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Hafnium and zirconium tetramethylnonanedionates as new MOCVD precursors for oxide films

S.V. Pasko[a,b], A. Abrutis[a,*], L.G. Hubert-Pfalzgraf[b,*]

[a]*Department of Chemistry, Vilnius University, Naugarduko 24, Vilnius, Lithuania*
[b]*Université Lyon 1, IRC, 2 av. A. Einstein, 69626 Villeurbanne Cédex, France*

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Abstract

New bulky Zr and Hf β-diketonates (2,2,8,8-tetramethyl-4,6-nonanedionates, tmnd) were synthesized and characterized by elemental analyses, ^{1}H NMR, FT-IR and mass spectrometry. A volatile copper compound $Cu(tmnd)_2$, an intermediate product of ligand synthesis, was isolated and characterized as well. The $M(tmnd)_4$ (M=Zr, Hf) compounds were tested as precursors for MOCVD of ZrO_2 and HfO_2 films. Preferentially (001)/(010)/(100) textured and in-plane oriented films of monoclinic oxides have been deposited by pulsed liquid injection MOCVD on R plane sapphire. Smooth films could be grown, especially on sapphire and at low temperature (500 °C). The films on Si(100) were polycrystalline and had rougher surface. XPS study showed 3–4 and 7–8 at.% of carbon in HfO_2 and ZrO_2 films, respectively. $Zr(tmnd)_4$ and $Hf(tmnd)_4$ lead to significantly higher growth rates of ZrO_2 and HfO_2 films at low temperature than conventional $Zr(thd)_4$ and $Hf(thd)_4$ precursors (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) and are attractive precursors for oxide films.

Keywords: Zirconium; Hafnium; Oxide; Thin films; β-diketonates; Chemical vapor deposition

1. Introduction

Hafnia and zirconia are among the most promising alternatives to silicon oxide in microelectronics applications due to their high chemical and thermal stability [1] and elevated dielectric constants [2]. Several orders of magnitude lower leakage currents were observed when HfO_2, ZrO_2 [3], or Al_2O_3-coated HfO_2 [4] films were used as insulating layers instead of SiO_2 films. Other applications of thin films of zirconia and hafnia are optical [5], protective [6] or thermal barrier [7,8] coatings, tunnel junctions [9], in solid oxide fuel cells [7] and in gas sensors [5–7,10].

Both physical methods (PVD)—e-beam evaporation [11], sputtering [9], and chemical ones—anodization [12], atomic layer deposition [5,13], chemical vapor deposition (CVD) [2–4,6,7,14–16]—have been used for the deposition of ZrO_2 and HfO_2 thin films. The latter is an advantageous technique if compared with physical methods due to possibility to grow uniform layers on large, different-shaped substrates, and easy composition control in multimetal oxide films, especially for liquid injection MOCVD [2].

The metal organic precursors used for CVD of MO_2 (M=Zr, Hf) are [2,16]: alkoxides $M(OR)_4$ [OR=O^tBu [4,7]; ONep (neopentoxide, M=Zr) [17]; mmp (1-methoxy-2-methyl-2-propanolate) [6]], $M(O^tBu)_2(mmp)_2$ [6]; $Hf_3O(ONep)_{10}$ [18]; amides—$M(NEt_2)_4$ [15]; β-diketonates such as acetylacetonate (acac), trifluoroacetylacetonate, hexafluoroacetylacetonate [14], 2,2,6,6-tetramethyl-3,5-heptanedionate (thd) [14,19]; 2,7,7-trimethyl-3,5-octanedionate (tod) [20], and mixed-ligand species, e.g., $[Zr(OR)_{4-x}X_x]_m$, (X=acac, R=$CH(CF_3)_2$, x=1 [2]; X=thd, R=^{i}Pr, ^{t}Bu, x=1,2 [21]).

β-diketonates are among the most often used precursors due to their air stability and volatility. One of their drawbacks is a too high thermal stability implying that oxide films can be

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* Corresponding authors. Tel.: +3705 2331004; fax: +3705 2330987.
E-mail address: adulfas.abrutis@chf.vu.lt (A. Abrutis).

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only deposited at relatively high temperatures. Sufficient deposition rates at low temperatures can be achieved by the use of other precursors, such as alkoxides [22]; however, their drawback is air sensitivity. An alternative is the use of β-diketonates with substituents allowing to achieve higher deposition rates compared to conventional precursors, such as M(thd)$_n$ [20]. Thus, we focused here on the synthesis of new sterically hindered β-diketonates RC(O)CHC(O)R containing bulky neopentyl moieties (R=Nep=CH$_2^t$Bu) and performed preliminary studies of their applicability as precursors for liquid injection MOCVD.

2. Experimental

2.1. Synthesis and characterization

Syntheses were performed under argon using Schlenk tubes and vacuum line techniques. 2,2,8,8-tetramethyl-4,6-nonanedione (tmndH) and Cu(tmnd)$_2$ were synthesized by a procedure similar to that described [20,23]. The copper complex, an intermediate used for purification of the ligand, was isolated (74% yield) and characterised. 2,2,6,6-tetramethyl-3,5-heptanedione (thdH), methylneopentylketone and 3,3-dimethylbutyrylchloride were used as received. Phenyl 3,3-dimethylbutyrate was synthesized as reported [23]. Solvents were purified by standard methods. FT-IR spectra were recorded with a Perkin-Elmer Paragon 500 Spectrometer as Nujol mulls. ^{1}H NMR experiments were performed using a Bruker 250 MHz spectrometer. The ESR spectra (X-band, 9.44 GHz microwave power 10 mW, modulation frequency 100 kHz at rt) were obtained with a Varian E9 ESR spectrometer; the spectra were referenced to dpph (2,2-diphenyl-1-picrylhydrazyl, g=2.0035, H=3314 G). Electron impact mass spectra were obtained using a Thermofinnigan MAT95XL spectrometer at 70 eV. Elemental analyses were performed at Vilnius University.

2.1.1. Characterization of tmndH and Cu(tmnd)$_2$

TmndH: ^{1}H NMR (CDCl$_3$ δ (ppm)): 1.00 (s, 17.7 H, ^{t}Bu), 2.13 (s, 3.9 H, CH$_2$), 5.39 (s, 0.98 H, CH), 9.67 (s, 0.98 H, OH enol). The diketone form (~2%) was characterized by the peaks at 1.10 (s, 0.31H, Bu^t), 2.23 (s, 0.07 H, CH$_2$ (Nep)), and 3.49 ppm (s, 0.04 H, CH$_2$ (dik)). IR, cm^{-1}: 3180 w (vOH); 1606 vs (vC=O, vC=C).

Cu(tmnd)$_2$: IR, cm^{-1}: 1598 w, 1561 vs., 1522 s (vC=O, vC=C); 488 m (vCu–O). ESR: (0.041 M hexane, rt): $\langle g\rangle$=2.124, $\langle A\rangle$=79.0 G; (0.009 M hexane, 77 K): $g_{\parallel}$=2.225, $g_{\perp}^{1}$=2.034, $g_{\perp}^{2}$=2.026, $A_{\parallel}$=175 G, $A_{\perp}^{1}$=32.7 G, $A_{\perp}^{2}$=29.7 G. Cu(tmnd)$_2$ sublimes at 120–130 °C/10^{-4} Torr.

2.1.2. Synthesis and characterization of Zr(tmnd)$_4$ (**1**)

A solution of 0.42 g (1.98 mmol) tmndH in 3 ml toluene was added to 0.15 g (0.46 mmol) of Zr(OPr^n)$_4$ in 4 ml toluene. The reaction mixture was evaporated after stirring for 23 h at rt and sublimed at 220–230 °C/3.8 · 10^{-2} Torr (0.37 g, 86%). Anal. (**1**) Found: C, 67.28; H, 10.08. Calc. for C$_{52}$H$_{92}$O$_8$Zr: C, 66.69; H, 9.90. ^{1}H NMR (CDCl$_3$ δ (ppm)): 0.95 (s, 72H, ^{t}Bu), 1.91 (s, 16H, CH$_2$), 5.27 (s, 4H, CH). IR, cm^{-1}: 1586 vs, 1520 vs. (vC=O, vC=C); 559 m (vZr–O). EI-MS: (M=Zr(tmnd)$_4$), M$^{+\cdot}$ (0.078%), M$^{+\cdot}$–Me$_2$C=CH$_2$ (0.038%), M$^{+\cdot}$–^{t}Bu–CH=C=O (0.35%), M$^{+\cdot}$–tmnd$^{\cdot}$ (100%), M$^{+\cdot}$–tmnd$^{\cdot}$–NepC≡CH (54%).

Zr(thd)$_4$ (81%) was synthesized by the same procedure.

2.1.3. Synthesis and characterization of Hf(tmnd)$_4$ (**2**)

A solution of 0.42 g (2.00 mmol) of tmndH in 5 ml toluene was added to a suspension of 0.16 g (0.50 mmol) of HfCl$_4$ in 5 ml toluene. Anhydrous NH$_3$ was bubbled through the reaction mixture three times for 15 min. After stirring at rt for 24 h, NH$_4$Cl was filtered off, the filtrate evaporated and sublimed at 200–210 °C/3 · 10^{-2} Torr (0.25 g, 49%). Anal. (**2**) Found: C, 61.71; H, 9.22. Calc. for C$_{52}$H$_{92}$HfO$_8$: C, 61.01; H, 9.06. ^{1}H NMR (CDCl$_3$ δ (ppm)): 0.95 (s, 72H, ^{t}Bu), 1.92 (s, 16H, CH$_2$), 5.25 (s, 4H, CH). IR, cm^{-1}: 1588 vs, 1522 vs (vC=O, vC=C); 562 m (vHf–O).

Hf(thd)$_4$ (88%) was synthesized by the same procedure.

All β-diketonates were soluble in hydrocarbons (except Cu(tmnd)$_2$), ethers, less in alcohols and acetonitrile.

2.2. CVD experiments and films characterization

Pulsed injection MOCVD technique [24,25], elaborated commonly at LMGP-Grenoble and Vilnius University, was applied for the study of the new compounds as possible precursors for oxide film deposition. This technique is based on repetitive injections of precise microdoses of solution of a volatile metal–organic precursor to a heated evaporator, flash evaporation, vapor transport by a carrier gas (Ar+O$_2$), and vapor decomposition on a hot substrate. Its advantage over conventional MOCVD is easy and reproducible control of precursor feeding rate (and consequently growth rate and film thickness) by changing injection parameters (injection frequency and drop size, concentration of the solution). Detailed description of this technique is given elsewhere [25,26].

The deposition conditions are presented in Table 1. The substrates (R plane sapphire and Si (100)) were cleaned in

Table 1
Deposition conditions of ZrO$_2$ and HfO$_2$ films

Precursors	M(tmnd)$_4$, M(thd)$_4$ (M=Zr, Hf)
Substrates	Sapphire (R plane) and Si (100)
Evaporator temperature	280 °C
Substrate temperature	500 and 700 °C
Ar flow	54 l/h
O$_2$ flow	36 l/h
Total pressure	5 Torr
Solvent	Toluene
Precursor concentration	0.05 M
Injection duration	3 ms
Injection frequency	2 Hz
Microdose mass	3 mg