Mononuclear precursor for MOCVD of HfO₂ thin films†

Arne Baunemann,a Reji Thomas,a Ralf Becker,a Manuela Winter,a Roland A. Fischer,a Peter Ehrhart,a Rainer Waserb and Anjana Devi†a

a Inorganic Materials Chemistry Group, Lehrstuhl für Anorganische Chemie II, Ruhr-University Bochum, Universitätstr. 150, D-44780 Bochum, Germany. E-mail: anjana.devi@ruhr-uni-bochum.de; Fax: +49 234 3224174; Tel: +49 234 3224150
b Institut für Festkörperforschung/EKM, Forschungszentrum Jülich gmbh, D-52425 Jülich, Germany

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We report the precursor characteristics of a novel mononuclear mixed alkoxide compound [Hf(OiPr)2(tbaoac)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.† There are several reports where thin films of HfO₂ have been produced by laser ablation, sputtering, sol–gel, ALD and CVD processes.‡ 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.† The hafnium center is highly unsaturated because it is only fourfold coordinated complexes [Hf(acac)₄] and [Hf(thd)₄] (acac = acet-ylacetonate, 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((fcl)₂] (fcl = trifluoroacetylacetone). The drawback of this precursor is the incorporation of fluoride into the gate oxide layer that cannot be avoided.† Amido precursors of the type [Hf(NRR')₂] (R, R' = alkyl) have also been established not only for the MOCVD of HfO₂ thin films but also for atomic layer deposition (ALD) processes.¶ 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(OBu)₂(smm)₂] and [Hf(OPr)₂(thd)₂] (mmp = 1-methoxy-2-methyl-2-propanoate).§

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-diketoether, Htaoac (thaoc = tert-butylacetacetate) 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(OPr)₂(thaoac)₂](I). 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 I 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 alkoxo groups (Fig. 1). The methyl groups at the thiobacig ligand are stronger donors than the tert-butoxy groups. Therefore the tert-buty-moieties of the β-ketoesters are trans to the isopropoxy groups (strong electron donators). 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 Hf–O and the Hf–O1 bond lengths causes the two chelating ligands to form an angle of 83.82(19)° for the O1–H1–O5A bond and even 79.28(18)° for the O5–H5–O1A bond. To neutralise the stress caused by this compression of the β-ketoester rings, the two isopropoxy groups form angles larger than 90° (O6–H6–O6A = 102.6(3)°). These data correspond to the data reported for the analogous Zr complex [Zr(thaoc)₂(OPrPr)₂].

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/SiO₂/p–Si(100) MIS structures shown in Fig. 3 were evaluated for the gate oxide application. The C–V curve shows small hysteresis (ΔVfb = 13 mV) with a loop in the

† 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/

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In summary, the novel mononuclear mixed alkoxide of Hf has been synthesized 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

1 [HI(OPr)2(baoc)] was synthesized by dissolving [HI(OPr)3] (10 mmol, 4.14 g) in 80 ml hexane and 1 ml (13 mmol) isopropanol. During refluxing of the mixture (T = 80 °C), tert-butylacetate (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 °C/0.07 Torr resulted in a pure white compound. Yield: 5.1 g (8.3 mmol, 80% based on [HI(OPr)3]); mp (uncorrected): 44 °C; anal.: calcd. for C22H40HfO8, C: 43.24; H: 6.60%; HR NMR: (room temperature (RT), 62.5 MHz, C2D2): δ 1.37 (18H, s, C(CH3)3, baoc), 1.41 (12H, d, CH2CH2:OPr), 1J = 6.28 Hz), 1.75 (6H, s, CH(CH3)3, baoc), 4.71 (2H, sept, CH2CH2:OPr), 5.06 (2H, s, CH baoc). 1H NMR: (RT, 62.5 MHz, C2D2): δ 25.68 (CH, baoc), 27.39 (CH2:OPr), 28.47 (C(CH3)3, baoc), 71.18 (CH2:OPr), 81.24 (OC(CH3)3), baoc), 90.45 (CH baoc); 173.92 (CO baoc). 186.15 (OCCH3 baoc). El mass spectrum (70 eV): m/z 612 [M]+, 553 [M−OPr]+, 497 [M−OPr−isobutene(CH3)3]+, 435 [M−baoc]+, 441 [M−OPr−2C2H5]+, 397 (calcd. 396) [M−OPr−baoc]+, 355 (calcd. 353) [M−OPr−baoc], −Pr]+.

§ Single crystal X-ray diffraction: data collection for [HI(OPr)2(t-baoc)] was performed on a Bruker-AXS-SMART (CCDC 1000) diffractometer, equipped with a cryogenic nitrogen cold stream to prevent loss of solvent and using graphite monochromated Mo-Kα radiation (0.71073 Å). The structures were solved by direct methods and refined anisotropically.