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Synthesis, structural characterization, and volatility evaluation of zirconium and hafnium amidate complexes

Mahesh C. Karunarathne, Joseph W. Baumann, Mary Jane Heeg, Philip D. Martin, Charles H. Winter*

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

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Treatment of tetrakis(dimethylamido)zirconium or tetrakis(dimethylamido)hafnium with four equivalents of N-*tert*-butylacetamide, N-isopropylisobutyramide, N-isopropylacetamide, N-methylacetamide, or N-*tert*-butylformamide in refluxing toluene, followed by sublimation of the crude products at 105−125 °C/0.05 Torr, afforded tetrakis(N-*tert*-butylacetamido)zirconium (81%), tetrakis(N-isopropylisobutyramido)zirconium (87%), tetrakis(N-isopropylacetamido)zirconium (51%), tetrakis(N-*tert*-butylacetamido)hafnium (83%), tetrakis(N-isopropyliso-butyramido)hafnium (79%), tetrakis(N-isopropylacetamido)hafnium (67%), tetrakis(N-methylacetamido)zirconium (5%), and tetrakis(N-*tert*-butylformamido)zirconium (1%) as colorless crystalline solids. The structural assignments for the new complexes were based upon spectral and analytical data and by X-ray crystal structure determinations for tetrakis(N-*tert*-butylacetamido)zirconium, tetrakis(N-isopropylacetamido)zirconium, tetrakis(N-isopropylacetamido)hafnium, tetrakis(N-methylacetamido)zirconium, and tetrakis(N-*tert*-butylformamido)zirconium. These complexes are monomeric in the solid state, with eight-coordinate metal centers surrounded by four κ^2-N,O-amidate ligands. Six of the eight new complexes undergo sublimation on a preparative scale from 130 to 140 °C at 0.05 Torr, with 84.5−95.8% sublimed recoveries and 0.68−3.06% nonvolatile residues. Tetrakis(N-methylacetamido)zirconium and tetrakis(N-*tert*-butylformamido)zirconium decompose extensively upon attempted sublimation. Solid state decomposition temperatures for the zirconium complexes range between 218 and 335 °C and 290−360 °C for the hafnium complexes. Tetrakis(N-isopropylisobutyramido)zirconium, tetrakis(N-*tert*-butylacetamido)hafnium, and tetrakis(N-isopropylacetamido)hafnium exhibit the highest solid state decomposition temperatures in the series, possess good volatility, and have useful properties for chemical vapor deposition and atomic layer deposition precursors.

1. Introduction

HfO_2 is widely used as the gate dielectric material in metal oxide semiconductor field-effect transistors [1,2]. Moreover, ternary and quaternary HfO_2-based materials are of significant interest as advanced high-κ material substitutes in future microelectronics devices [3–10]. ZrO_2 [10–15] and other zirconium-containing high-κ materials [16–20] are also structurally compatible with silicon semiconductors and are of interest as alternative gate dielectrics in future transistor structures. Zirconium- and hafnium-based thin films are also components in capacitors [4–7,21], tunnel junctions [22–24], and optical coatings [25–27], due to their high dielectric constants, low leakage currents, interface compatibility with Si and SiO_2, high chemical and thermodynamic stability in contact with Si at elevated temperatures, large band gap energies, and high refractive indices.

Atomic layer deposition (ALD) [28–30] has been widely used to grow ZrO_2 and HfO_2 films, for several reasons. The self-limited growth mechanism of ALD gives constant growth rates per cycle, which allows sub-nanometer control over film thicknesses [28–30]. The dielectric layers used in transistor structures need to be <10 nm thick, and the thicknesses and uniformities must be precisely controlled. The surfaces must also be atomically smooth to avoid the accumulation of trapped interface charges [1a]. Moreover, the self-limited ALD growth mechanism enables high conformal coverage in nanoscale features, since growth occurs in a

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* Corresponding author.
E-mail address: chw@chem.wayne.edu (C.H. Winter).

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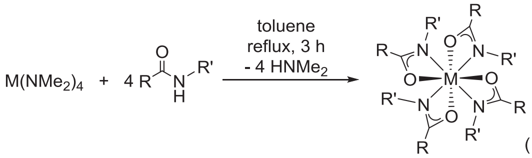
layer-by-layer fashion [28–30]. Applications such as resistive random access memories and vertical transistor designs require perfect growth of conformal dielectric coatings in high aspect features as well as excellent film thickness control [24,31]. ALD precursors must combine volatility, thermal stability at the film growth temperature, and high reactivity toward a second reagent to afford the desired thin film material [28–30]. The tetragonal and cubic phases of ZrO_2 and HfO_2 have higher κ values than the monoclinic phase or amorphous films, and growth of the tetragonal and cubic phases is favored at deposition temperatures of >300 °C [32–34]. Additionally, growth at >300 °C affords higher density films with better crystallinity, compared to films grown at lower temperatures. Precursors containing many different ligands have been used in the ALD growth of ZrO_2 and HfO_2 films [32–34], of which selected examples include halides [35,36], dialkylamides [37–39], alkoxides [40–42], cyclopentadienyls [32–34,43–47], and others [48–51]. Zirconium and hafnium halides have high thermal stabilities and high growth rates, but form corrosive HX as a reaction byproduct, lead to undesired halogen impurities in the films, and are powders that can lead to particle incorporation into the films [32–36]. Dialkylamides have good volatility, high reactivity, and high growth rates, but carbon and nitrogen incorporation in the films can be a problem and their low thermal stabilities limit deposition temperatures to <300 °C [32–34,37–39]. Cyclopentadienyl-based precursors can have high thermal stabilities, but growth rates are often lower than those of halides and dialkylamides and the reactivities are not as high as those of dialkylamides [32–34,43–47]. For these reasons, there is continuing interest in the development of new precursors for ZrO_2 and HfO_2 films that combine volatility, high thermal stability, high reactivity toward oxygen sources, and high growth rates in ALD processes.

In contemplating new directions for zirconium and hafnium ALD precursors, we sought to identify ligands that would confer high thermal stabilities. Organic amides have strong C-N and C-O bonds due to delocalization, and are widely used in organic polymers that exhibit high thermal stabilities [52]. Amidate ligands derived from deprotonation of organic amides containing N-H bonds therefore might lead to new classes of highly thermally stable precursors. Zirconium and hafnium complexes containing amidate ligands have been reported recently, mostly within the context of catalyst development for organic transformations [53–64]. Most of these zirconium and hafnium complexes contain mixed ligand sets with amidates and other ligands. Only a few complexes of the formula $M(amidate)_4$ (M = Zr, Hf) have been reported [51,53,64]. Herein we describe the synthesis, structure, properties, volatility, and thermal stability of zirconium and hafnium amidate complexes of the formula $M(RC(O)NR')_4$ (M = Zr(IV), Hf(IV)). Many of these new complexes sublime at moderate temperatures under reduced pressures and have decomposition temperatures above 300 °C. These properties suggest that the new amidate complexes may serve as useful ALD and chemical vapor deposition (CVD) precursors.

2. Results and discussion

2.1. Synthesis of new complexes

Treatment of tetrakis(dimethylamido)zirconium with four equivalents of N-*tert*-butylacetamide, N-isopropylisobutyramide, or N-isopropylacetamide in refluxing toluene, followed by sublimation of the crude products at 110–120 °C/0.05 Torr, afforded tetrakis(N-*tert*-butylacetamido)zirconium (**1**, 81%), tetrakis(N-isopropylisobutyr-amido)zirconium (**2**, 87%), and tetrakis(N-isopropylacetamido)zirconium (**3**, 51%), respectively, as colorless crystalline solids (eq 1). Similar treatment of tetrakis(dimethylamido)hafnium with the same amides afforded tetrakis(N-*tert*-butylacetamido)hafnium (**4**, 83%), tetrakis(N-isopropylisobutyramido)hafnium (**5**, 79%), and tetrakis(N-isopropylacetamido)hafnium (**6**, 67%), as colorless crystalline solids (eq 1). The synthesis of lower molecular weight complexes was explored by treatment of tetrakis(dimethylamido)zirconium with N-methylacetamide and N-*tert*-butylformamide in refluxing toluene, to afford tetrakis(N-methylacetamido)zirconium (**7**) and tetrakis(N-*tert*-butylformamido)zirconium (**8**), respectively (eq 1). Sublimation of the crude product mixtures afforded very low yields of **7** (~5%) and **8** (~1%), although the products were obtained as high purity single crystals. The syntheses were repeated, but **7** and **8** were extracted with hexane from the crude reaction residues obtained upon removal of the toluene. Filtration through a pad of Celite, followed by removal of the hexane under reduced pressure, afforded the products with ~95% purity by ^1H NMR and in much higher yields (**7**, 77%; **8**, 47%). Accordingly, **7** and **8** appear to decompose substantially upon sublimation. The lower thermal stabilities of **7** and **8**, compared to **1**–**6**, may arise because of the smaller amidate carbon and nitrogen atom substituents, which allow more access to the polar, reactive zirconium-oxygen and zirconium-nitrogen bonds. Additional experiments were conducted in which tetrakis(dimethylamido)zirconium was treated in refluxing toluene with four equivalents of the primary organic amides acetamide, isobutyramide, and trimethylacetamide or the secondary organic amide N-isopropylformamide. Analysis of the crude products by ^1H NMR showed complex mixtures, and these reactions were not pursued further.



(1)

1, M = Zr, R = Me, R' = tBu, 81%
2, M = Zr, R = iPr, R' = iPr, 87%
3, M = Zr, R = Me, R' = iPr, 51%
4, M = Hf, R = Me, R' = tBu, 83%
5, M = Hf, R = iPr, R' = iPr, 79%
6, M = Hf, R = Me, R' = iPr, 67%
7, M = Zr, R = Me, R' = Me, 5%
8, M = Zr, R = H, R' = tBu, 1%

The structural assignments for **1**–**8** were based upon spectral and analytical data and by X-ray crystal structure determinations for **1**, **3**, **6**, **7**, and **8**, as described below. Due to poor quality crystals, structure determinations for **2** and **5** were not possible. A low precision X-ray crystal structure determination of **4** revealed a molecular structure similar to that of **1**. Complexes **1**, **3**, **4**, **6**, **7**, and **8** are monomeric in the solid state, with eight-coordinate metal centers surrounded by four κ^2-N,O-amidate ligands. Complexes **2** and **5** likely possess similar molecular structures. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**–**8** in benzene-d_6 are consistent with the solid state structure assignments and show only one set of resonances for all four amidate ligands in the same chemical environment. Complexes **1** and **2** were reported recently [64]. The NMR spectra for **1** and **2** described herein are identical to the previously reported values. In the present study, melting points were observed for **1** (255–258 °C) and **2** (285–288 °C), whereas the previous paper [64] stated that the complexes did not melt up to their decomposition temperatures.

2.2. X-ray structural aspects

The X-ray crystal structures of **1**, **3**, **6**, **7**, and **8** were determined to establish the geometries about the metal centers and the

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