Title: CYCLOPENTADIENYL TYPE HAFNIUM AND ZIRCONIUM PRECURSORS AND USE THEREOF IN ATOMIC LAYER DEPOSITION

Abstract: Precursors suitable for chemical vapour deposition, especially ALD, of hafnium oxide or zirconium oxide, have the general formula (I): (R Cp)₂MR₂ wherein Cp represents a cyclopentadienyl ligand, R is H or a substituting alkyl group, alkoxy group or amido group of the Cp ligand, R' and R" are an alkyl group, an alkoxy group or an amido group and M is hafnium or zirconium.
This invention concerns chemical vapour deposition, especially atomic layer deposition (ALD) and precursors therefor.

In ALD, thermal decomposition of the precursors is undesirable as the mechanism is purely a chemical reaction on the growth surface. Alternate precursors are applied with a self-limiting reaction depositing one monolayer at a time in an extremely uniform manner. Any thermal breakdown of the precursor means that the self-limiting growth is lost and so the layers formed are not good.

For ALD of hafnium based oxide materials, tetrakis(ethylmethyl)hafnium (IV) (hafnium methylethylamide, Hf(NEtMe)₄) is reportedly the best available precursor but is not sufficiently stable for use in ALD in practice.

An alternative hafnium precursor has been proposed, namely, bis(cyclopentadienyl) hafnium (IV) dimethyl (Cp₂HfMe₂). This precursor is, however, a solid having low volatility and so suffers from transport problems.

An object of this invention is to provide precursors suitable for chemical vapour deposition, especially ALD, of hafnium oxide and zirconium oxide and a method of depositing hafnium oxide or zirconium oxide.

According to a first aspect of the invention there is provided a use for a precursor in the atomic layer deposition (ALD) of hafnium oxide or zirconium oxide, wherein the precursor has the general formula:

\[(R'Cp)₂MR₂\]
2

wherein Cp represents a cyclopentadienyl ligand, $R^1$ is a substituting alkyl group, alkoxy group or amido group of the Cp ligand, $R^2$ is an alkyl group, an alkoxy group or an amido group and $M$ is hafnium or zirconium.

A second aspect of the present invention provides a method of depositing hafnium oxide or zirconium oxide by atomic layer deposition using a precursor of the general formula:

$$(R^1\text{Cp})_2MR^2R^3$$

wherein Cp represents a cyclopentadienyl ligand, $R^1$ is a substituting alkyl group, alkoxy group or amido group of the Cp ligand, $R^2$ and $R^3$ are the same or different and are selected from alkyl groups, alkoxy groups and amido groups and $M$ is hafnium or zirconium.

Preferably the $R^2$ and $R^3$ ligands have 1 to 4 carbon atoms, especially 1 or 2 carbon atoms. In one preferred embodiment the precursor used in the invention is bis(methylcyclopentadienyl) hafnium (IV) dimethyl, $(\text{MeCp})_2\text{HfMe}_2$. This compound has been found to be a low melting point solid with slightly higher volatility than the above-mentioned prior art precursors. Bis(methylcyclopentadienyl) zirconium (IV) dimethyl, $(\text{MeCp})_2\text{ZrMe}_2$, is an example of a preferred zirconium oxide precursor. An alternative is bis(methylcyclopentadienyl) hafnium (IV) methyl ethyl, $(\text{MeCp})_2\text{HfMe}(\text{Et})$.

According to yet a third aspect of the invention there is provided novel precursors suitable for chemical vapour deposition, especially ALD, of hafnium oxide or zirconium oxide having the formula:

$$(\text{Cp}_2\text{MR}^4\text{R}^5)$$
wherein $R^4$ and $R^5$ are the same or different and selected from alkoxy groups and amido groups, Cp represents a cyclopentadienyl ligand and M is hafnium or zirconium.

Preferably, the precursor contains at least one alkoxy ligand. Preferred precursor of this formula are when $R^4$ and $R^5$ are the same especially bis(cyclopentadienyl)bis(methoxy) hafnium (IV), $Cp_2Hf(OMe)_2$, wherein Me represents a methyl group and the zirconium equivalent, $Cp_2Zr(OMe)_2$.

A fourth aspect of the present invention provides novel precursors suitable for chemical vapour deposition, especially ALD of hafnium oxide or zirconium oxide having the formula:

$$(R^6Cp_2MR^4OR^5)$$

wherein Cp represents a cyclopentadienyl ligand, $R^4$ is selected from an alkyl group and an alkoxy group, $R^2$ is an alkyl group and $R^6$ is a H, substituting alkyl group, alkoxy group or amido group of the Cp ligand and M is hafnium or zirconium.

Preferably, the $R^4$ and $R^5$ ligands have 1 to 4 carbon atoms, especially 1 or 2, ideally 1. $R^6$ is preferably H or an alkyl group having 1 or 2 carbon atoms, especially Me.

Preferred precursors include those where $R^4$ is an alkoxy group, particularly bis(methylcyclopentadienyl)bis(methoxy) hafnium (IV), $(MeCp)_2Hf(OMe)_2$, and its equivalent zirconium components. Alternatively, preferred precursors are those that contain three different ligands, i.e., having the formula:

$$(R^6Cp)_2MR^4OR^5$$
as defined above but wherein R^4 is not an alkoxide group, particularly bis(methylcyclopentadieny1)methyl methoxy hafnium (IV), (MeCp)_2Hf(OMe)Me wherein Me represents a methyl group and the equivalent zirconium components.

Deposition of hafnium oxide or zirconium oxide from precursors according to the third and fourth aspects of the invention is preferably by means of ALD but other deposition techniques, wherein two reactant sources are delivered to a substrate in a controlled sequence, may be used, such as atomic vapour deposition (AVD) and atomic layer epitaxy (ALE). Typically the precursor may be delivered to a substrate in pulses alternating with pulses of a suitable oxygen source, such as H_2O, O_2 or ozone.

The precursor may be delivered to the substrate by any suitable means, examples of which include conventional bubbling of carrier gas, vapour draw or other techniques using neat compounds. Alternatively compound solutions may be prepared and injected into evaporators to put them in the vapour phase for delivery to a growth chamber.

It is envisaged that ALD using this precursor will be suitable for applications such as DRAM and CMOS for memory and logic applications in silicon chips.

This invention will be further described by means of the accompanying drawings, in which:

Figure 1 shows TGA data for purified (MeCp)_2HfMe_2;

Figure 2 is a vapour pressure plot for dimethylhafnocene derivatives;

Figures 3 and 3a are plots of growth rate as a function of deposition temperature for deposition from (CpMe)_2HfMe_2 with O_3 and H_2O;
Figures 4 and 4a are plots of growth rate as a function of \((\text{CpMe})_2\text{HfMe}_2\) pulse length at deposition temperature of 350\(^\circ\)C (and 400\(^\circ\)C) using water and ozone as oxygen sources;

Figure 5 is a plot of growth rate (mm/cycle) versus growth temperature (\(^\circ\)C) for atomic layer deposition using \(\text{HfCp}_2\text{Me}_2\) and \((\text{MeCp})_2\text{HfMe}_2\);

Figure 6 shows proton NMR for \(\text{Cp}_2\text{Hf(OMe)}_2\);

Figure 7 shows proton NMR for \((\text{MeCp})_2\text{Hf(OMe)Me}\); and

Figure 8 is a comparison of TGA data for various Hf precursors; and

Figures 9 and 10 are plots of growth rate using \((\text{MeCp})_2\text{Hf(OMe)Me}\) as a function of deposition temperature (\(^\circ\)C) and pulse length (sec), using ozone as the oxygen source.

This invention will now be further described by means of the following Examples.

Example 1

Preparation of bis(methylcyclopentadienyl) hafnium (IV) dimethyl, \((\text{MeCp})_2\text{HfMe}_2\)
(MeCp)\textsubscript{2}HfMe\textsubscript{2} was prepared in a one-pot method as follows. The reaction of 2 equivalents of methylcyclopentadiene with 4 equivalents of MeLi solution in Et\textsubscript{2}O, followed by the treatment with 1 equivalent of HfCl\textsubscript{4} gave brown liquid crude product in 87% yield. The product was purified by vacuum distillation of crude product at 80 - 120 °C/0.3 - 0.5 torr to give a wax-like compound (68%). Melting point ~30-40C. Elemental analysis of this compound was in good agreement with theory (%): C : 45.40 (cal: 45.80); H: 5.40 (cal: 5.45)

Note the reaction scale was targeted to yield 100g of purified product. Increased batch size may be achieved by directly scaling quantities and using appropriately sized equipment.

Thermal behaviour of the product was tested with a thermal gravimetric analyzer (TGA) with temperature increases of 20 °C/min and 40 °C/min. The graph (Figure 1) showed that purified (MeCp)\textsubscript{2}HfMe\textsubscript{2} started to vapourise at 50 °C and finish at 300 °C with less than 4% non-volatile residues.

The vapour pressure of (MeCp)\textsubscript{2}HfMe\textsubscript{2} was tested in the temperature range of 30 °C to 70 °C and the plot is in the following Figure 2, which compares the known source Cp\textsubscript{2}HfMe\textsubscript{2} with (MeCp)\textsubscript{2}HfMe\textsubscript{2} and shows a beneficial improvement in volatility for the new compound.

Example 2

Report on ALD studies on (MeCp)\textsubscript{2}HfMe\textsubscript{2}

The equipment used was a standard ALD reactor (Microchemistry F-120) operating at a pressure of 2-3 mbar. The (MeCp)\textsubscript{2}HfMe\textsubscript{2} precursor was observed to
melt at 43-44°C under these conditions and could be suitably evaporated at about 60°C to allow controlled introduction to the growth chamber.

Several runs have been performed to deposit on Si(100) with H_2O and O_3 as the oxygen source. Growth rate against deposition temperature is shown in Figures 3 and 3a.

Growth rate at 350°C is 0.36 Å/cycle, which is slightly lower than with Cp_2HfMe_2/H_2O process (Niinistö J. et al. J. Mater. Chem. 2005). Films could be grown at 300°C but growth rate is rather low. At 350°C and 400°C the ALD type saturative growth seems to be dominant as shown in Figures 4 and 4a.

Uniformity was good (+− 1 nm) over the substrate are (5 x 10 cm^2) for all trials.

Figure 5 is a plot of ALD performance for Cp_2HfMe_2 and (MeCp)_2 HfMe_2. It is clear that the addition of a methyl group to the Cp ring has a profound effect on the temperature range over which the ALD self-limiting growth process holds true. For the prior art compound Cp_2HfMe_2, the self-limiting regime ends around 400°C as demonstrated by a steep rise in growth. In contrast, (MeCp)_2 HfMe_2 clearly remains self-limiting up to 500°C. This dramatic change observed with the new precursor for ALD was not expected.

Example 3

Preparation of bis(cyclopentadienyl)bis(methoxy) hafnium (IV),

(Cp)_2Hf(OMe)_2
Synthesis of this compound involved a two stage process starting from hafnium tetra-amide and substituting first the Cp and then alkoxide groups as follows. Hf(NMe₂)₄ (58g, 0.16mol) was dissolved in toluene (500mls), and CpH (27mls, 0.41mol) was added and the mixture heated to reflux for 2 hours. Another 20mls of CpH was added and the mixture reheated to reflux for another 2 hours. An aliquot was taken for NMR, which showed the right integrations for Cp₂Hf(NMe₂)₂. The solvent was removed to give a yellow/brown solid in 60g (94%) yield.

Cp₂Hf(NMe₂)₂ (30g, 0.075mol) was dissolved in toluene (250mls) and MeOH (6mls, 4.8g, 0.15mol) added slowly. The solution was heated to reflux for 2 hours then the solvent removed under vacuum to give a dark brown oil. The oil was dried under vacuum, which then became a very thick immobile oil. The product was extracted in toluene and transferred to a sublimation flask. The solvent was removed under vacuum and the product sublimed onto a cold finger.

A white crystalline solid was collected at 60-70°C @ 0.5 torr. ¹H NMR analysis of the crystals showed only the 2 major peaks expected for Cp₂Hf(OMe)₂ (Figure 6).
Example 4

Preparation of bis(methylyclopentadienyl)methylmethoxy hafnium (IV),
(MeCp)₂Hf(OMe)Me

9.3g (0.025 moles) of (Me-Cp)₂HfMe₂ was dissolved in 60 ml of toluene. 2.2ml (0.052 moles) of anhydrous methanol was added. The reaction was stirred overnight and volatiles removed in vacuo.

Yield: 9.6g (96%) yellow liquid.

Elemental Analysis: Calc C, 43.93 H, 5.27; Found C, 43.53 H, 5.24. NMR see Figure 7. The peaks observed are as expected for the product.

It should be noted that further addition of methanol did not change the product and full substitution of the alkoxide for the alkyl group could not be achieved by this method.

The liquid nature of this precursor results in it being much more suited to the vapour delivery approach commonly employed in ALD compared with prior art precursors.

Figures 9 and 10 illustrate the growth data for this precursor against the deposition temperature (°C) and pulse time (sec) respectively.
Example 5

Comparison of TGA data.

A comparison of TGA data for a number of compounds is given in Figure 8 to highlight the improvements achieved by molecular tailoring. The MeCp derivatives are clearly superior to unsubstituted Cp compounds with much reduced residues implying greater thermal stability and the ability to vapourise without decomposition.

It is expected that other substituted Cp derivatives in combination with different alkoxide and alkyl groups will have similar properties and by careful choice of the precise groups involved optimised precursors can be isolated for each deposition process.
CLAIMS

1. The use of a precursor in atomic layer deposition of hafnium oxide or zirconium oxide, wherein the precursor has the general formula:

\[(R^1\text{Cp})_2\text{MR}^2\]

wherein Cp represents a cyclopentadienyl ligand, \(R^1\) is a substituting alkyl group, alkoxy group or amido group of the Cp ligand, \(R^2\) is an alkyl group, an alkoxy group or an amido group and M is hafnium or zirconium.

2. The use of a precursor as claimed in claim 1, wherein the precursor is Bis(methylcyclopentadienyl) hafnium (IV) dimethyl, \((\text{MeCp})_2\text{HfMe}_2\).

3. The use of a precursor as claimed in claim 1, wherein the precursor is Bis(methylcyclopentadienyl) zirconium (IV) dimethyl \((\text{MeCp})_2\text{ZrMe}_2\).

4. The use of a precursor as claimed in claim 1, wherein the precursor is bis(methylcyclopentadienyl) hafnium methyl ethyl, \((\text{MeCp})_2\text{HfMe(Et)}\).

5. The use of a precursor as claimed in claim 1, wherein the precursor is bis(methylcyclopentadienyl) zirconium (IV) methyl ethyl, \((\text{MeCp})_2\text{ZrMe(Et)}\).

6. The novel precursor bis(methylcyclopentadienyl) hafnium (IV) methyl ethyl, \((\text{MeCp})_2\text{HfMe(Et)}\).

7. The novel precursor bis(methylcyclopentadienyl) zirconium (IV) methyl ethyl, \((\text{MeCp})_2\text{ZrMe(Et)}\).

8. A precursor suitable for chemical vapour deposition, especially ALD, of hafnium oxide or zirconium oxide having the formula:

\[(\text{Cp}_2\text{MR}^4\text{R}^5)\]
wherein $R^4$ and $R^5$ are the same or different and selected from alkoxy groups and amido groups, Cp represents a cyclopentadienyl ligand and M is hafnium or zirconium.

9. A precursor as claimed in claim 8 wherein $R^4$ and $R^5$ have 1 to 4 carbon atoms.

10. A precursor as claimed in claim 8 or 9 wherein the precursor contains at least one alkoxide group.

11. A precursor as claimed in claim 8, 9 or 10 wherein $R^4$ and $R^5$ are the same.

12. The precursor Bis(cyclopentadienyl)bis(methoxy) hafnium (IV), Cp$_2$Hf(OMe)$_2$, wherein Me represents a methyl group.

13. The precursor Bis(cyclopentadienyl)bis(methoxy) zirconium (IV), Cp$_2$Zr(OMe)$_2$, wherein Me represents a methyl group.

14. The use of a precursor in atomic layer deposition of hafnium oxide or zirconium oxide having the formula:

$$(R^6\text{Cp})_2\text{MR}^4R^5$$

wherein Cp represents a cyclopentadienyl ligand, $R^4$ and $R^5$ are the same or different selected from alkyl groups, and alkoxy groups $R^6$ is a substituting alkyl group, alkoxy group or amido group of the Cp ligand and M is hafnium or zirconium.

15. The use of a precursor as claimed in claim 14 wherein $R^4$ and $R^5$ have 1 to 4 carbon atoms.

16. The use of a precursor as claimed in claim 14 or 15 wherein $R^6$ is H or an alkyl group having 1 to 2 carbon atoms.
17. The use of a precursor as claimed in any one of claims 14 to 16 wherein R⁴ is an alkoxide group.

18. A precursor suitable for chemical vapour deposition, especially ALD of hafnium oxide or zirconium oxide, having the general formula:

\[(R^6\text{Cp})_2MR^4\text{OR}^5\]

wherein Cp represents a cyclopentadienyl ligand, R⁴ is an alkyl or alkoxide group, R⁵ is an alkyl group and R⁶ is a H, substituting alkyl group or amido group of the Cp ligand and M is hafnium or zirconium.

19. A precursor as claimed in claim 18 wherein R⁴ is an alkoxide group.

20. The precursor Bis(methylcyclopentadienyl)bis(methoxy) hafnium (IV), (MeCp)₂Hf(OMe)₂, wherein Me represents a methyl group.

21. The precursor Bis(methylcyclopentadienyl)bis(methoxy) zirconium (IV), (MeCp)₂Zr(OMe)₂, wherein Me represents a methyl group.

22. A precursor as claimed in claim 18 wherein R⁴ is an alkyl group.

23. The precursor Bis(methylcyclopentadienyl)methyl methoxy hafnium (IV), (MeCp)₂Hf(OMe)Me, wherein Me represents a methyl group.

24. Bis(methylcyclopentadienyl)methyl methoxy zirconium (IV), (MeCp)₂Hf(OMe)Me, wherein Me represents a methyl group.

25. A method of depositing hafnium oxide or zirconium oxide by chemical vapour deposition, especially by ALD, using a precursor as claimed in any one of claims 6 to 13 and 18 to 24.

26. A method as claimed in claim 25, wherein the precursor is delivered to a substrate in pulses alternating with pulses of an oxygen source.
27. A method as claimed in claim 26, wherein the oxygen source is selected from, H$_2$O, O$_2$ or ozone.

28. A method as claimed in claim 25, 26 or 27, wherein the precursor is delivered to the substrate by bubbling of carrier gas, vapour draw or other techniques using neat compounds.

29. A method as claimed in claim 25, 26 or 27, wherein precursor compound solutions are prepared and injected into evaporators to put them in the vapour phase for delivery to a growth chamber.

30. The use of precursors according to any one of claims 6 to 13 and 18 to 24 in ALD techniques for applications including DRAM and CMOS for memory and logic applications in silicon chips.
Vapour pressure of dimethyl hafnocene

(\text{MeCp})_2\text{HfMe}_2
y = -3072.1x + 8.0218
R^2 = 0.9327

\text{Cp}_2\text{HfMe}_2
y = -3142.9x + 8.062
R^2 = 0.9997

Temperature 1/T(K-1)
(CpMe)₂Hf(CH₃)₂/H₂O

$T_{\text{Growth}} = 400^\circ\text{C}$

Growth rate $A/\text{(cycle)}^{-1}$

Pulse time $/\text{s}$

FIG 4

(CpMe₂)HfMe₂/O₃

$T_{\text{Growth}} = 400^\circ\text{C}$

Growth rate $A/\text{(cycle)}$

Pulse time (sec)

FIG 4a
Growth data for $(\text{MeCp})_2\text{Hf(OMe)Me/O}_3$

**FIG 9**

Growth data for $(\text{MeCp})_2\text{Hf(OMe)Me/O}_3$

**FIG 10**

**SUBSTITUTE SHEET (RULE 26)**
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/18
ADD. C23C16/455

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

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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</table>

Y

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1-3, 14, 15

X

Further documents are listed in the continuation of Box C.

* 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 document but published on or after the international filing date
  *L* Document which may throw doubts on priori 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 data 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.

*X* Document member of the same patent family

Date of the actual completion of the international search
6 September 2006

Date of mailing of the international search report
29/09/2006

Name and mailing address of the ISA/
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Authorized officer
Schuhmacher, Jörg

Form: PCT/ISA/210 (second sheet) (April 2003)
<table>
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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>NIINISTO J ET AL: &quot;Structural and dielectric properties of thin ZrO2 films on silicon grown by atomic layer deposition from cyclopentadienyl precursor&quot; JOURNAL OF APPLIED PHYSICS AIP USA, vol. 95, no. 1, 1 January 2004 (2004-01-01), pages 84-91, XP002397605 ISSN: 0021-8979 abstract</td>
<td>16</td>
</tr>
<tr>
<td>Y</td>
<td>CODATO SIMONE ET AL: &quot;MOCVD growth and characterization of ZrO2 thin films obtained from unusual organo-zirconium precursors&quot; ADV MATER.; ADVANCED MATERIALS 1999 WILEY-VCH VERLAG BERLIN GMBH, WEINHEIM, GER, vol. 11, no. 11, 1999, pages 159-164, XP002397606 page 160</td>
<td>1-3,14, 15</td>
</tr>
</tbody>
</table>
INTERNATIONAL SEARCH REPORT

Box II  Observations where certain claims were found unsearchable (Continuation of Item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. [ ] Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III  Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [x] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (January 2004)
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1 partial, 2-7, 14 partial, 15 partial, 16 partial, and (25-30) partial

Precursors and use thereof in atomic layer deposition of hafnium oxide or zirconium oxide, the precursor having the general formula:

R(Cp)2MR'R''

wherein Cp represents a cyclopentadienyl, R is a substituting alkyl, alkoxy or amido group of the Cp ligand and R' and R'' are alkyl groups

2. claims: 1 partial, 8-13, 14 partial, 15 partial, 16 partial, 17-24, and (25-30) partial

Precursors and use thereof in atomic layer deposition of hafnium oxide or zirconium oxide, the precursor having the general formula:

R(Cp)2MR'R''

wherein Cp represents a cyclopentadienyl, R is hydrogen or a substituting alkyl, alkoxy or amido group of the Cp ligand and R' and R'' are alkyl groups, alkoxy groups or amido groups, and at least R' or R'' is an alkoxy or amido group