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We report the precursor characteristics of a novel mononuclear mixed alkoxide compound [Hf(OⁱPr)₂(tbaoc)₂] and its application towards MOCVD of HfO₂ thin films in a production tool CVD reactor.

Hafnium dioxide is one of the promising candidates to replace SiO₂ as the gate oxide material in the submicron generation of complementary metal oxide semiconductor (CMOS) devices because of its relatively high dielectric constant and stability.¹ There are several reports where thin films of HfO₂ have been produced by laser ablation, sputtering, sol-gel, ALD and CVD processes.² MOCVD is one of the appealing techniques for the deposition of thin films of various materials as it possesses some inherent advantages. The metalorganic compounds used as precursors for this process play a pivotal role in the resulting properties of the films obtained.

Several precursors have been tried for the CVD of HfO₂ films and among them alkoxides and β-diketonates of Hf have been extensively used. However, there are some limitations associated with these precursors. The homoleptic hafnium ethoxide and isopropoxide compounds tend to oligomerize and are therefore less suitable for MOCVD applications. Hafnium *tert*-butoxide exhibits a much higher volatility due to its monomeric structure (sterical demand of the *tert*-butyl groups). Hence, it is utilized in MOCVD.³ The hafnium center is highly unsaturated because it is only fourfold substituted and hafnium favours the coordination number eight. This results in a high sensitivity towards moisture and air. The low coordination number also reduces the shelf life of hafnium alkoxides in solution and limits the usage for liquid injection CVD. To increase the stability of the compounds, bidentate ligands, mainly β-diketonate ligands could be introduced. The eight coordinated complexes [Hf(acac)₄] and [Hf(thd)₄] (acac = acetylacetonate, thd = 2,2,6,6-tetramethyl-3,5-heptadionate) are less sensitive towards moisture but at the same time they display a low volatility. It is possible to increase the volatility of these homoleptic compounds using fluorinated ligands. An example is [Hf(tfac)₄] (tfac = trifluoroacetylacetonate). The drawback of this precursor is the incorporation of fluorine into the gate oxide layer that cannot be avoided.⁴ Amido precursors of the type [Hf(NRR')₄] (R, R' = alkyl) have also been established not only for the MOCVD of HfO₂ thin films but also for atomic layer deposition (ALD) processes.⁵ In general a compromise has to be made between the stability and the volatility and a coordination number of eight seems to be favourable. Examples of hafnium complexes with the coordination number six or with fluxional ligand systems are [Hf(mmp)₄], [Hf(OⁱBu)₂(mmp)₂] and [Hf(OⁱPr)₂(thd)₂] (mmp = 1-methoxy-2-methyl-2-propanolate).⁶

Our approach to the synthesis of volatile precursors for the MOCVD of HfO₂ is the introduction of specific changes in the ligand sphere of already established Hf-key structures (β-diketonates like acac and thd). By using the β-diketoester, Htbaoc (tbaoc = *tert*-butylacetoacetate) the Lewis acidity of the metal

center is expected to be enhanced and the system should be more stabilized. In this communication, we report the synthesis[‡] and structural characterisation[§] of the mononuclear mixed-alkoxide compound [Hf(OⁱPr)₂(tbaoc)₂](**1**). The precursor exhibits a high degree of solubility in organic solvents and possesses promising thermal properties for CVD applications. Thin films of HfO₂ were grown in a production tool liquid injection MOCVD reactor and the observed electrical properties of the films seem promising for gate oxide applications.

Compound **1** is a white crystalline solid with a low melting point of 44 °C and the synthesis can be easily scaled up with high yields.

From single crystal X-ray diffraction studies, the complex was found to be monomeric and crystallizes in the monoclinic space group *C2/c*. The ligands are oriented in *cis*-geometry due to the stronger *trans* effect of the alkoxy groups (Fig. 1). The methyl groups at the tbaoc ligand are stronger donors than the *tert*-butoxy groups. Therefore the *tert*-butyl-moieties of the β-ketoesters are *trans* to the isopropoxy groups (strong electron donors). The Hf–O bonds *trans* to the isopropoxy groups are lengthened (Hf1–O5 = 2.200(5) Å, Hf1–O1 = 2.081(6) Å). The difference in the Hf1–O5 and the Hf1–O1 bond lengths causes the two chelating ligands to form an angle of 83.82(19)° for the O1–Hf1–O5A bond and even 79.28(18)° for the O5–Hf1–O5A bond. To neutralise the stress caused by this compression of the β-ketoester rings, the two isopropoxy groups form angles greater than 90° (O6–Hf1–O6A = 102.6(3)°). These data correspond to the data reported for the analogous Zr complex [Zr(tbaoc)₂(OⁱPr)₂].⁷

Thermal analysis (simultaneous TG/DTA) was carried out to test the suitability of the precursor for CVD applications. The compound sublimates at relatively low temperatures (70–90 °C, from isothermal studies using TG) and the decomposition temperature is around 225 °C and hence suitable for MOCVD applications and low temperature deposition.

Crystalline HfO₂ films with monoclinic phase were obtained in the susceptor temperature range 500–750 °C as can be seen in Fig. 2 and films were amorphous below 500 °C.

Capacitance–voltage (*C*–*V*) and current–voltage (*I*–*V*) characteristics of the Pt/HfO₂/SiO_x/p–Si(100) MIS structures shown in Fig. 3 were evaluated for the gate oxide application. The *C*–*V* curve shows small hysteresis (Δ*V*_{fb} = 13 mV) with a loop in the

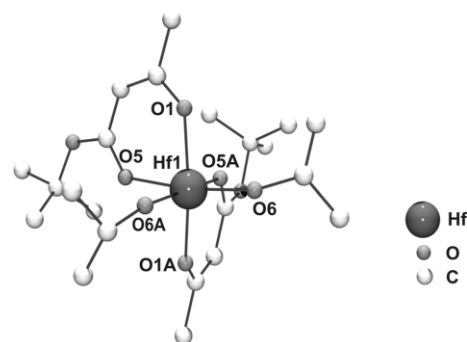


Fig. 1 Molecular structure of [Hf(OⁱPr)₂(tbaoc)₂] in the solid state.

† Electronic supplementary information (ESI) available: TG/DTA, and isothermal studies, RBS and AFM data of HfO₂ film. See <http://www.rsc.org/suppdata/cc/b4/b405015k/>

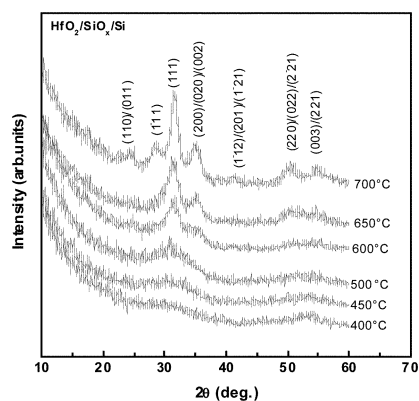


Fig. 2 XRD patterns of HfO₂ films on Si substrates deposited at various susceptor temperatures in a MOCVD production tool.

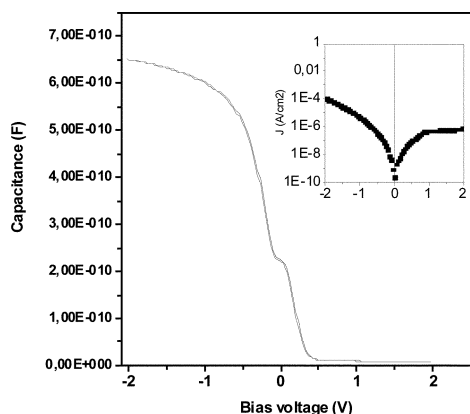


Fig. 3 C–V and I–V characteristics of HfO₂/SiO_x/Si deposited at 700 °C in a MOCVD production tool.

anticlockwise direction, indicating oxide trapping of electrons injected into the oxide at positive voltage and subsequent ejection of trapped electrons at the negative bias. This effect corresponds to a density of rechargeable oxide traps $\sim 1 \times 10^{11} \text{ cm}^{-2}$. Equivalent oxide thickness (EOT) calculated from the accumulation capacitance was about 2.6 nm for the 3 nm thickness HfO₂ films. Average flatband voltage was about 0.32 V. Interface trapped charges, vital in the degradation of the MOS device, were calculated from the slope of C–V curve at the flat band voltage, and was found to be $7.0 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$, comparable with the SiO₂ based MOS devices without the forming gas anneal. Leakage current density at –1 V was about $4.6 \times 10^{-6} \text{ A cm}^{-2}$, less than the corresponding SiO₂ based structures.

In summary, the novel mononuclear mixed alkoxide of Hf has been synthesised and structurally characterised. Application of this compound as a precursor in a production tool MOCVD reactor resulted in HfO₂ thin films exhibiting electrical properties which are promising for device applications.

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Notes and references

‡ [Hf(OⁱPr)₂(tbaoc)₂] was synthesized by dissolving [Hf(OⁱPr)₄] (10 mmol, 4.14 g) in 80 ml hexane and 1 ml (13 mmol) isopropanol. During refluxing of the mixture ($T = 80^\circ\text{C}$), *tert*-butylacetoacetate (20 mmol, 3.32 ml) diluted in 5 ml hexane was added slowly. After a refluxing period of 2 h, the solvent was removed *in vacuo* yielding a slightly yellow, viscous product. Short-path distillation of the product at $85^\circ\text{C}/0.07$ Torr resulted in a pure white compound. Yield: 5.1 g (8.3 mmol, 80% based on [Hf(OⁱPr)₄]); mp (uncorrected): 44°C ; anal.: calcd. for C₂₂H₄₀HfO₈, C: 43.24; H: 6.60; found: C: 42.64 H: 6.63%; ¹H NMR: (room temperature (RT), 250 MHz,

C₆D₆): δ 1.37 (18H, s, C(CH₃)₃ tbaoc), 1.41 (12H, d, CH(CH₃)₂ OⁱPr, $J = 6.28$ Hz), 1.75 (6H, s, CH₃ tbaoc), 4.71 (2H, sept., CH(CH₃)₂ OⁱPr), 5.06 (2H, s, CH tbaoc). ¹³C{¹H}NMR: (RT, 62.5 MHz, C₆D₆): δ 25.68 (CH₃ tbaoc), 27.39 (CH₃ OⁱPr), 28.47 (C(CH₃)₃ tbaoc), 71.18 (CH OⁱPr), 81.24 (OC(CH₃)₃ tbaoc), 90.45 (CH tbaoc); 173.92 (CO tbaoc). 186.15 (OCCH₃ tbaoc). EI-mass spectrum (70 eV): m/z 612 [M]⁺, 553 [M – OⁱPr]⁺, 497 [M – OⁱPr, – isobutene (C₄H₈)]⁺, 455 [M – tbaoc]⁺, 441 [M – OⁱPr, – 2 C₄H₈]⁺, 397 (calcd. 396) [M – OⁱPr, – tbaoc]⁺, 355 (calcd. 353) [M – OⁱPr, – tbaoc, – ⁱPr]⁺.

§ Single crystal X-ray diffraction: data collection for [Hf(OⁱPr)₂(tbaoc)₂] was performed on a Bruker-AXS-SMART (CCD 1000) diffractometer, equipped with a cryogenic nitrogen cold stream to prevent loss of solvent and using graphite monochromated Mo–K α radiation (0.71073 Å). The structures were solved by direct methods and refined anisotropically with SHELXL-97 program suite. CCDC 236724. See <http://www.rsc.org/suppdata/cc/b4/b405015k/> for crystallographic data in .cif or other electronic format. Crystallographic data for [Hf(OⁱPr)₂(tbaoc)₂] (red. $0.48 \times 0.42 \times 0.38$ mm), C₂₂H₄₀HfO₈, $M_r = 611.02$, monoclinic, $a = 9.872(3)$, $b = 15.312(4)$, $c = 18.599(4)$ Å, $\beta = 97.548(7)^\circ$, $U = 2787.1(12)$ Å³, $T = 213(2)$ K, space group C2/c, $Z = 4$, 7901 reflections collected, 2471 unique ($R_{\text{int}} = 0.127$) which were used in all calculations. The final $wR(F^2)$ was 0.0953 (all data). Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) was carried out using a Seiko TG/DTA 6300S11 in an argon atmosphere (300 mL min^{-1} , sample size ~ 10 mg, ambient pressure, RT–500 °C, heating rate of 5°C min^{-1}).

Film depositions were performed in an AIXTRON 2600G3 planetary reactor equipped with a TRIJET liquid injection system, which allows deposition on 5×6 in. wafers simultaneously.⁸ The precursor was dissolved in *n*-butylacetate (0.05 mol). The deposition conditions: substrate temperature 350–750 °C, vaporisation temperature 170–240 °C, reactor pressure 1.0–1.5 mbar, O₂ flow of 200 sccm, period 0.32 s and opening time 0.8 ms. Films were deposited on p-type silicon wafers without removing the native oxide layer. Film thickness was calculated by measuring the areal mass of the film's Hf atoms from the X-ray fluorescence (RIGAKU ZSX-100e). The crystal structure of the films was characterized using an X-ray diffractometer (Philips Analytical) employing grazing incidence and Cu–K α radiation. Surface morphology of the films was studied with AFM (SIS Picostation) and the RMS roughness was around 0.1 nm. The composition of the films deposited were analysed by Rutherford back scattering and X-ray photoelectron spectroscopy. Electrical properties of the films were studied after sputter deposition and patterning of Pt top electrodes. Electrode annealing was done at 400 °C in N₂ atmosphere and the area used for the electrical characterization was 0.0491 mm². C–V and I–V characteristics of the films in the MIS configuration were obtained, using a HP8284 LCR meter and a 617 Keithley programmable electrometer, respectively.

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