

Example 1: Synthesis of $CpZr((-N(Me)-CH_2-CH_2-)_3N)$

To a 100mL flask submerged in an ice bath and filled with 7.6g, 0.03mol of $CpZr(NMe_2)_3$ in 40 mL of heptane, tris[(2-methylamino)ethyl]amine, 4.96g, 0.03mol in 20mL heptane was added dropwise via a cannula. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight before filtration. Solvent was then removed by vacuum to collect the crude product in quantitative yield. The pure product was collected by recrystallization in ether-pentane. The overall yield was around 80%. The NMR^{1}H spectrum is provided in **FIG 4**. ^1H NMR (270MHz, C_6D_6, ppm): δ 6.30 (s, 5H, C_5H_5), 3.13 (s, 15H, CH_3), 3.57 (t, 6H, CH_2), and 2.54 (t, 6H, CH_2).

The solid left approximately 2% residual mass during open cup vacuum thermogravimetric analysis (TGA) measured at a temperature rising rate of 10°C/min. These results are shown in **FIG 5**, which is a TGA graph illustrating the percentage of weight loss upon temperature increase for both atmospheric and vacuum open cup. **FIG 5** also includes the Differential Thermal Analysis (DTA) showing the differential temperature with increasing temperature. These analyses were performed using a protective N_2 flow of 20 mL/minute. The atmospheric TGA/DTA also had a 200 mL/minute N_2 carrier flow. The low amount of residue demonstrated by the TGA results for $CpZr((-N(Me)-CH_2-CH_2-)_3N)$ are promising for vapor deposition applications.

Example 2: Synthesis of $CpZr((-N(iPr)-CH_2-CH_2-)_3N)$

In a 50mL flask, 5.30g, 0.02mol of $CpZr(NMe_2)_3$ and 5.00g, 0.02mol tris[(2-isopropylamino)ethyl]amine were mixed together at room temperature for a few days under nitrogen conditions. Crystals formed during this time. The formed crystals were analyzed by NMR and confirmed the formation of $CpZr((-N(iPr)-CH_2-CH_2-)_3N)$ in quantitative yield. The NMR^{1}H spectrum is provided in **FIG 6**. ^1H NMR (270MHz, C_6D_6, ppm): δ 6.23 (s, 5H, C_5H_5), 4.23 (h, 3H, *CH*),3.06 (t, 6H, CH_2), 2.50 (t, 6H, CH_2), 1.10 (d, 18H, CH_3).

The solid left approximately 32% residual mass during open cup atmospheric thermogravimetric analysis (TGA) measured at a temperature rising rate of 10°C/min. These results are shown in **FIG 7**, which is a TGA graph illustrating the percentage of weight loss upon temperature increase. **FIG 7** also includes the Differential Thermal Analysis (DTA) showing the differential temperature with increasing temperature. These analyses were performed using a protective N_2 flow of 20 mL/minute and a N_2 carrier flow of 200 mL/minute.

<u>Example 3</u>: Synthesis of $MeCpZr((-N(Me)-CH_2-CH_2-)_3N)$

To a 100mL flask submerged in an ice bath and filled with 8g, 0.03mol of $MeCpZr(NMe_2)_3$ in 40 mL of heptane, tris[(2-methylamino)ethyl]amine, 4.98g, 0.03mol in 20mL heptane was added dropwise via a cannula. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was then removed by vacuum to collect the crude product in quantitative yield. The pure product was collected by recrystallization in ether-pentane. The overall yield was around 60%. The NMR^{1}H spectrum is provided in **FIG 8**. ^1H NMR (270MHz, C_6D_6, ppm): δ 6.27-6.11 (m, 4H, $CH_3C_5H_4$), 3.17 (s, 9H, CH_3), 3.09 (t, 6H, CH_2), 2.56 (t, 6H, CH_2), 2.31 (s, 3H, $CH_3C_5H_4$).

The solid left approximately 3% residual mass during open cup vacuum thermogravimetric analysis (TGA) measured at a temperature rising rate of 10°C/min. These results are shown in **FIG 9**, which is a TGA graph illustrating the percentage of weight loss upon temperature increase for both atmospheric and vacuum open cup. **FIG 9** also includes the Differential Thermal Analysis (DTA) showing the differential temperature with increasing temperature. These analyses were performed using a protective N_2 flow of 20 mL/minute and a N_2 carrier flow of 200 mL/minute.

Comparative Example 1: Synthesis of $Me_2N\text{-}Zr((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$

To a 100mL flask submerged in an ice bath and filled with 7.1g, 0.03mol of $Zr(NMe_2)_4$ in 40 mL of heptane, tris[2-(methylamino)ethyl]amine, 5.0g, 0.03mol in 20mL heptane was added dropwise via a cannula. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was then removed by vacuum to collect the crude product in quantitative yield. The NMR^{1}H spectrum is provided in **FIG 10**. ^{1}H NMR (270MHz, C_6D_6, ppm): δ 3.09 (t, 6H, CH_2), 3.08 (s, 9H, CH_3), 3.07 (s, 6H, CH_3), 2.56 (t, 6H, CH_2).

The solid left approximately 51% residual mass during open cup atmospheric thermogravimetric analysis (TGA) measured at a temperature rising rate of 10°C/min. These results are shown in **FIG 11**, which is a TGA graph illustrating the percentage of weight loss upon temperature increase. **FIG 11** also includes the Differential Thermal Analysis (DTA) showing the differential temperature with increasing temperature. These analyses were performed using a protective N_2 flow of 20 mL/minute and a N_2 carrier flow of 200 mL/minute.

Comparative Example 2: Synthesis of $Et_2N\text{-}Zr((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$

To a 100mL flask submerged in an ice bath and filled with 20g, 0.05mol of $Zr(NEt_2)_4$ in 40 mL of heptane, tris[2-(methylamino)ethyl]amine, 9.92g, 0.05mol in 30mL heptane was added dropwise via a cannula. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was then removed by vacuum to collect the crude product in quantitative yield. The pure product was received by vacuum distillation with a boiling point around 144°C at a vacuum of 6mTorr. The overall yield was around 80%. The NMR^{1}H spectrum is provided in **FIG 12**. ^{1}H NMR (270MHz, C_6D_6, ppm): δ 3.44 (q, 4H, CH_2CH_3), 3.09 (t, 6H, CH_3NCH_2), 3.09 (s, 9H, CH_3NCH_2), 2.59 (t, NCH_2), 1.22 (t, CH_2CH_3).

The solid left approximately 49% residual mass during open cup atmospheric thermogravimetric analysis (TGA) measured at a temperature rising rate of 10°C/min. These results are shown in **FIG 13**, which is a TGA graph illustrating the percentage of weight loss upon temperature increase. **FIG 13** also includes the Differential Thermal Analysis (DTA) showing the differential temperature with increasing temperature. These analyses were performed using a protective N_2 flow of 20 mL/minute and a N_2 carrier flow of 200 mL/minute.

Comparative Example 3: Synthesis of $Me_2N\text{-}Zr((\text{-}N(iPr)\text{-}CH_2\text{-}CH_2\text{-})_3N)$

To a 100mL flask submerged in an ice bath and filled with 4.9g, 0.02mol of $Zr(NMe_2)_4$ in 20 mL of heptane, tris[2-(isopropylamino)ethyl]amine, 4.99g, 0.02mol in 10mL heptane was added dropwise via a cannula. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was then removed by vacuum to collect the crude product in quantitative yield. The pure product was collected by vacuum sublimation when an oil bath was heated to around 180ºC@6mTorr. The NMR^{1}H spectrum is provided in **FIG 14**. ^{1}H NMR (270MHz, C_6D_6, ppm): δ 3.97 (h, 3H, $(CH_3)_2\mathit{CH}$), 3.08 (t, 6H, $\mathit{CH_2}$), 2.95 (s, 6H, $N(\mathit{CH_3})$), 2.54 (t, 6H, $\mathit{CH_2}$), 1.15 (d, 18H, $(\mathit{CH_3})_2CH$).

The solid left approximately 19.5% residual mass during open cup atmospheric thermogravimetric analysis (TGA) measured at a temperature rising rate of 10°C/min. These results are shown in **FIG 15**, which is a TGA graph illustrating the percentage of weight loss upon temperature increase. **FIG 15** also includes the Differential Thermal Analysis (DTA) showing the differential temperature with increasing temperature. These analyses were performed using a protective N_2 flow of 20 mL/minute and a N_2 carrier flow of 200 mL/minute.

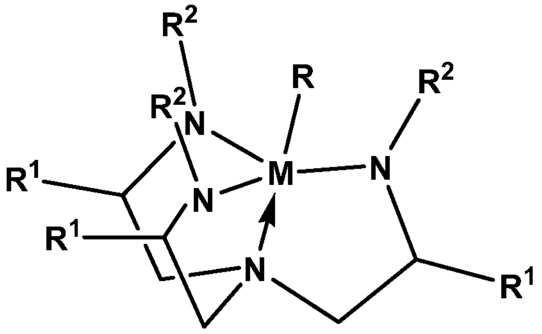
Comparative Example 4: Synthesis of $Me_2N\text{-}Ti((\text{-}N(Me)\text{-}CH_2\text{-}CH_2\text{-})_3N)$

To a 500mL flask submerged in an ice bath and filled with 12.0g, 0.03mol of $Ti(NMe_2)_4$ in 200 mL of heptane, tris[2-(methylamino)ethyl]amine, 10.8g, 0.05mol in 100mL heptane was added dropwise via a cannula. Upon completion of addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was then removed by vacuum to collect the crude product in quantitative yield. The pure product was collected by vacuum distillation with a boiling point around 110-115°C at a vacuum of 35mTorr. The NMR^{1}H spectrum is provided in **FIG 16**. ^{1}H NMR (270MHz, C_6D_6, ppm): δ 3.29 (s, 9H, $\mathit{CH_3}$), 3.28 (s, 6H, $N(\mathit{CH_3})_2$), 3.17 (t, 6H, $\mathit{CH_2}$), 2.59 (t, 6H, $\mathit{CH_2}$).

It will be understood that many additional changes in the details, materials, steps, and arrangement of parts, which have been herein described and illustrated in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims. Thus, the present invention is not intended to be limited to the specific embodiments in the examples given above and/or the attached drawings.

We claim:

1. A Group 4 transition metal-containing film forming composition comprising a Group 4 transitional metal-containing azatrane precursor having the following formula:



wherein M is selected from Group 4 transition metals consisting of Ti, Zr, or Hf; R is a halide, Cp, alkyl or silyl substituted Cp, disilylamino, trialkylsiloxy, amidinate, or DAD; each R^1 is independently H or a C1 to C6 hydrocarbyl group; and each R^2 is independently a C1 to C6 hydrocarbyl group.

2. The Group 4 transition metal-containing film forming composition of claim 1, wherein the Group 4 transitional metal-containing azatrane precursor is selected from the group consisting of Cl-Ti((-N(Me)-CH_2-CH_2-)$_3$N), Cl-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), Cl-Ti((-N(Me)-CHMe-CH_2-)$_3$N), Cl-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), Cp-Ti((-N(Me)-CH_2-CH_2-)$_3$N), Cp-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), Cp-Ti((-N(Me)-CHMe-CH_2-)$_3$N), Cp-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), MeCp-Ti((-N(Me)-CH_2-CH_2-)$_3$N), MeCp-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), MeCp-Ti((-N(Me)-CHMe-CH_2-)$_3$N), MeCp-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), EtCp-Ti((-N(Me)-CH_2-CH_2-)$_3$N), EtCp-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), EtCp-Ti((N(Me)-CHMe-CH_2-)$_3$N), EtCp-Ti((N(iPr)-CHMe-CH_2-)$_3$N), iPrCp-Ti((-N(Me)-CH_2-CH_2-)$_3$N), iPrCp-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), iPrCp-Ti((-N(Me)-CHMe-CH_2-)$_3$N), iPrCp-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), Me_5Cp-Ti((-N(Me)-CH_2-CH_2-)$_3$N), Me_5Cp-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), Me_5Cp-Ti((-N(Me)-CHMe-CH_2-)$_3$N), Me_5Cp-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), Me_3SiCp-Ti((-N(Me)-CH_2-CH_2-)$_3$N), Me_3SiCp-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), Me_3SiCp-Ti((-N(Me)-CHMe-CH_2-)$_3$N), Me_3SiCp-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), N^{iPr}Me-Amd-Ti((-N(Me)-CH_2-CH_2-)$_3$N), N^{iPr}Me-Amd-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), N^{iPr}Me-Amd-Ti((-N(Me)-CHMe-CH_2-)$_3$N), N^{iPr}Me-Amd-Ti((-N(iPr)-CHMe-CH_2-)$_3$N), tBuDAD-Ti((-N(Me)-CH_2-CH_2-)$_3$N), tBuDAD-Ti((-N(iPr)-CH_2-CH_2-)$_3$N), tBuDAD-Ti((-N(Me)-

CHMe-CH$_2$-)$_3$N), tBuDAD-Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$SiO-)Ti((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Ti((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Ti((-N(Me)-CHMe-CH$_2$-)$_3$N), or (Me$_3$SiO-)Ti((-N(iPr)-CHMe-CH$_2$-)$_3$N).

3. The Group 4 transition metal-containing film forming composition of claim 1, wherein the Group 4 transitional metal-containing azatrane precursor is selected from the group consisting of Cl-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cl-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cl-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Cl-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Cp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Cp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeCp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), MeCp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), EtCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), EtCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), EtCp-Zr((N(Me)-CHMe-CH$_2$-)$_3$N), EtCp-Zr((N(iPr)-CHMe-CH$_2$-)$_3$N), iPrCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), iPrCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), iPrCp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), iPrCp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_5$Cp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), Me$_3$SiCp-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), N^{iPr}Me-Amd-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), tBuDAD-Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), tBuDAD-Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), tBuDAD-Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), tBuDAD-Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N), (Me$_3$SiO-)Zr((-N(Me)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Zr((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), (Me$_3$SiO-)Zr((-N(Me)-CHMe-CH$_2$-)$_3$N), or (Me$_3$SiO-)Zr((-N(iPr)-CHMe-CH$_2$-)$_3$N).

4. The Group 4 transition metal-containing film forming composition of claim 1, wherein the Group 4 transitional metal-containing azatrane precursor is selected from the group consisting of Cl-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cl-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cl-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Cl-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), Cp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), Cp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), Cp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), Cp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), MeCp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), MeCp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), MeCp-Hf((-N(Me)-CHMe-CH$_2$-)$_3$N), MeCp-Hf((-N(iPr)-CHMe-CH$_2$-)$_3$N), EtCp-Hf((-N(Me)-CH$_2$-CH$_2$-)$_3$N), EtCp-Hf((-N(iPr)-CH$_2$-CH$_2$-)$_3$N), EtCp-

Hf((N(Me)-CHMe-CH_2-)$_3$N), EtCp-Hf((N(iPr)-CHMe-CH_2-)$_3$N), iPrCp-Hf((-N(Me)-CH_2-CH_2-)$_3$N), iPrCp-Hf((-N(iPr)-CH_2-CH_2-)$_3$N), iPrCp-Hf((-N(Me)-CHMe-CH_2-)$_3$N), iPrCp-Hf((-N(iPr)-CHMe-CH_2-)$_3$N), Me_5Cp-Hf((-N(Me)-CH_2-CH_2-)$_3$N), Me_5Cp-Hf((-N(iPr)-CH_2-CH_2-)$_3$N), Me_5Cp-Hf((-N(Me)-CHMe-CH_2-)$_3$N), Me_5Cp-Hf((-N(iPr)-CHMe-CH_2-)$_3$N), Me_3SiCp-Hf((-N(Me)-CH_2-CH_2-)$_3$N), Me_3SiCp-Hf((-N(iPr)-CH_2-CH_2-)$_3$N), Me_3SiCp-Hf((-N(Me)-CHMe-CH_2-)$_3$N), Me_3SiCp-Hf((-N(iPr)-CHMe-CH_2-)$_3$N), N^{iPr}Me-Amd-Hf((-N(Me)-CH_2-CH_2-)$_3$N), N^{iPr}Me-Amd-Hf((-N(iPr)-CH_2-CH_2-)$_3$N), N^{iPr}Me-Amd-Hf((-N(Me)-CHMe-CH_2-)$_3$N), N^{iPr}Me-Amd-Hf((-N(iPr)-CHMe-CH_2-)$_3$N), tBuDAD-Hf((-N(Me)-CH_2-CH_2-)$_3$N), tBuDAD-Hf((-N(iPr)-CH_2-CH_2-)$_3$N), tBuDAD-Hf((-N(Me)-CHMe-CH_2-)$_3$N), tBuDAD-Hf((-N(iPr)-CHMe-CH_2-)$_3$N), (Me_3SiO-)Hf((-N(Me)-CH_2-CH_2-)$_3$N), (Me_3SiO-)Hf((-N(iPr)-CH_2-CH_2-)$_3$N), (Me_3SiO-)Hf((-N(Me)-CHMe-CH_2-)$_3$N), or (Me_3SiO-)Hf((-N(iPr)-CHMe-CH_2-)$_3$N).

5. The Group 4 transition metal-containing film forming composition of claim 1, wherein R is Cp or alkyl- or silyl-substituted Cp.

6. The Group 4 transition metal-containing film forming composition of claim 5, wherein the Group 4 transitional metal-containing azatrane precursor is Me_5Cp-M((-N(Me)-CH_2-CH_2-)$_3$N), Me_5Cp-M((-N(iPr)-CH_2-CH_2-)$_3$N), Cp-M((-N(Me)-CHMe-CH_2-)$_3$N), or Cp-M((-N(iPr)-CHMe-CH_2-)$_3$N).

7. A method of depositing of a Group 4 transition metal-containing film on a substrate, comprising the steps of: introducing a vapor of the Group 4 transition metal-containing film forming composition of any one of claims 1 to 6 into a reactor having a substrate disposed therein and depositing at least part of the Group 4 transition metal-containing azatrane precursor onto the substrate.

8. The method of claim 7, further comprising introducing at least one reactant into the reactor.

9. The method of claim 8, wherein the reactant is selected from the group consisting of: O_2, O_3, H_2O, H_2O_2, NO, N_2O, NO_2, oxygen radicals thereof, and mixtures thereof.

10. The method of claim 8, wherein the reactant is a M'-containing precursor and the Group 4 transition metal-containing film is MM'_iO_x, wherein i ranges from 0 to 1; x ranges from 1 to 6; and M' is selected from a Group 3 element, a different Group 4 element (*i.e.*, M≠M'), a Group 5 element, a lanthanide, Si, Al, B, P or Ge.

11. The method of claim 8, wherein the Group 4 transition metal-containing film forming composition and the reactant are introduced into the reactor simultaneously and the reactor is configured for chemical vapor deposition.

12. The method of claim 8, wherein the Group 4 transition metal-containing film forming composition and the reactant are introduced into the chamber sequentially and the reactor is configured for atomic layer deposition.

13. The method of claim 8, wherein the precursor is used to form a DRAM capacitor

14. The method of claim 10, wherein the deposition is plasma enhanced.

15. The method of claim 11, wherein the deposition is plasma enhanced.

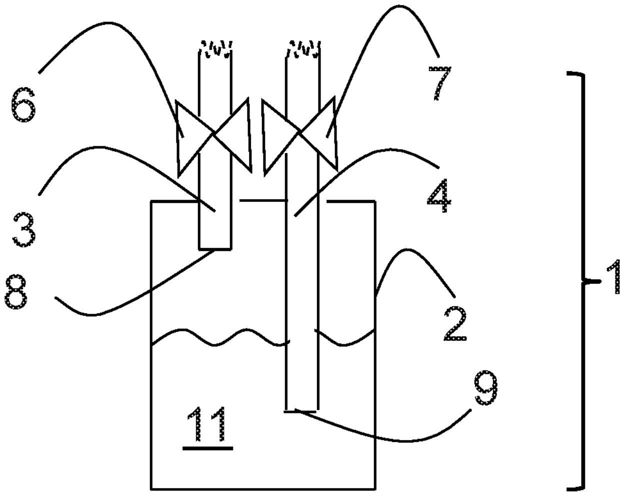


FIG 1

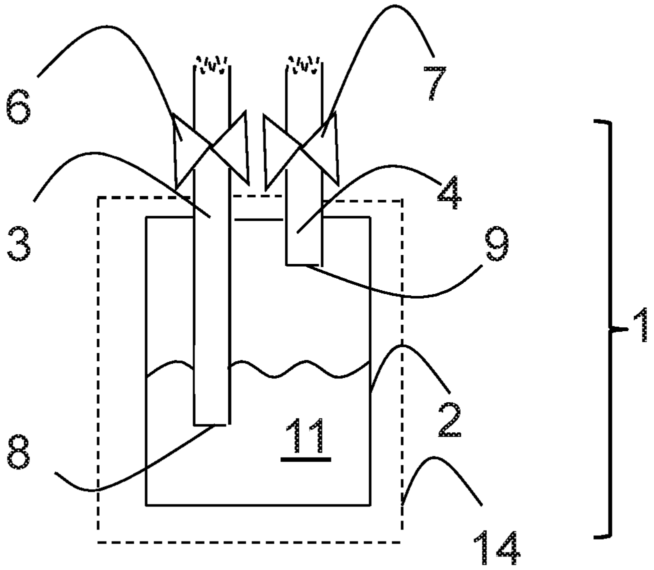


FIG 2

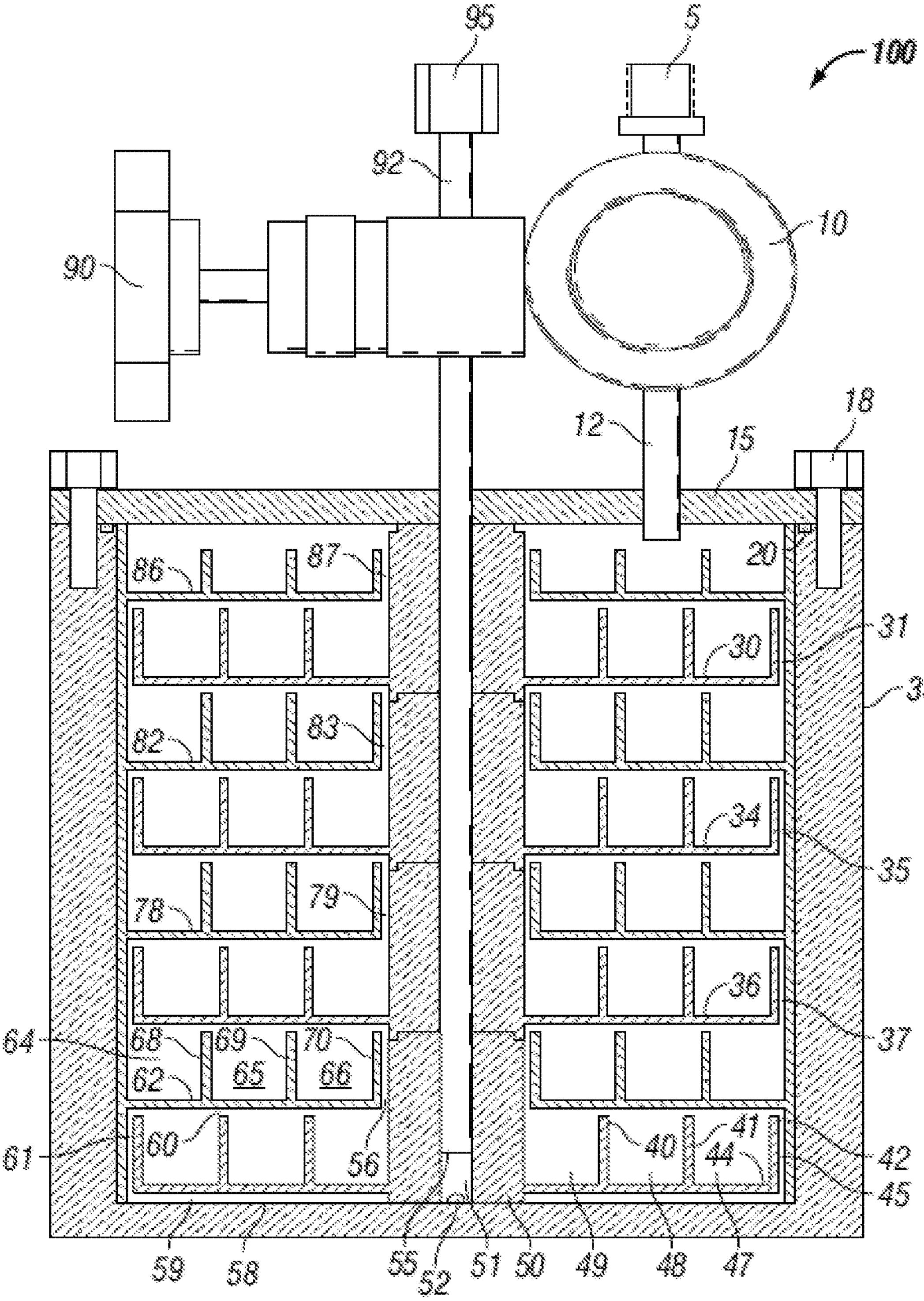
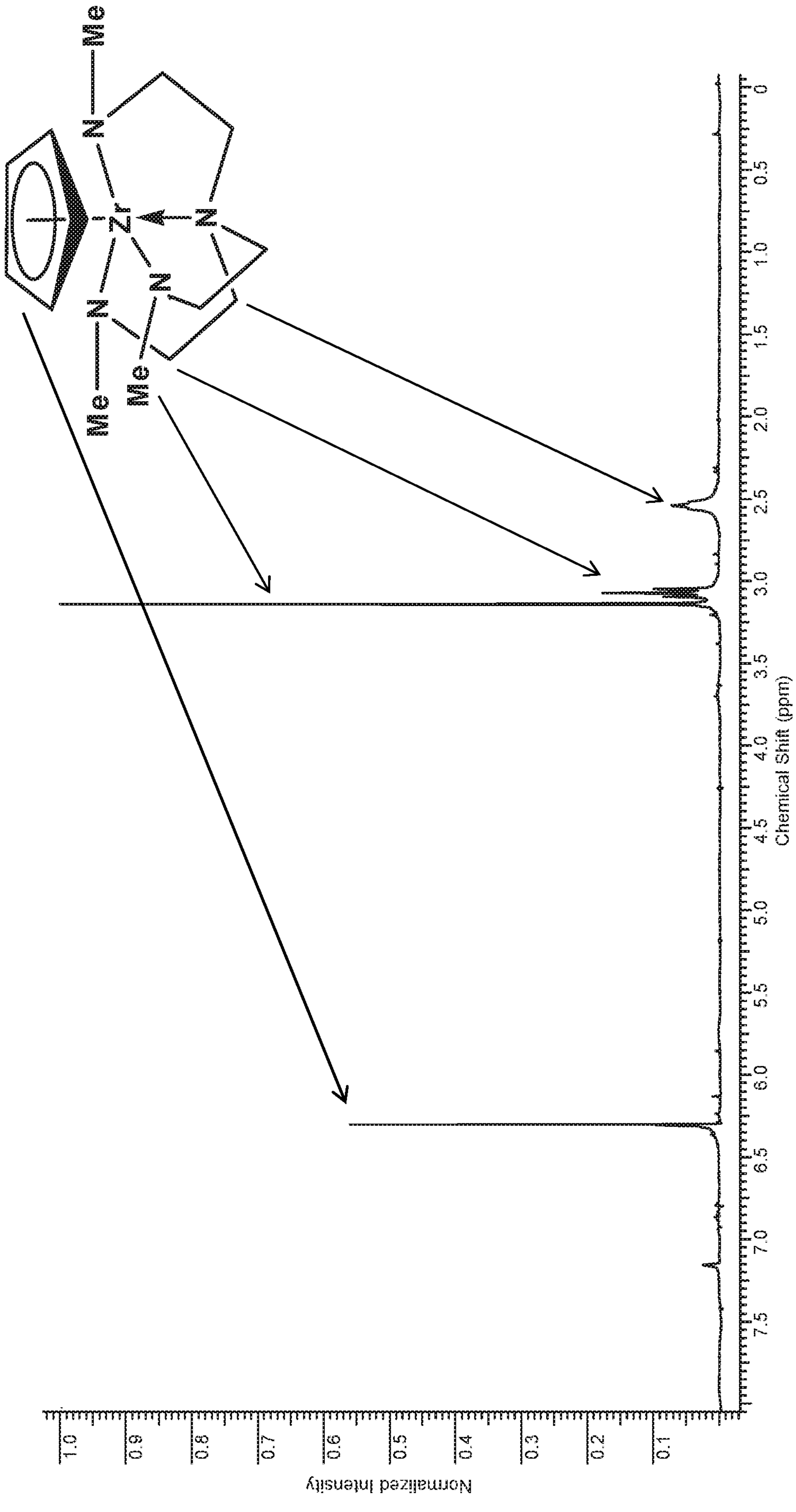

95
5
100
92
90
10
12
15
18
86
87
20
31
30
33
82
83
34
35
78
79
36
37
64
68
69
70
65
66
62
61
60
56
41
40
44
42
45
59
58
55
52
51
50
49
48
47

FIG 3



NMR Spectrum of Recrystallized Product in C_6D_6

FIG 4

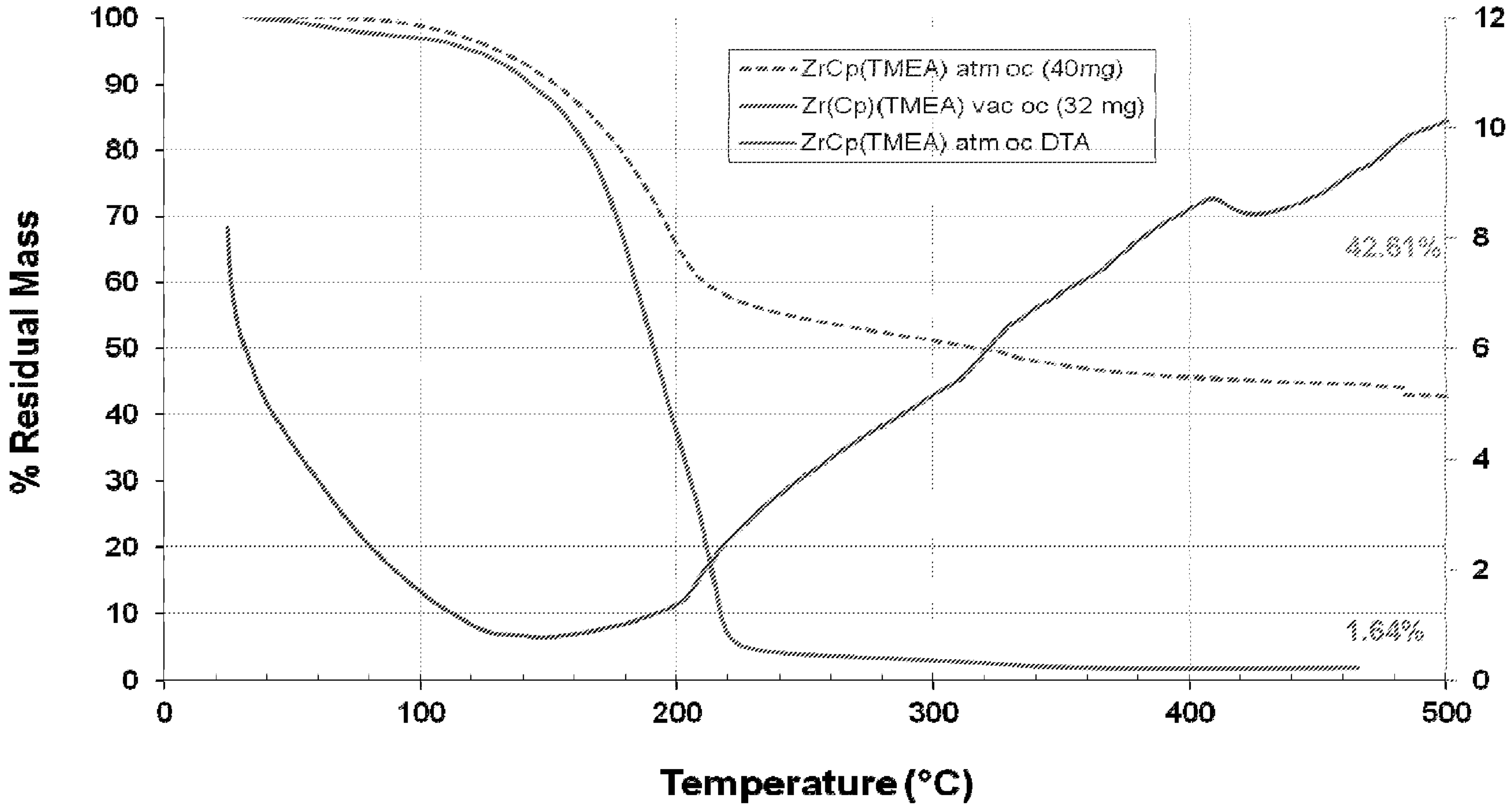
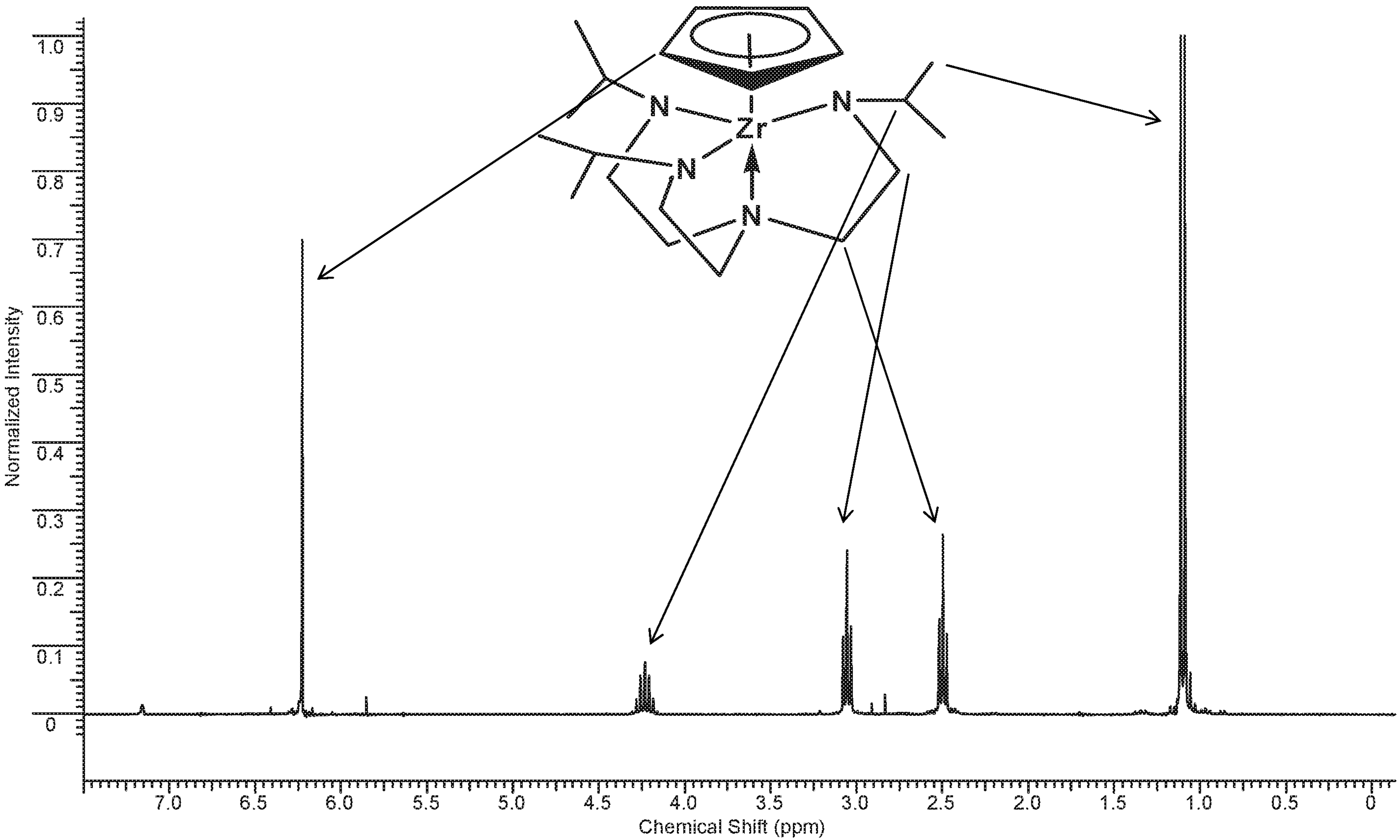

% Residual Mass
100
90
80
70
60
50
40
30
20
10
0
12
10
8
6
4
2
0
0
100
200
300
400
500
Temperature (°C)
ZrCp(TMEA) atm oc (40mg)
Zr(Cp)(TMEA) vac oc (32 mg)
ZrCp(TMEA) atm oc DTA
42.61%
1.64%

FIG 5



NMR Spectrum of Crystals Formed from Neat reactants in C_6D_6

FIG 6

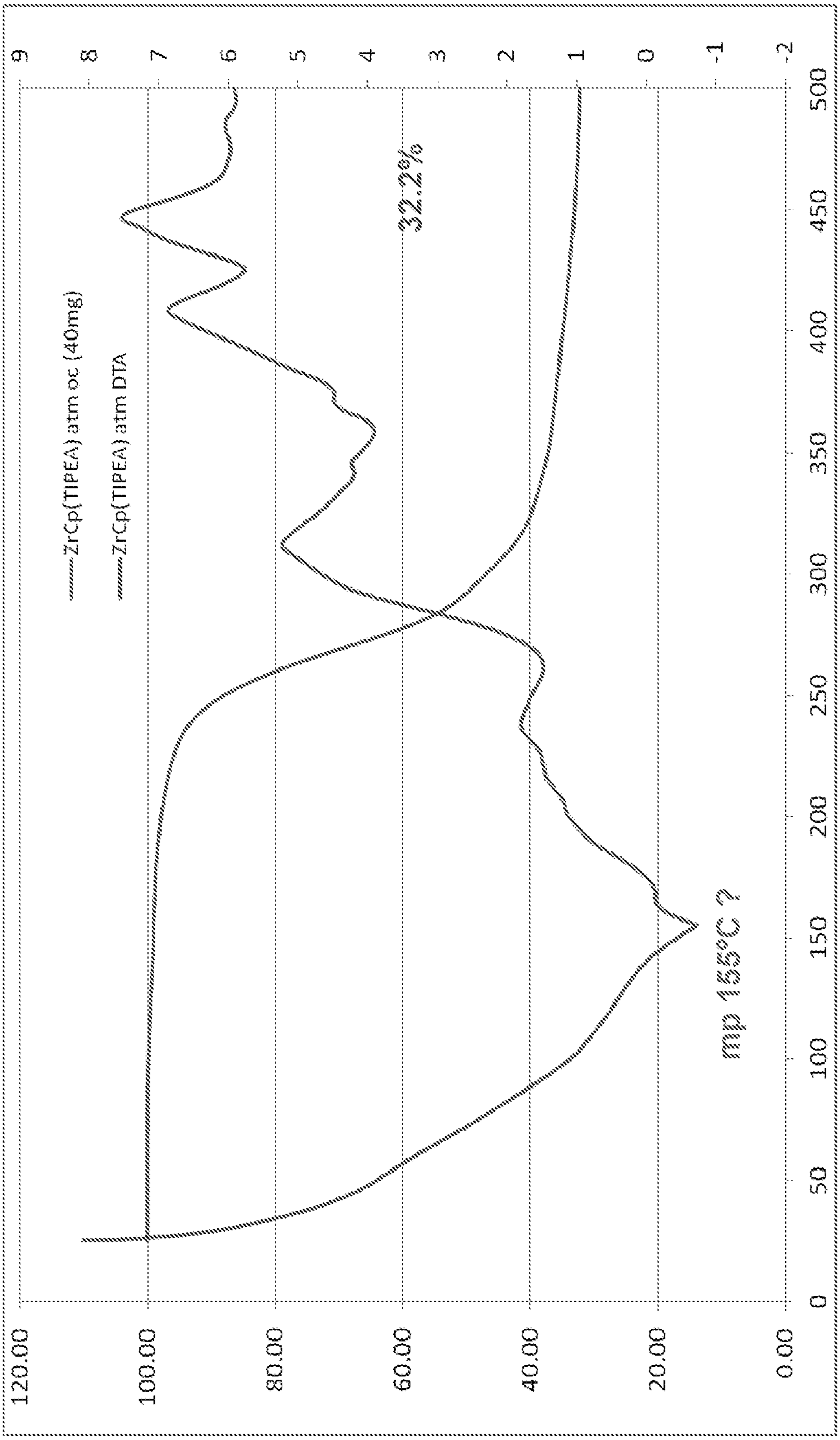

ZrCp(TIPEA) atm oc (40mg)
ZrCp(TIPEA) atm DTA
32.2%
mp 155°C ?
120.00
100.00
80.00
60.00
40.00
20.00
0.00
9
8
7
6
5
4
3
2
1
0
-1
-2
0
50
100
150
200
250
300
350
400
450
500

FIG 7

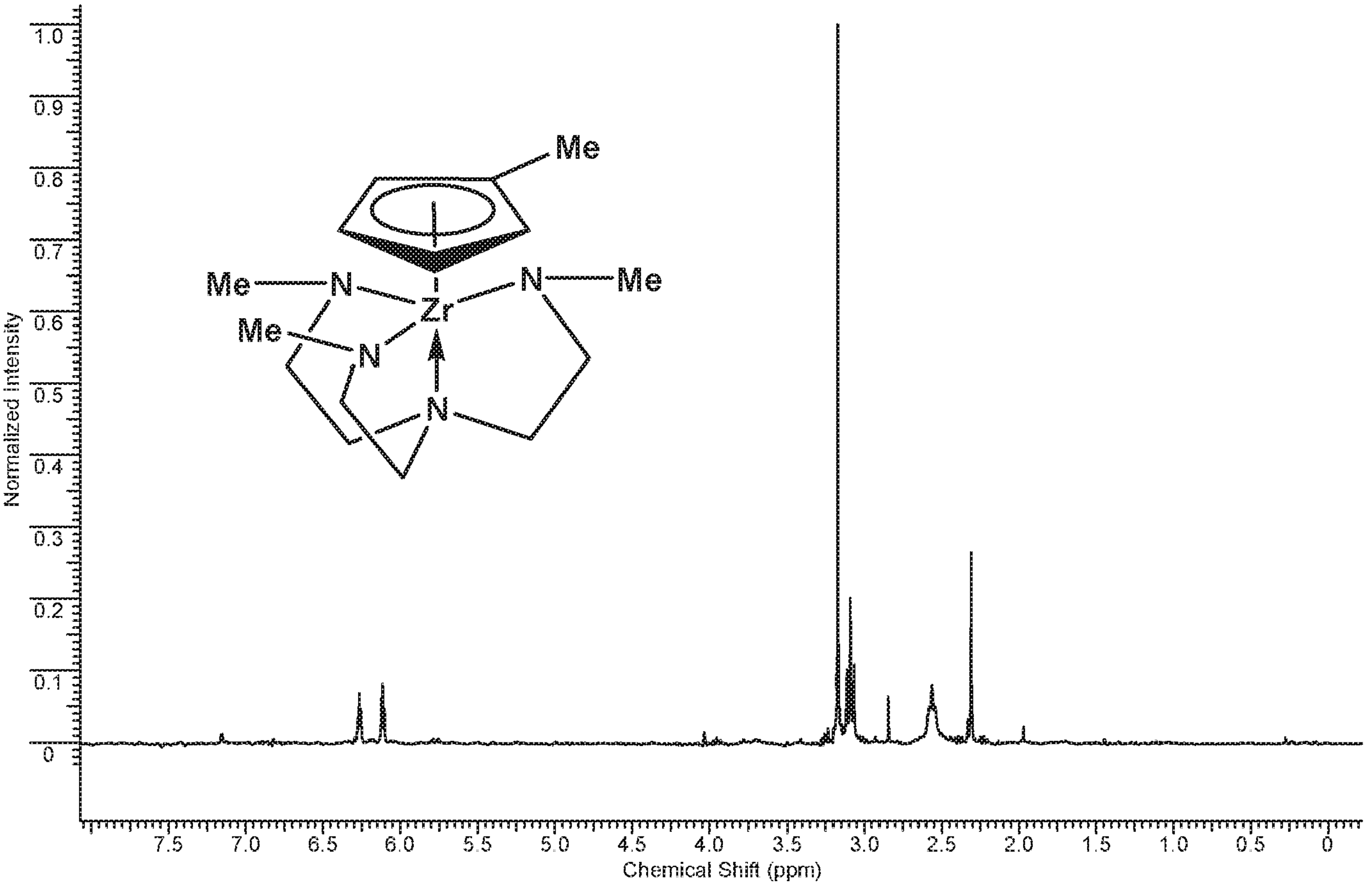

Me
Me
N
Zr
N
Me
Me
N
N
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

FIG 8

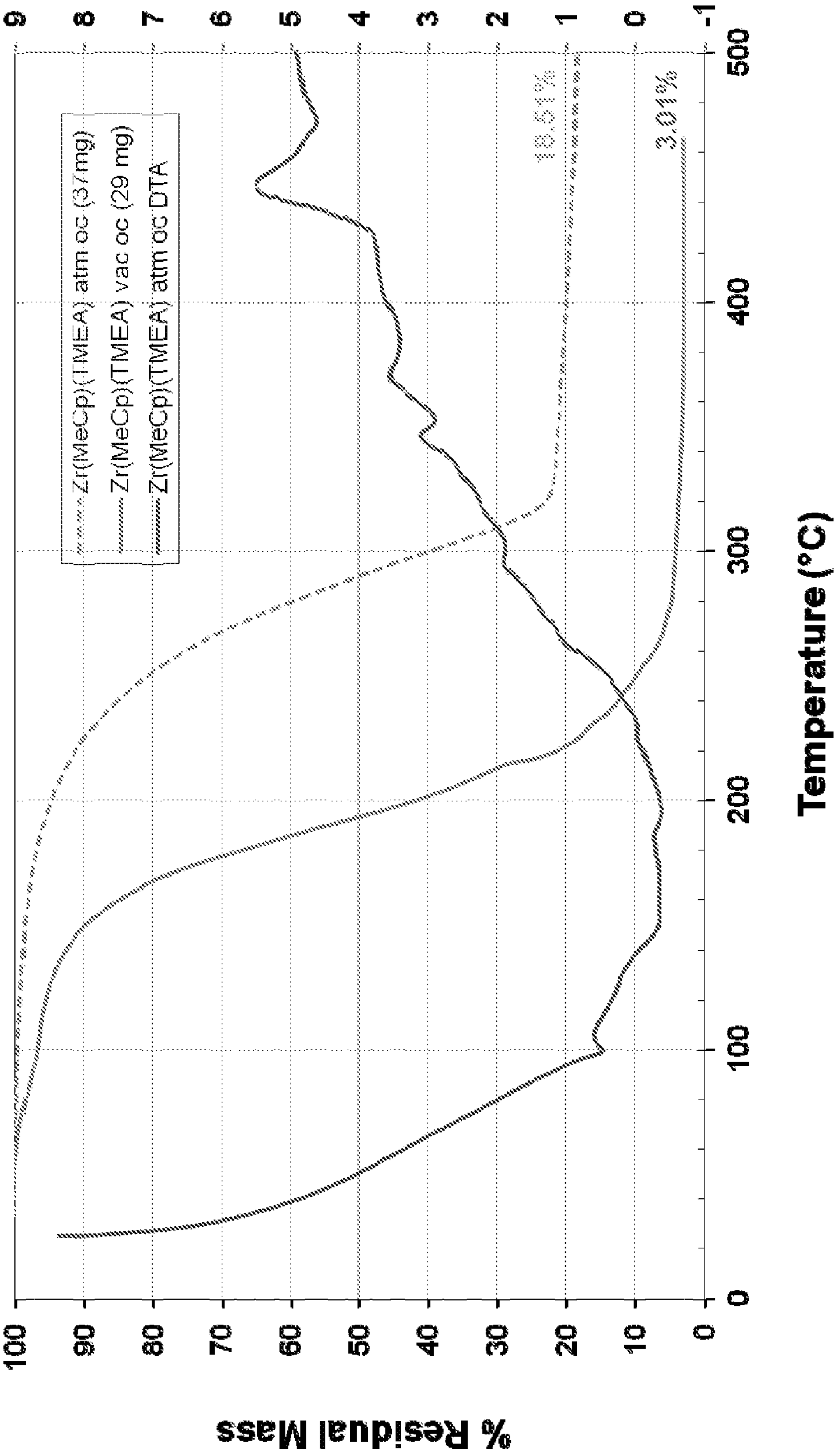
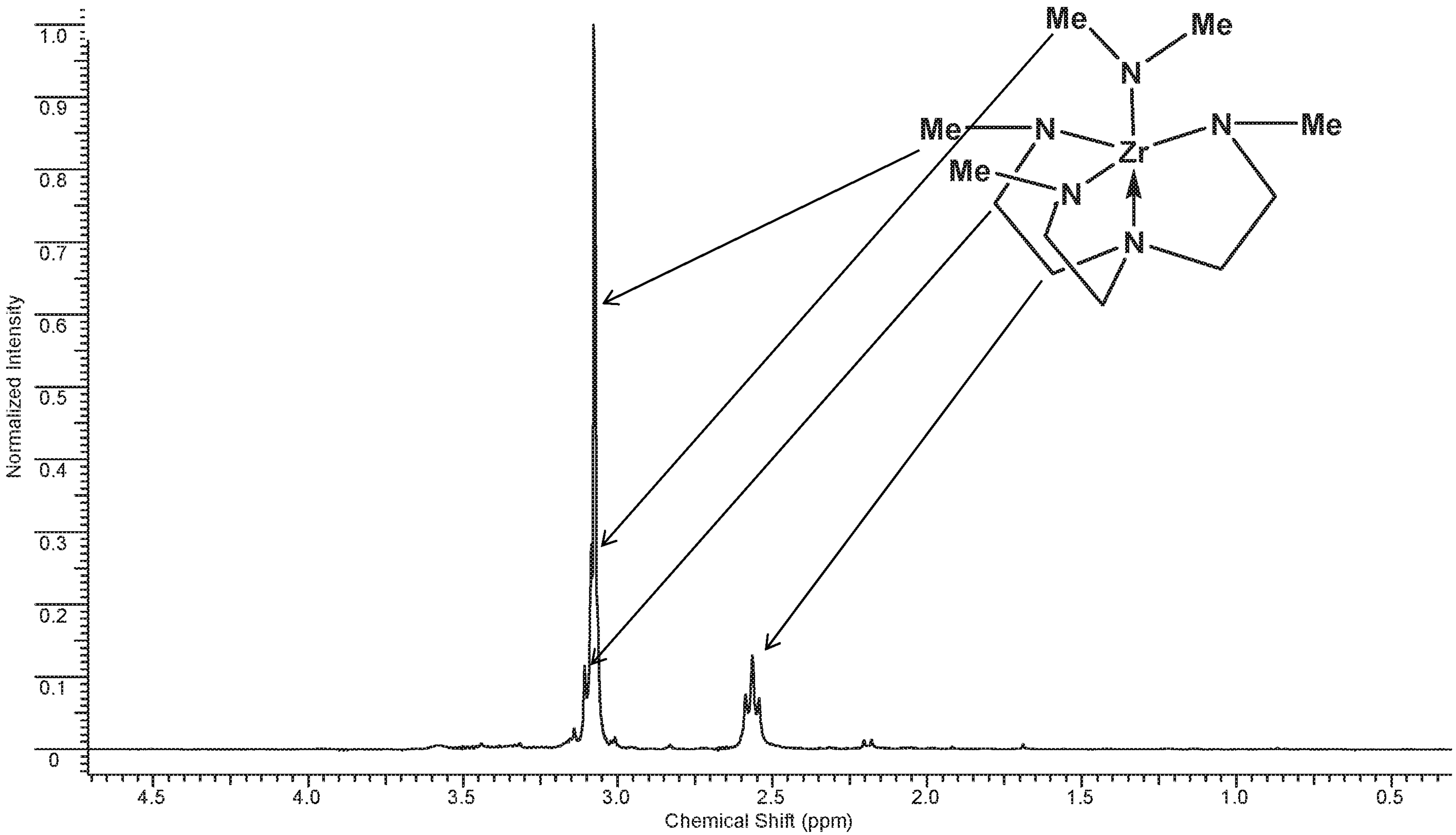

% Residual Mass
100
90
80
70
60
50
40
30
20
10
0
9
8
7
6
5
4
3
2
1
0
-1
0
100
200
300
400
500
Temperature (°C)
Zr(MeCp)(TMEA) atm oc (37mg)
Zr(MeCp)(TMEA) vac oc (29 mg)
Zr(MeCp)(TMEA) atm oc DTA
18.51%
3.01%

FIG 9



NMR Spectrum of Crude Product in C_6D_6

FIG 10

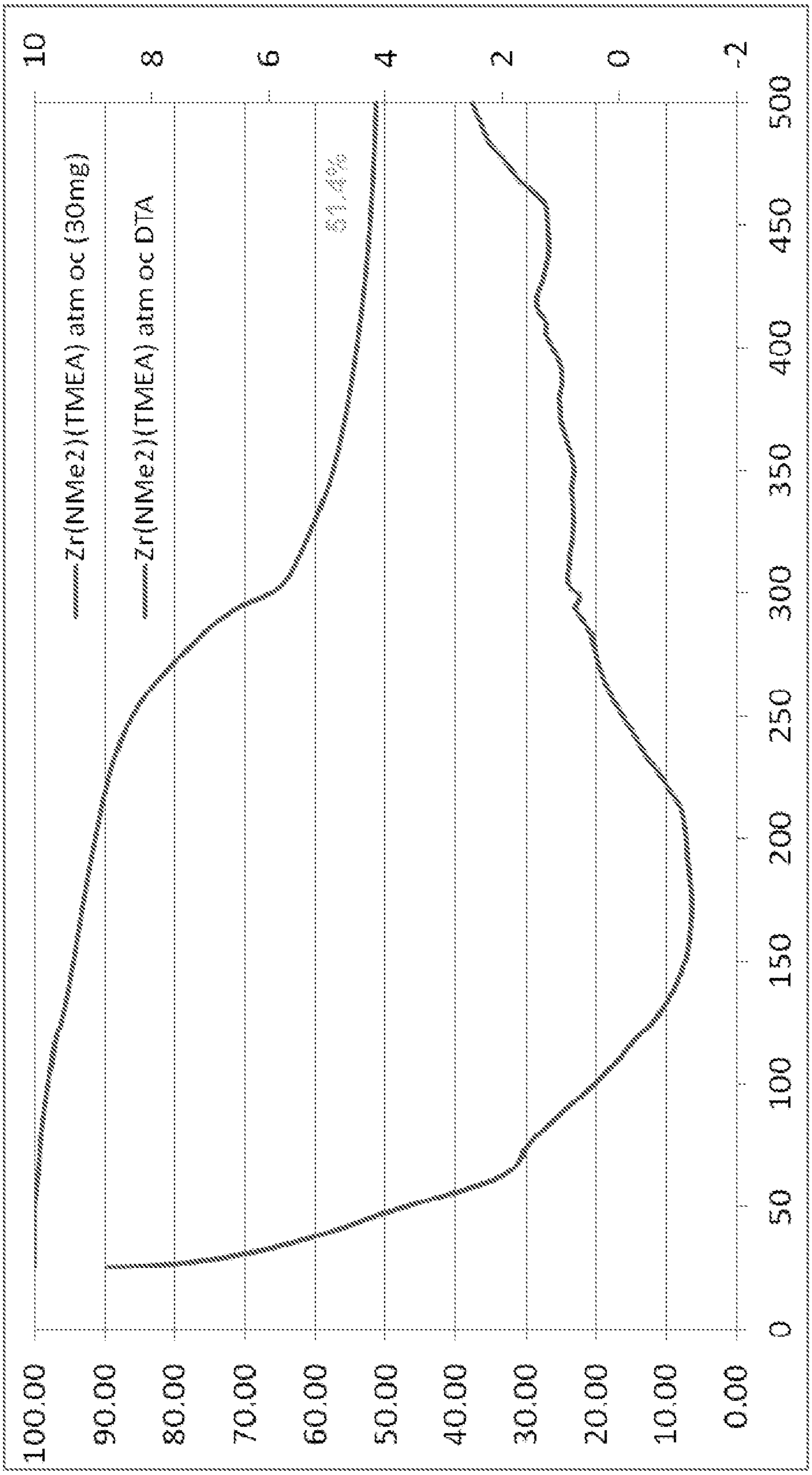
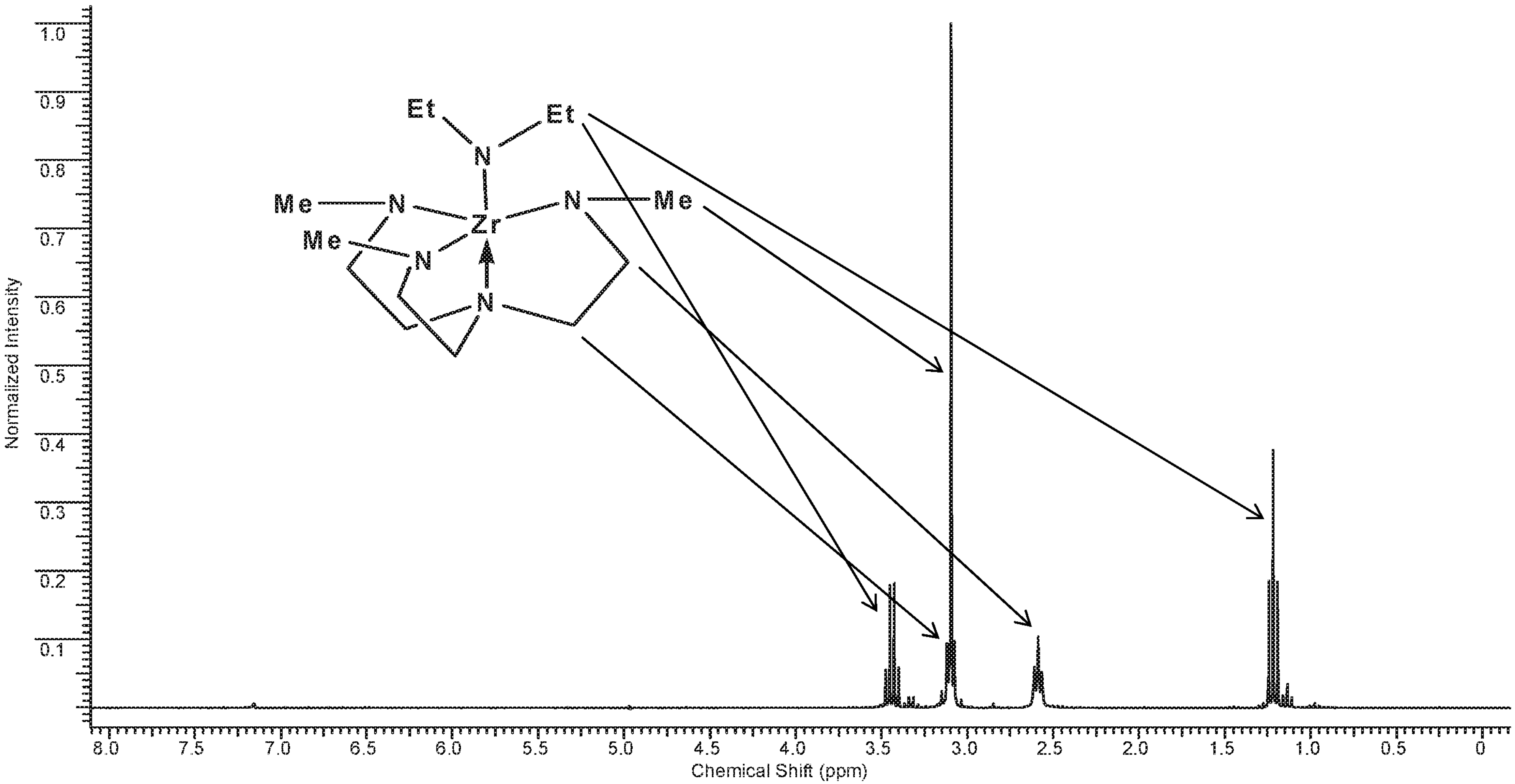

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
50
100
150
200
250
300
350
400
450
500
10
8
6
4
2
0
-2
Zr(NMe2)(TMEA) atm oc (30mg)
Zr(NMe2)(TMEA) atm oc DTA
51.4%

FIG 11



NMR Spectrum of Distilled Product in C_6D_6

FIG 12

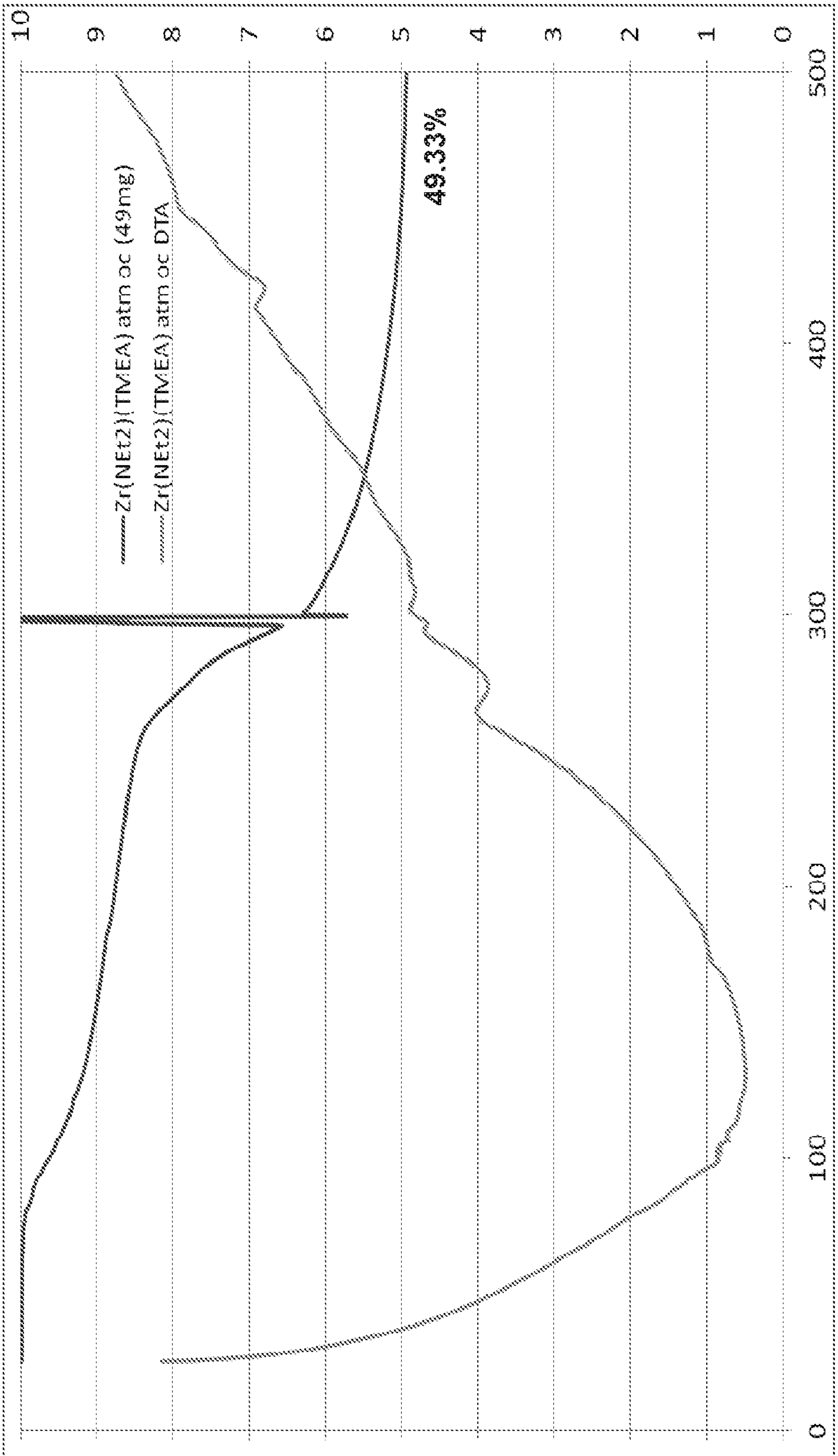
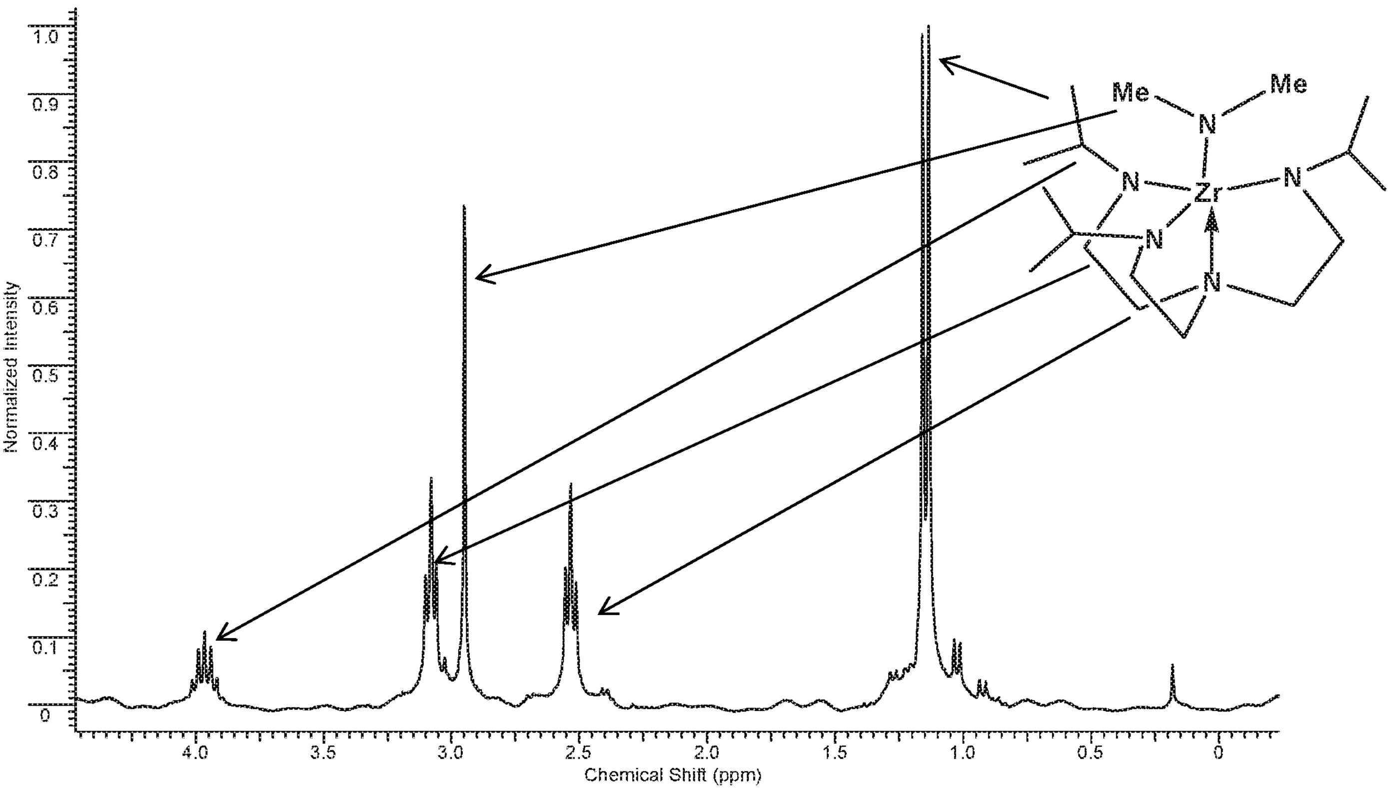
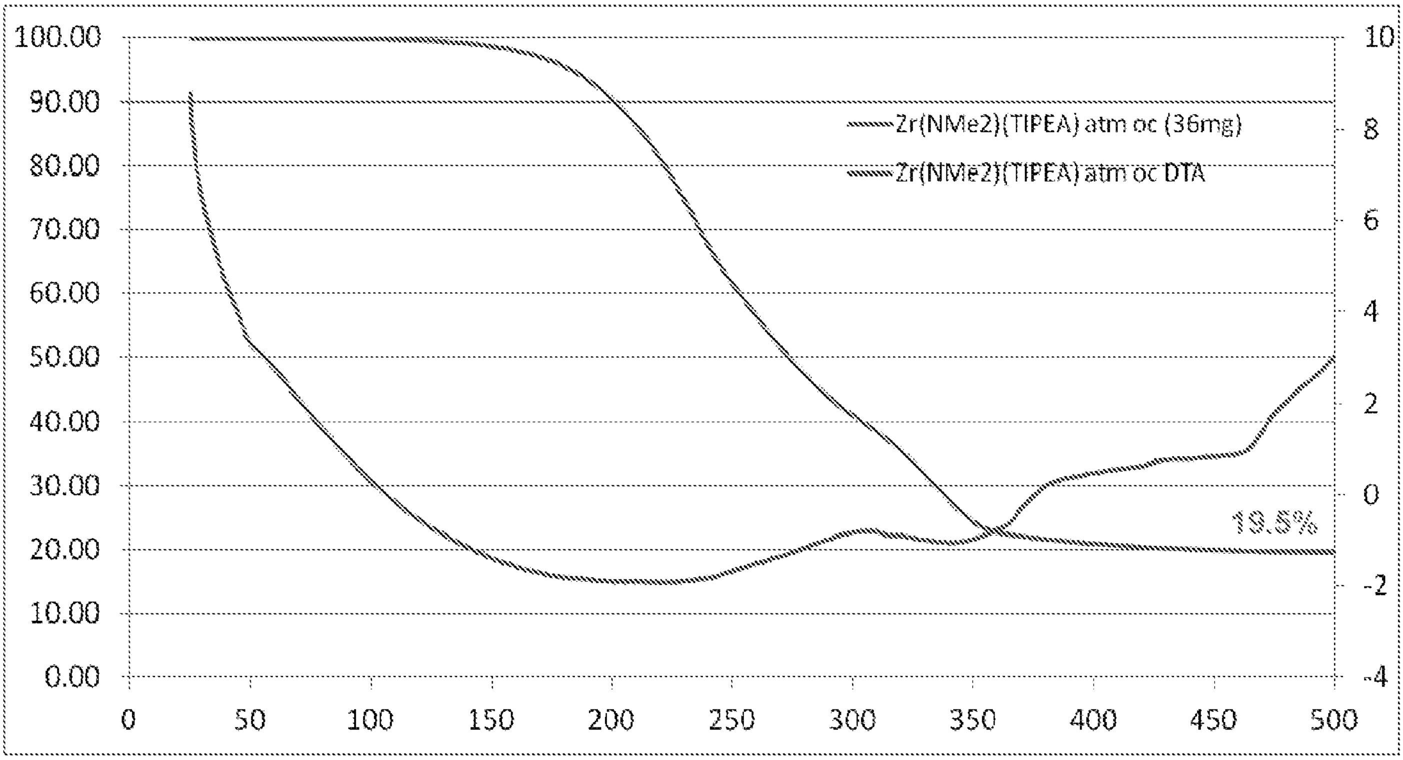

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
100
200
300
400
500
10
9
8
7
6
5
4
3
2
1
0
Zr(NEt2)(TMEA) atm oc (49mg)
Zr(NEt2)(TMEA) atm oc DTA
49.33%

FIG 13



NMR Spectrum of Crude Product in C_6D_6

FIG 14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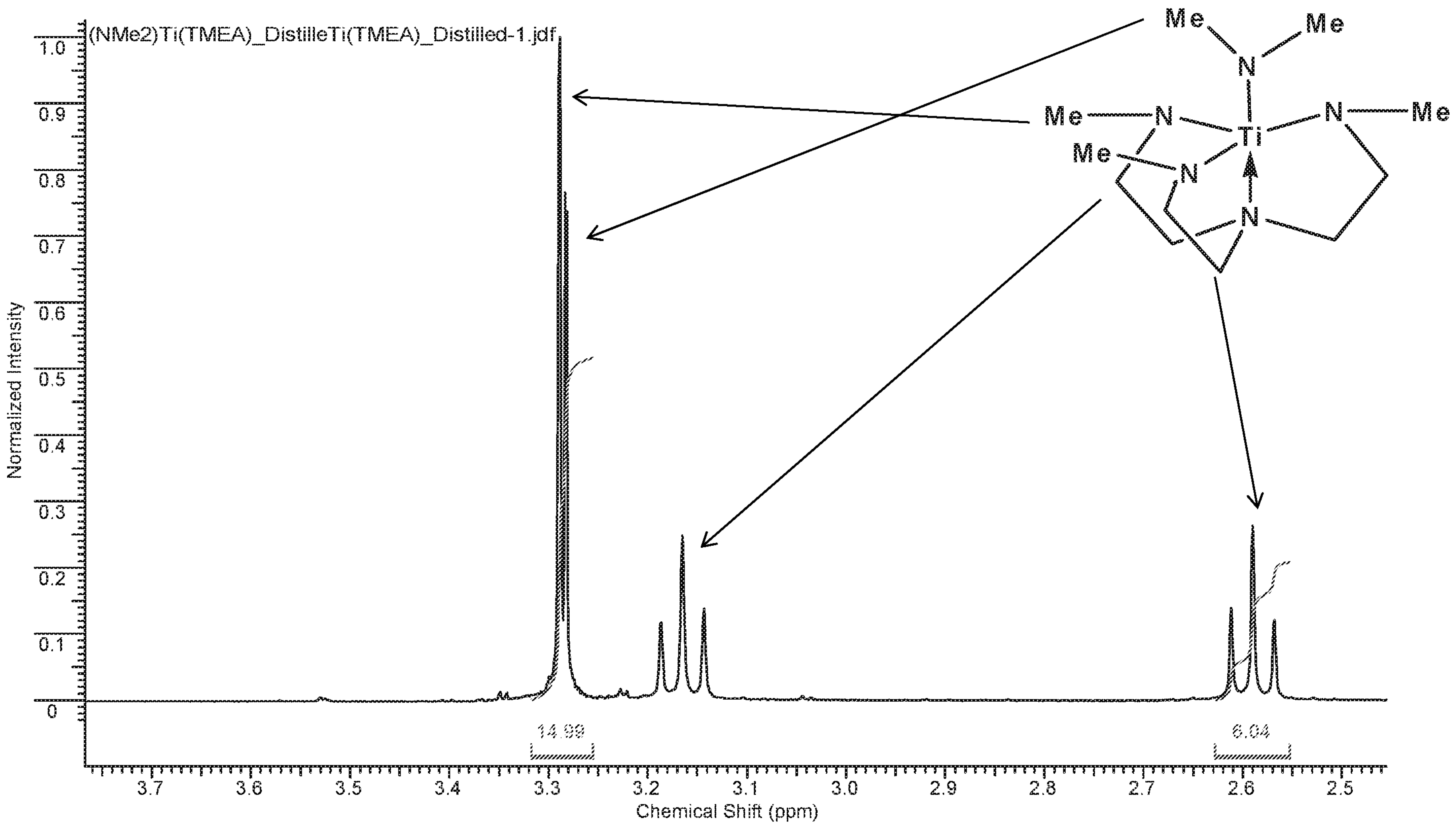
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
10
8
6
4
2
0
-2
-4
0
50
100
150
200
250
300
350
400
450
500
Zr(NMe2)(TIPEA) atm oc (36mg)
Zr(NMe2)(TIPEA) atm oc DTA
19.5%

FIG 15



NMR Spectrum of Distilled Product in C_6D_6

FIG 16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/026817

A. CLASSIFICATION OF SUBJECT MATTER

C23C 16/455(2006.01)i, C23C 16/18(2006.01)i, C23C 16/50(2006.01)i, C07F 7/28(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C23C 16/455; C07F 15/06; C07F 19/00; C07F 7/28; C23C 16/18; C23C 16/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: transition metal, Ti, Hf, Zr, depositing, precursor, halide, Cp, N

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JUNG et al., Atomic layer deposition of ZrO_2 thin film on Si(100) using $\{\eta 5:\eta 1\text{-}Cp(CH_2)_3NMe\}Zr(NMe_2)_2/O_3$ as precursors, This Solid Films, 2015, vol. 589, pp. 831-837 See page 831 and chart 1.	1-15
A	US 2015-0105573 A1 (ROMERO, PATRICIO E.) 16 April 2015 See paragraphs [0007], [0014]-[0016], claim 1 and figures 1, 2.	1-15
A	US 2013-0295298 A1 (L`AIR LIQUIDE, SOCIETE ANONYME POUR I`ETUDE ET I`EXPLOITATION DES PROCEDES GEORGES CLAUDE) 07 November 2013 See paragraph [0078] and claim 1.	1-15
A	US 2016-0137675 A1 (L`AIR LIQUIDE, SOCIETE ANONYME POUR L`ETUDE ET L`EXPLOITATION DES PROCEDES GEORGES CLAUDE) 19 May 2016 See paragraphs [0323], [0326] and claim 1.	1-15
A	BUTAKOFF et al., NEW TITANIUM AND ZIRCONIUM SANDWICH AND HALF-SANDWICH COMPLEXES CONTAINING THE $C5Me_4CH_2CH_2CH{=}CH_2$ (Cp=) LIGAND, Polyhedron, 1996, vol. 15, no. 3, pp. 489-499 See page 489 and scheme 1.	1-15

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 15 June 2017 (15.06.2017)	Date of mailing of the international search report **15 June 2017 (15.06.2017)**
Name and mailing address of the ISA/KR International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Authorized officer HAN, Joong Sub Telephone No. +82-42-481-3578

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2017/026817

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015-0105573 A1	16/04/2015	US 9067958 B2	30/06/2015
US 2013-0295298 A1	07/11/2013	US 9187511 B2	17/11/2015
US 2016-0137675 A1	19/05/2016	None	