Chemical vapor deposition of hafnium dioxide thin films from cyclopentadienyl hafnium compounds

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Abstract

Thin films of HfO_2 were grown by metal-organic chemical vapour deposition on fused quartz substrates in the temperature range of 400–500 °C using some bis(cyclopentadienyl)bis(alkoxide)hafnium (IV) precursors, namely $Cp_2Hf(O^iPr)_2$, $[Cp_2Hf\{OCH(CH_3)CH_2OCH_3\}_2]$, $[Cp_2Hf\{OC(CH_3)_2CH_2OCH_3\}_2]$ and $[Cp_2Hf\{OC(CH_2CH_3)_2CH_2OCH_3\}_2]$. These complexes, analyzed by nuclear magnetic resonance and thermogravimetric measurements, resulted pure and very stable towards air and moisture. The obtained films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy and atomic force microscopy. The deposits contained hafnium and oxygen in the right stoichiometric ratio with a low carbon contamination and they consisted of monoclinic HfO_2 phase (baddeleyite) with a granular surface morphology.
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1. Introduction

Hafnium dioxide (HfO_2) has been extensively studied to replace SiO_2 as the gate-oxide insulating material for sub-0.1 μm complementary metal oxide semiconductor devices [1] as the consequence of the dielectric properties of its polycrystalline films, its high permittivity and stability in contact with silicon, its density, heat of formation and relatively large band gap. The growing scientific and technological interest for HfO_2 is also due to the possibility of using it as insulating dielectric in capacitive elements in many memory devices, such as dynamic random access memory, and in thin-film electroluminescent applications [2]. Finally, HfO_2 thin films are challenging candidates for the production of protective and barrier coatings [3], mirrors [4], and sensors [5]. More specifically, samples with a large content of tetragonal phase, obtained under high-pressure and very fast crystallization conditions, present high hardness values [6].

HfO_2 thin films have been already prepared by sol-gel processes [7], Physical Vapour Deposition [8], Atomic Layer Deposition (ALD) [9], and Metal Organic Chemical Vapour Deposition (MOCVD) [10] techniques. Among them, MOCVD presents several advantages, such as uniform depositions even on non-planar device geometries, a great versatility and the possibility of carrying out film growth at relatively low temperatures. Nevertheless, the choice of a suitable precursor with an adequate volatility, a necessary condition for an efficient vapour phase transport, is still an open challenge. As a matter of fact, the precursors that have been employed in Chemical Vapour Deposition processes for the deposition of HfO_2 such as $HfCl_4$ [11], β-diketonates and their fluorinated complexes [12], $Hf(NO_3)_4$ [13] and $Hf(NEt_2)_4$ ($NEt_2 =$ diethylamide) [14], presented some drawbacks such as a low volatility, a great air and moisture sensitivity, high evaporation and deposition temperatures with a high carbon and fluorine contamination of the corresponding deposits.

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Other compounds, largely employed as precursors, are the tetra-alkoxide complexes which, however, present the problem of oligomerization which reduces their volatility. Nevertheless, the presence of bulky ligands on the molecular skeleton inhibits oligomerization, thus making hafnium (IV) t-butoxide [Hf(O^{t}Bu)$_4$] a suitable precursors for the deposition of oxide layers [15], even though an eventual drawback of such a molecule concerns to the presence of the unsaturated four-coordinate Hf center which makes it very sensitive to air and moisture. Hafnium precursors with improved chemico-physical properties have been synthesized using donor functionalized alkoxide ligands. In particular, it has been demonstrated that when alkyl groups are bonded on α-carbon of the ligand, the formation of mononuclear complexes such as Hf (dmae)$_4$ (dmae=dimethylaminoethoxide), Hf(mmp)$_4$ (mmp=1-methoxy-2-methyl-2-propanolate), Hf(mp)$_4$ (mp=3-methyl-3-pentoxide) and Hf(O^{t}Bu)$_2$(mmp)$_2$ is preferred [16]. In the last few years, fully saturated hafnium homoleptic Hf(dmae)$_4$ [17], Hf (mmp)$_4$ [18] and Hf(mp)$_4$ [19] and heteroleptic alkoxide compounds such as: Hf(O^{t}Bu)$_2$(mmp)$_2$ [20] and Hf(O^{i}Pr)$_2$ (tbaoac)$_2$ (tbaoac=ter-butylacetoacetato) [21] have been used. Moreover, the tetrahydroxyldiethylamide Hf(ONEt$_2$)$_4$ [22], more stable than the coordinatively unsaturated Hf(NEt$_2$)$_4$, and multi-nuclear compounds like Hf$_3$O(ONep)$_{10}$ (Nep=neopentyl) [23] have been also investigated and employed.

An alternative class of precursors could be represented by the cyclopentadienyl complexes coordinatively saturated with dialkoxide or dialkylamide ligands. In this regard, it deserves to mention that some hafnocene compounds with a series of bicyclo [2.2.1]heptanolates ligands {Cp$_2$Hf(OBL)$_2$, (Cp=cyclopentadie-nyl, OBL=borneol), Cp$_2$Hf(ONBL)$_2$ (ONBL=norborneol)} [24] and of alkyl and dialkylamide moieties {Cp$_2$Hf(L)$_2$ (L=Me, N (Me)$_2$, N(Et)$_2$} [25,26] and more recently the bismethylcyclo-pentadienyl complexes (MeCp)$_2$HfMe$_2$ [27] and (MeCp)$_2$HfMe (OMe), (MeCp=methylcyclopentadienyl) [27,28] have been already investigated and used.

In this contribution bis(cyclopentadienyl)bis(alkoxide)hafnium (IV) complexes with different steric hindrance, namely bis (cyclopentadienyl)bis(isopropoxy)hafnium(IV) [(C$_5$H$_5$)$_2$Hf{OCH (CH$_3$)$_2$}$_2$] (1), bis(cyclopentadienyl)bis(1-methoxy-2-propoxy)haf-nium(IV) [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)CH$_2$OCH$_3$}$_2$] (2), bis(cyclopen-tadienyl)bis(1-methoxy-2-methyl-2-propoxy)hafnium(IV) [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$] (3) and bis(cyclopentadienyl) bis(3-methylmethoxy-3-pentoxy)hafnium(IV) [(C$_5$H$_5$)$_2$Hf{OC (CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$] (4) have been synthetized, characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and thermo-gravimetric measurements (TG) and used as MOCVD precursors for the deposition of HfO$_2$ thin films on fused quartz. The layers were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

2. Experimental details

2.1. General techniques

All the reactions for the precursor syntheses were carried out in dry-box under N$_2$ atmosphere. Hafnium (IV) chloride (99.9%) was purchased from Strem and used without further purification.

Diethylamine was distilled from calcium hydride, n-hexane and toluene from potassium-benzophenone. Fresh cyclopentadiene was obtained from the cracking at 170 °C of dicyclopentadiene (Aldrich) and used at once. Butyllithium was purchased from Aldrich. The commercial 2-propanol, 1-methoy-2-propanol and 1-methoxy-2-methyl-2-propanol (Aldrich) were further anhydri-fied by distillation at room pressure over CaH$_2$. The 3-methylmethoxy-3-pentanol was obtained as reported in literature [29].

^{1}H NMR experiments were carried out on a Bruker 300 MHz spectrometer and C$_6$D$_6$ as a solvent, while the ^{13}C NMR DEPT experiment was used with a 135° pulse to distinguish the primary and tertiary carbon atoms from the secondary ones.

HfO$_2$ thin films were deposited in a low-pressure hot wall MOCVD reactor equipped with a Pyrex tube (ext. ∅=50 mm) heated by a tubular furnace. The carrier gas was N$_2$ (flow rate=125 sccm), flowing through a bubbler containing the hafnium precursor thermostatically set to a temperature suitable for an efficient vaporization and thermal stability. The reactant gas (O$_2$+H$_2$O) was introduced in the main flow in the vicinity of the reaction zone, with a flow rate of 250 sccm. Prior entering into the reaction chamber, oxygen was bubbled into a 500 cm^3 flask containing 250 cm^3 of distilled water kept at 30 °C. The amount of released water was constant for all the depositions and it was 20 g×h^{-1}. For all the experiments, the total pressure was kept at 6 Pa and the growth temperature ranged between 400 °C and 500 °C. Prior to each deposition experiment, the substrate (fused quartz) was cleaned with hot trichloroethylene and rinsed with acetone in order to minimize the surface contamination.

The XRD patterns were recorded in 2θ/ω method with an X'Pert PW 3710 Philips instrument using Cu K$_\alpha$ radiation. A parallel plate collimator was used in front of the detector. Phase identification was performed with the support of the standard ICDD files. The average crystallite size was estimated by means of the Scherrer's formula.

XPS measurements were performed by using an Escalab Mk II spectrometer, equipped with a standard Al Kα excitation source (hν=1486.6 eV) and a five channeltron detection system. The binding energy (BE) scale was calibrated by referring to the C 1 s peak (BE=285.0 eV) of the surface contamination. The accuracy of the measured BE was±0.1 eV. XPS data were collected at a chamber pressure of ~1×10^{-7} Pa, increased up to ~1×10^{-5} Pa during the depth profiling carried out by means of an ion gun (Ar$^+$) whose energy was fixed at 2.0 keV.

AFM characterization of the surface morphology was realized with a Park Scientific Instrument-Model CP by using silicon cantilever tips with nominal curvature radius of 10 nm in contact mode.

Film thicknesses were determined by using a KLA Tencor Alpha-Step IQ surface profiler used to analyze the film height steps on partially masked samples.

Thermogravimetric analysis was carried out using a High Resolution TGA 2950 (TA Instruments) thermobalance. A working N$_2$ flux of 100 cm^3 min^{-1} was used. The TG profiles were recorded in the 20–1000 °C temperature range using an open platinum pan loaded with about 5 mg of each sample. The

heating rate was varied dynamically during the ramp in response to the derivative of weight change from 50 °C/min to 0.1 °C/min. The balance resolution is 1 μg.

2.2. Precursor synthesis

[(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)$_2$}$_2$] (**1**). To a stirred solution of Hf (NEt$_2$)$_4$ (obtained by reaction of an excess of NH(CH$_2$CH$_3$)$_2$ with butyllithium 1.6 M in n-hexane and HfCl$_4$), (2.06 g, 4.41 mmol) in toluene (40 cm^3), 3 ml of CpH (32.56 mmol) in toluene (20 cm^3) were added dropwise. The solution was boiled under reflux for 20 h and then the solvent and the ammine were removed in vacuo to give the Cp$_2$Hf(NEt$_2$)$_2$ as a yellow pure solid. To a stirred solution of this product (0.703 g, 1.55 mmol) dissolved in n-hexane (40 cm^3), 0.188 g (3.10 mmol) of 2-propanol diluted in n-hexane (5 cm^3) were slowly added dropwise. After 24 h the solvent was removed in vacuo giving **1** as a solid white product. ^{1}H NMR (C$_6$D$_6$, 25 °C) δ [ppm]: 5.97 (s, 10H, [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)$_2$}$_2$]), 4.14 (s, 2H, [(C$_5$H$_5$)$_2$Hf {OCH(CH$_3$)$_2$}$_2$]), 1.11 (d, 12H, [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)$_2$}$_2$]).

[(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)CH$_2$OCH$_3$}$_2$] (**2**). The complex was synthesized by the dropwise addition of 1-methoxy-2-propanol (0.268 g, 3 mmol) diluted in n-hexane (5 cm^3) to a stirred solution of Cp$_2$Hf(NEt$_2$)$_2$ (0.677 g, 1.50 mmol) in n-hexane (40 cm^3). After 24 h the solvent was removed in vacuo giving **2** as orange oil. ^{1}H NMR (C$_6$D$_6$, 25 °C) δ [ppm]: 6.04 (s, 10H, [(C$_5$H$_5$)$_2$ Hf{OCH(CH$_3$)CH$_2$OCH$_3$}$_2$]), 4.22 (m, 2H, [(C$_5$H$_5$)$_2$Hf{OCH (CH$_3$)CH$_2$OCH$_3$}$_2$]), 3.21 (s, 6H, [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$) CH$_2$OCH$_3$}$_2$]), 3.07 (m, 4H, [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$) CH$_2$OCH$_3$}$_2$]), 1.15 (d, 6H, [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$) CH$_2$OCH$_3$}$_2$]). ^{13}C NMR DEPT (C$_6$D$_6$, 25 °C) δ [ppm]: 21.68 [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)CH$_2$OCH$_3$}$_2$], 58.51 [(C$_5$H$_5$)$_2$Hf{OCH (CH$_3$)CH$_2$OCH$_3$}$_2$], 75.51 [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)CH$_2$OCH$_3$}$_2$], 80 [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)CH$_2$OCH$_3$}$_2$], 110.69 [(C$_5$H$_5$)$_2$Hf {OCH(CH$_3$)CH$_2$OCH$_3$}$_2$].

[(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$] (**3**). The complex was synthesized by the dropwise addition of 1-methoxy-2-methyl-2-propanol (0.301 g, 2.88 mmol) diluted in n-hexane (5 cm^3) to a stirred solution of Cp$_2$Hf(NEt$_2$)$_2$ (0.652 g, 1.44 mmol) in n-hexane (40 cm^3). After 24 h the solvent was removed in vacuo giving **3** as an orange oil. ^{1}H NMR (C$_6$D$_6$, 25 °C) δ [ppm]: 1.24 (s, 6H, [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]), 3.08 (s, 4H, [(C$_5$H$_5$)$_2$ Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]), 3.21 (s, 6H, [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$ CH$_2$OCH$_3$}$_2$]), 6.05 (s, 10H, [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]). ^{13}C NMR DEPT (C$_6$D$_6$, 25 °C) δ [ppm]: 27.75 [(C$_5$H$_5$)$_2$Hf{OC (CH$_3$)$_2$CH$_2$OCH$_3$}$_2$], 58.73 [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$], 83.06 [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$], 110.73 [(C$_5$H$_5$)$_2$Hf {OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$].
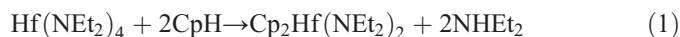
[(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$] (**4**). The complex was synthesized by the dropwise addition of 3-methylmethoxy-3-pentanol (0.380 g, 2.87 mmol) diluted in n-hexane (5 cm^3) to a stirred solution of Cp$_2$Hf(NEt$_2$)$_2$ (0.650 g, 1.435 mmol) in n-hexane (40 cm^3). After 24 h the solvent was removed in vacuo giving **4** as a yellow oil. ^{1}H NMR (C$_6$D$_6$, 25 °C) δ [ppm]: 0.95 (t, 12H, [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]), 1.60 (q, 8H, [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]), 3.17 (s, 6H, [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]), 3.32 (s, 4H,

[(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]), 6.13 (s, 10H, [(C$_5$H$_5$)$_2$ Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]). ^{13}C NMR DEPT (C$_6$D$_6$, 25 °C) δ [ppm]: 8.31 [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$], 30 [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$], 58.54 [(C$_5$H$_5$)$_2$Hf{OC (CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$], 79.06 [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$ CH$_2$OCH$_3$}$_2$], 110.78 [(C$_5$H$_5$)$_2$Hf{OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}$_2$].

3. Results and discussion

3.1. Precursors synthesis and characterization

The hafnium precursors 1, 2, 3 and 4 were obtained, in good yields and purity, as air stable products by following a simple two steps procedure based on the known displacement reaction order R < NR$_2$ < Cp << OR [30].

$$Hf(NEt_2)_4 + 2CpH \rightarrow Cp_2Hf(NEt_2)_2 + 2NHEt_2 \qquad (1)$$

$$Cp_2Hf(NEt_2)_2 + 2ROH \rightarrow Cp_2Hf(OR)_2 + 2NHEt_2 \qquad (2)$$

{Cp = cyclopentadienyl, Et = ethyl, R = –CH(CH$_3$)$_2$,–CH(CH$_3$) CH$_2$OCH$_3$,–C(CH$_3$)$_2$CH$_2$OCH$_3$,–C(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$}.

The four precursors were analyzed by thermogravimetric investigation under a N$_2$ flux. Corresponding thermal curves are displayed in Fig. 1. Compound 1 began to sublime at about 30 °C with a monotonic weight loss up 170 °C leaving a residue of about 50% which remained stable up to 1000 °C. The presence of such large residue and its thermal stability up to 1000°C is probably indicative of its nature as HfO$_2$. Compound 2 underwent a weight loss in the temperature range of 100–210 °C due to its sublimation; after that, it showed a further small weight loss up to 310 °C, presumably due to its decomposition. Above 310 °C, it generated a residue stable up to 1000 °C and corresponding to ~30% of the starting material. Compound 3 showed a two step thermal curve; the former corresponded to a weight loss of 10% between 100–200 °C due to an initial sublimation of the sample, while the latter, taking place in the temperature range of 250–270 °C, corresponded to an almost complete sublimation. The residue was stable *up to* 1000 °C and corresponded to about the
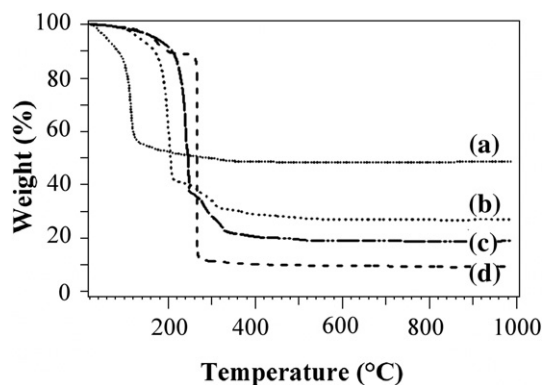

Fig. 1. Thermogravimetric curves of precursors 1 (a), 2 (b), 3 (d) and 4 (c) under a N$_2$ atmosphere.

Table 1
Experimental conditions for the growth of HfO$_2$ thin films

Precursor	Evaporation temperature (°C)	Growth temperature (°C)	Deposition time (min)	Thickness (nm)	Growth rate (nm/min)
Cp$_2$Hf(OCH(CH$_3$)$_2$)$_2$ (1)	100	400, 450, 500	60	100, 130, 180	1.7, 2.2, 3.0
Cp$_2$Hf(OCH(CH$_3$)CH$_2$OCH$_3$)$_2$ (2)	120	400, 450, 500	60	50, 80, 130	0.8, 1.3, 2.2
Cp$_2$Hf(OC(CH$_3$)$_2$CH$_2$OCH$_3$)$_2$ (3)	120	400, 450, 500	60	60, 180, 200	1.0, 3.0, 3.3
Cp$_2$Hf(OC(CH$_2$CH$_3$)$_2$CH$_2$OCH$_3$)$_2$ (4)	140	400, 450, 500	60	30, 40, 40	0.5, 0.6, 0.6

10% of the starting material. Finally, compound 4 was characterized by a weight loss curve similar to that of compound 2. The sample sublimated in the temperature range of 100–250 °C, and then it decomposed up to 340 °C giving a residue stable up to 1000 °C and corresponding to ~20% of the starting material. The obtained residues were reasonably constituted of hafnium oxide formed by the reaction at high temperature with the oxygen coming from the thermal decomposition of the alkoxy-alkoxide moiety.

It deserves to mention that precursors started to sublime at relatively low temperatures from the TG curves. Compounds 1 sublimed as well as decomposed at low temperature, while precursors 2, 3, 4 were less volatile, but more thermally stable than precursor 1, as they started to lose weight at higher temperatures. This is confirmed also from the deposition experiments below described.

As already reported in the literature [18], also in the present case the ^{1}H and ^{13}C NMR DEPT peaks of 1, 2, 3, and 4 in deuterated benzene solution did not show any evidence of line broadening, thus indicating that molecules were not fluxional and, probably, mononuclear in solution, being their oligomerization inhibited by the steric hindrance of the four ligands. Unfortunately, the lack of structural data did not allow to confirm the coordinative saturation of the Hf centre by the two cyclopentadienyl and alkoxy-alkoxide ligands, which in any case would be consistent with the high stability in air of these complexes.

3.2. MOCVD of HfO$_2$ thin films

Thin films of HfO$_2$ with various thicknesses were grown by using 1, 2, 3 and 4 as precursors under an atmosphere of oxygen mixed with water vapour as reactant gases. The presence of a protic acid as water facilitate the removal of the Cp and OR groups as CpH and ROH and favours a clean precursor decomposition minimizing the carbon contamination within the films [31]. The obtained films were colourless and well adherent to the substrate with a uniform, crack-free surface (experimental conditions are reported in Table 1). Complexes 1, 2, 3 and 4 were all characterized by a volatility lower than that of other commercial compounds like Hf(O^{t}Bu)$_4$ or Hf(NEt$_2$)$_4$; nevertheless, they were more stable as a consequence of the higher coordination degree of the Hf centre. In particular, compound 1, which showed the highest volatility along the investigated series (see Fig. 1), possessed the highest growth rate at the lowest investigated temperature. Rising the temperature (400 °C), it thermally decomposed in homogeneus gas phase giving a less growth efficiency, while com-

pound 3, less volatile than 1 but more thermally stable, resulted to possess the highest deposition rate.

Film microstructure was preliminarily investigated by XRD measurements. All the films were polycrystalline with a monoclinic HfO$_2$ baddeleyite structure (ICDD pattern 01-078-
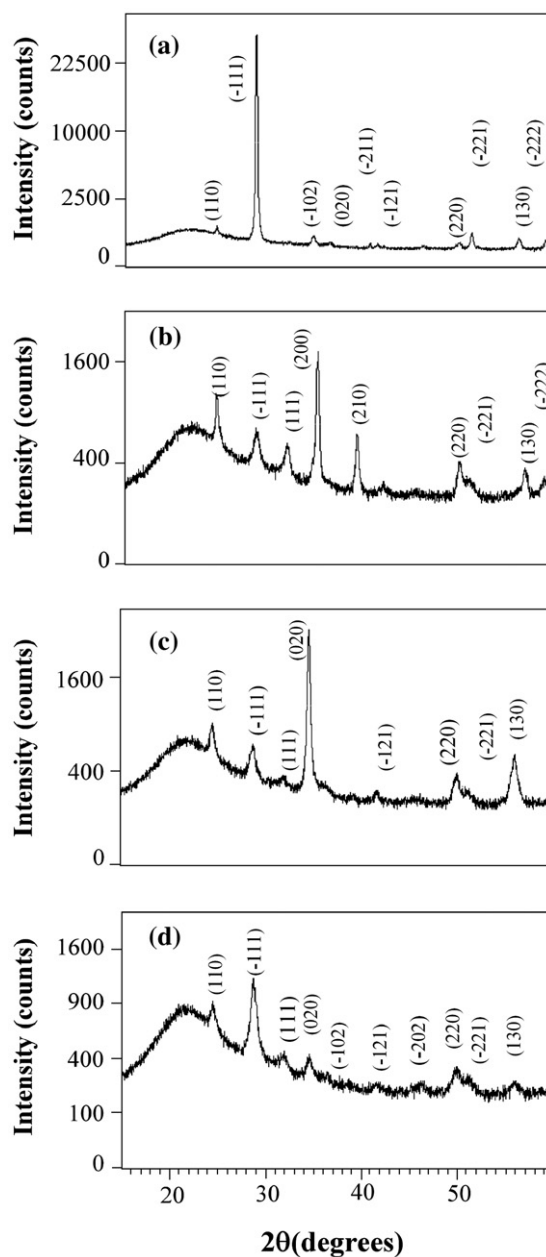

Fig. 2. XRD patterns of HfO$_2$ thin films grown at 450 °C starting from precursor 1 (a), 2 (b), 3 (c) and 4 (d).

0050). XRD patterns of films grown at 450 °C are displayed in Fig. 2. The sample, grown with precursor 1 (Fig. 2a), clearly showed a (−111) preferential orientation independently of the growth temperature. The average crystallite size, estimated from the analysis of the most intense (−111) signal, underwent a progressive increase from 60 to 68 nm rising the deposition temperature from 400 to 500 °C. At variance to that, films deposited with precursor 2 at 400 °C were characterized by XRD peaks hardly detectable, while those obtained at 450 °C (Fig. 2b) and 500 °C showed a (200) (crystallite size=30 nm) and a (−111) preferential orientation (crystallite size=41 nm), respectively. The use of precursor 3 gave rise to further preferential orientations as a function of the deposition temperature, i.e. (110) (crystallite size=22 nm) at 500 °C, (020) (crystallite size=22 nm) at 450 °C (Fig. 2c), and (−111) (crystallite size=15 nm) at 400 °C. Finally, analogously to films grown from 1, those obtained from 4 showed a (−111)
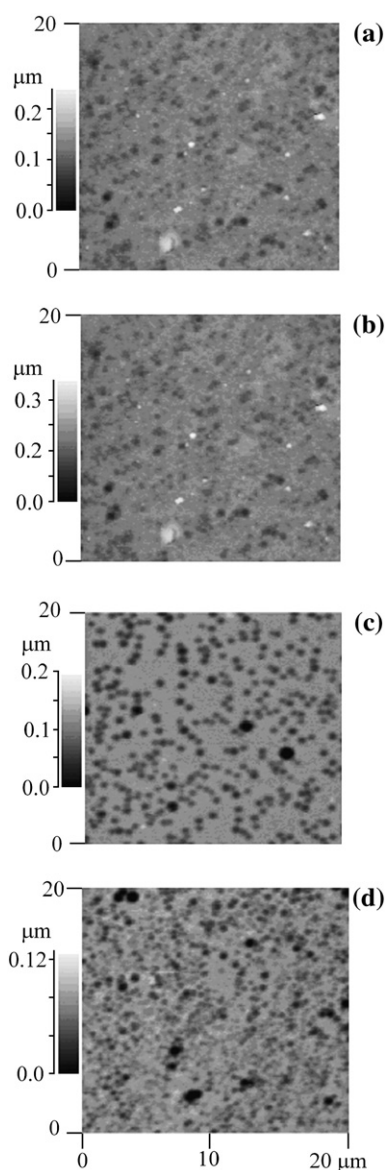

Fig. 3. AFM images (20×20 μm^2) of the HfO_2 thin films grown at 450 °C by using precursor 1 (a), 2 (b), 3 (c) and 4 (d).
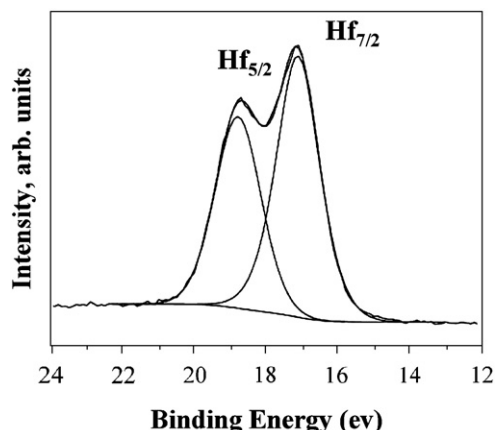

Fig. 4. Representative XPS spectrum of Hf 4f region of the HfO_2 film deposited at 450 °C by using precursor 4.

preferential orientation (crystallite size=15 nm at 500 °C; 12 nm at 450 °C; 11 nm at 400 °C) (Fig. 2d) at every deposition temperature.

It can be noticed that the crystalline grain size of all the films increased with temperature independently of the employed precursors.

Film surface morphology was investigated by AFM. Representative images in a 20×20 μm^2 area of films deposited at 450 °C are reported in Fig. 3. The inspection of the figures testified that film topography was dominated by the presence of globular grains, with no discernible cracks but with some holes (black colour), more evident for samples grown from 3 and 4 (images c and d). The root-mean-square roughness (rms) values were 14.0, 24.0, 19.0 and 13.0 nm, for films deposited by using precursors 1, 2, 3 and 4, respectively. Dividing the rms by the film thickness (t), a rms/t ratio of 0.107 ± 0.002 (1), 0.300 ± 0.002 (2), 0.105 ± 0.002 (3), and 0.325 ± 0.002 (4) was obtained, which, in our case, decreased increasing the deposition rate (see Table 1). In the investigated substrate temperature range the growth rate depended on the temperature, for all precursors, and it increased as the substrate temperature raised. In any case higher growth rate and lower rms were obtained for compounds 1 and 3. This behaviour can be due to the lower thermal stability
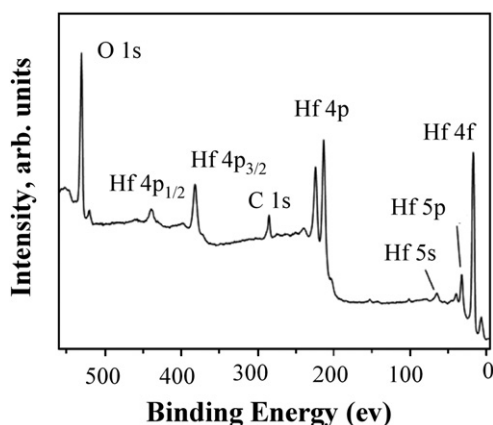

Fig. 5. XPS survey spectrum of the HfO_2 film deposited at 450 °C by using precursor 4.
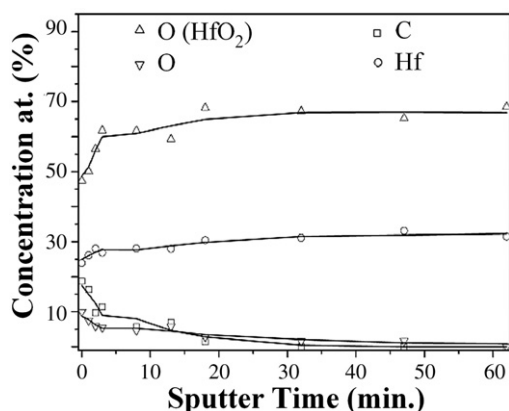
Fig. 6. XPS depth profile of the HfO$_2$ film deposited at 450 °C by using precursor 4.

of these compounds, which decomposed more easily than compounds 2 and 4 giving higher growth rates. Therefore, for the lower growth rates obtained with precursors 2 and 4, the atomic species produced on the growth surface have more time to diffuse and to agglomerate, while for higher growth rate, showed by precursors 1 and 3 the diffusing atoms were blocked by newly deposited atoms giving a smoother morphology [32].

Composition and purity of the deposited films were determined by XPS analysis. In this regard, it is pointed out that the BE value of the Hf 4 f$_{7/2}$ main peak in the Hf 4f spectra, very similar for all films (Fig. 4), lied between 16.9 and 17.4 eV (depending on the precursor), confirming that hafnium was in the +4 oxidation state. Incidentally, it has to be noted that this value is a little higher than that (16.7 eV) corresponding to pure HfO$_2$ films [33].

The XPS survey spectrum and the depth profile of the film obtained from 4 at 450 °C are reported in Figs. 5 and 6, respectively. At the surface, the O:Hf ratio calculated from the normalized peak areas corresponding to Hf 4f and O1s orbitals was slightly higher than 2 (O:Hf=2.1–2.6), most probably as consequence of the presence of super-stoichiometric species containing oxygen in excess, a quite common feature in metal-oxide films deposited by MOCVD. All the samples contained a superficial carbon contamination in the range 16–22 at.% that was completely removed after few cycles of ion sputtering (depth of few nm). Also the O:Hf ratio in the bulk corresponded to that of the stoichiometric HfO$_2$ sample after the ion sputtering process (Ar$^+$ of 2.0 keV energy). These results suggested that the surface contamination did not derive from the growth process.

4. Conclusions

Bis(cyclopentadienyl)bis(alkoxide)hafnium (IV) precursors were synthetized and characterized by NMR and thermogravimetric measurements. These compounds, thanks to the coordinative saturation of the Hf centre, were more stable towards air compared to the usually employed Hf(O^{t}Bu)$_4$. Among them, the precursors which possessed the highest growth rate were [(C$_5$H$_5$)$_2$Hf{OCH(CH$_3$)$_2$}$_2$] and [(C$_5$H$_5$)$_2$Hf{OC(CH$_3$)$_2$CH$_2$OCH$_3$}$_2$]. Thin films of HfO$_2$ grown by MOCVD on fused quartz substrates at three different temperatures were well

adherent to the substrate, colorless and crack-free. Structural and compositional measurements showed the formation of monoclinic (baddeleyite) polycrystalline HfO$_2$ with the right stoichiometry and with a carbon contamination limited to the outermost layers. All the films were characterized by a granular surface morphology, with quite high roughness values. Nevertheless, the films obtained with precursors 1 and 3 at high growth rates resulted smoother suggesting that an increase of the growth rate, obtained by a good choice of the growth parameters such as a rise of the temperature or of the partial pressure of the oxidant could overcome the problem. The tested precursors presented a low thermal stability as shown from the presence of large residues after TGA so that they could be more suitable if used with the liquid injection MOCVD and the ALD techniques. In any case, on the basis of these findings, the present results demonstrated the amenability and feasibility of the proposed MOCVD approach for the synthesis of HfO$_2$ films by using precursors with favourable chemical-physical properties of stability and ease of handling, thus opening intriguing perspectives for eventual large-scale technological applications.

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