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Chemical Vapor Deposition of Phase-Pure Uranium Dioxide Thin Films from Uranium(IV) Amidate Precursors

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### **Uranium Chemistry**

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## **Chemical Vapor Deposition of Phase-Pure Uranium Dioxide Thin Films from Uranium(IV) Amidate Precursors**

Mark D. Straub, Jennifer Leduc, Michael Frank, Aida Raauf, Trevor D. Lohrey, Stefan G. Minasian, Sanjay Mathur,\* and John Arnold\*

**Abstract:** Homoleptic uranium(IV) amidate complexes have been synthesized and applied as single-source molecular precursors for the chemical vapor deposition of  $UO_2$  thin films. These precursors decompose by alkene elimination to give highly crystalline phase-pure  $UO_2$  films with an unusual branched heterostructure.

he efficiency and safety profiles of nuclear reactors are heavily impacted by the surface chemistry of the fuel materials used in the reactor core.<sup>[1]</sup> Defect formation and void swelling in UO<sub>2</sub> fuel pellets dramatically reduce the lifetime and energy output of these materials, but the direct study of the surface oxidation processes that cause these defects can be challenging due to the chemical complexity and extreme radioactivity of spent fuels.<sup>[1-3]</sup> Due to their large active surface areas, phase-pure UO2 thin films can serve as an excellent model systems for the chemical and physical changes that occur at the grain boundaries of bulk UO<sub>2</sub> fuel pellets. Uranium oxide thin films have been fabricated using both solution<sup>[4-6]</sup> and sputtering<sup>[7-10]</sup> methods; however, achieving stoichiometric control in the resulting films has been challenging due to the wide array of accessible uranium oxide phases and the facile interconversion of these phases at grain boundaries.<sup>[5,11]</sup> Consequently, many published studies on uranium oxide have been performed using materials with a varying degree of amorphous or polycrystalline character.<sup>[12]</sup> McClesky and co-workers have used an innovative polymerassisted deposition technique from  $UO_2(NO_3)_2$  precursors to produce  $UO_2$  and  $U_3O_8$  thin films; epitaxial matching of the desired uranium oxide phase to the substrate, followed by annealing at 1000 °C, resulted in phase-pure films.<sup>[12,13]</sup> Chemical vapor deposition (CVD) is an additional promising route with the added benefit that the direct synthesis of uranium oxide films from a single-source molecular precursor

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could facilitate an enhanced tunability of the growth process through rational control of the decomposition mechanism and rate.<sup>[14]</sup> However, the preparation of phase-pure thin films in a CVD process can be challenging, since the precursors must be both sufficiently volatile and decompose cleanly by a single mechanism to minimize the formation of side products.<sup>[15]</sup>

The last few decades have yielded an enormous amount of research of volatile transition metal and lanthanide complexes, which are used as molecular precursors for the CVD of metal oxide, nitride, sulfide, and carbide thin films.<sup>[14,16-22]</sup> In contrast to the myriad quantity of CVD precursors that have been described for these metals, only a small handful of uranium oxide CVD precursors have ever been reported. The first gas-phase synthesis of uranium oxide thin films was accomplished by heating a uranyl β-diketonate precursor above 400 °C in the presence of  $O_2$  or  $H_2O$ ; however, the oxidizing environment of these reactive gases prevented the formation of phase-pure UO<sub>2</sub> films.<sup>[23]</sup> In a more recent single-source process, films containing a mixture of uranium oxides were synthesized via thermal CVD from fluorinated uranium heteroarylalkenolate precursors.<sup>[24]</sup> We sought to develop a class of volatile, non-fluorinated precursors with an easily-accessible thermal decomposition pathway to UO<sub>2</sub>, thereby minimizing the heat required to form phase-pure UO2 films. Based on previous research in our group<sup>[25]</sup> and promising results from related transition-metal systems,[26-28] we turned to uranium amidate complexes to meet these requirements. Amidate ligand substituents can be readily varied to cover a wide range of steric and electronic properties, enabling control over the geometry, thermal stability, volatility, and decomposition mechanisms of the resulting metal complexes. Using new U<sup>IV</sup> amidate precursors with a well-defined decomposition mechanism, we synthesized crystalline, phase-pure UO<sub>2</sub> films via CVD.

The amide proligands N-*tert*-butylisobutyramide (H-(ITA)) (1) and N-*tert*-butylpivalamide (H(TTA)) (2) were synthesized according to literature methods<sup>[29]</sup> and purified by sublimation. Deprotonation of 1 and 2 with KN(SiMe<sub>3</sub>)<sub>2</sub> in THF generated the corresponding potassium amidates K-(ITA) (3) and K(TTA) (4) in high yield. As we have observed previously in related systems,<sup>[25]</sup> using these potassium amidates directly for the metalation of uranium led to the formation of undesirable -ate complexes, resulting in poor yields of the anticipated products. This was overcome by adding 18-crown-6 to 3 and 4 to give the crowned potassium amidates K(ITA)(18c6) (5) and K(ITA)(18c6) (6) in near-quantitative yield (Scheme 1); these ligand salts performed much more favorably for the metalation of uranium.

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**Scheme 1.** Synthesis of the crowned potassium amidates K(ITA)(18c6)(5) and K(TTA)(18c6) (6).

The homoleptic amidate complexes U(ITA)<sub>4</sub> (7) and U(TTA)<sub>4</sub> (8) were synthesized by treating UI<sub>4</sub>(1,4-dioxane)<sub>2</sub> with four equivalents of 5 or 6, respectively (Scheme 2). We also synthesized 7 and 8 via a protonolysis route with  $[(Me_3Si)_2N]_2U[\kappa^2-(C,N)-CH_2Si(Me)_2N(SiMe_3)]$  and 1 or 2, but yields were lower using this method. Green crystals of 7 and teal crystals of 8 suitable for X-ray diffraction were grown from Et<sub>2</sub>O and pentane, respectively.



Scheme 2. Synthesis of  $U(ITA)_4$  (7) and  $U(TTA)_4$  (8).

Although the proligands 1 and 2 are sterically comparable, we observed different molecular geometries for 7 and 8. Crystallographic analysis of 7 showed this molecule to be eightfold coordinated and  $D_{2d}$ -symmetric, with all four amidate ligands chelated ( $\kappa_2$ -N,O) to the uranium center. By comparison, 8 is sixfold coordinated and  $C_1$ -symmetric, with two ( $\kappa_2$ -N,O) amidate ligands and two ( $\kappa_1$ -O) amidate ligands bound to the uranium center. This difference in geometry can possibly be attributed to the higher electrondonating effect of the *tert*-butyl vs. *iso*-propyl substituents on the amidate backbone, disfavoring electron donation from the lone pairs on all four nitrogen atoms to the uranium center in 8; however, it is also possible that the larger steric bulk of the C-<sup>1</sup>Bu substituent contributes to the lower coordination number of 8.

The U–O and U–N bond lengths (Table 1) in **7** are comparable to the analogous U–O and U–N bonds of the chelated amidates in **8** (2.284(4) and 2.296(4) Å for U–O). However, the U–O bonds of the O-bound amidates in **8** are substantially shorter (2.123(5) and 2.135(4) Å), suggesting an



**Figure 1.** 50% probability thermal ellipsoid view of U(ITA)<sub>4</sub> (7) (left) and U(TTA)<sub>4</sub> (8) (right). Hydrogen atoms are omitted for clarity.

Table 1:	Selected	bond	lengths	in	7	and	8
					-		-

Atoms	Bond lengths (Å)	Bond lengths (Å)			
	7	8			
U1-01	2.333(2)	2.123(5)			
U1-O2	2.350(2)	2.135(4)			
U1-O3	2.366(2)	2.284(4)			
U1-04	2.346(2)	2.296(4)			
U1-N1	2.499(3)	-			
U1-N2	2.507(2)	-			
U1-N3	2.502(2)	2.495(5)			
U1-N4	2.493(3)	2.457(5)			
C101	1.307(4)	1.375(9)			
C2O2	1.311(3)	1.361(7)			
C3-O3	1.296(4)	1.323(7)			
C4-04	1.303(4)	1.323(7)			
C1-N1	1.305(4)	1.141(11)			
C2-N2	1.292(4)	1.240(9)			
C3-N3	1.296(4)	1.297(8)			
C4N4	1.310(4)	1.309(9)			

increased localization of electron density on the oxygen atoms of these ligands when bound  $\kappa_1$ -O. Providing further support for this claim, the O-bound ligands in **8** also possess longer C–O bonds (1.375(9) and 1.361(7) Å) and shorter C–N bonds (1.141(11) and 1.240(9) Å for C–N) than their chelated counterparts (1.323(7) and 1.323(7) Å for C–O; 1.297(8) and 1.309(9) Å).

The thermal decomposition of the precursors was further investigated using thermogravimetric (TG) analysis (Figure 2). Precursor **7** showed an onset of decomposition at 85 °C, while precursor **8** showed it at 70 °C. The experimentally detected overall weight losses of **7** (65.0%) and **8** (62.7%) are lower than the theoretical values of 66.5% and



*Figure 2.* Thermograms of **7** (left) and **8** (right) collected under nitrogen at a heating rate of  $5^{\circ}$ C min<sup>-1</sup>.

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68.8% for the formation of  $UO_2$ , suggesting a potential incorporation of carbon impurities; this mass difference is substantially more prominent for precursor **7** than for precursor **8**. An in-depth discussion on the TG analysis can be found in the Supporting Information.

To elucidate the decomposition mechanism of these precursors to uranium oxide, solid samples of **7** and **8** were heated to 300 °C in sealed J-Young tubes under a nitrogen atmosphere. The tubes were then cooled with liquid nitrogen to condense volatile decomposition products, and  $C_6D_6$  was added for NMR analysis. Three main products were visible in the resulting <sup>1</sup>H NMR spectra of the decomposed precursors: the amides **1** or **2**, isobutyronitrile (from **7**) or pivalonitrile (from **8**), and isobutylene. A small amount of insoluble black uranium oxide precipitate was also observed. These products are consistent with an alkene elimination mechanism (Scheme 3), as reported previously for related homoleptic  $Zr^{IV}$  amidates.<sup>[26]</sup> We also observed slow formation of the same products by heating solutions of **7** and **8** to 150 °C in  $[D_8]$ toluene over the course of multiple days.

In the first decomposition step, isobutylene elimination from a nitrogen atom generates a hemiamidate intermediate (**D-1**). This hemiamidate then undergoes protonolysis with another amidate ligand to promote the elimination of one equivalent each of amide and nitrile, leaving an oxygen atom bound to the uranium center (**p-2**). Because this is a lowcoordinate system, it is likely that the intermediate **p-2** aggregates prior to the elimination of additional ligands. A second iteration of this process yields  $UO_2$  and one more equivalent each of isobutylene, amide, and nitrile.

Complexes 7 and 8 were both tested as UO<sub>2</sub> thin film precursors in a cold-wall thermal CVD reactor. We were interested to determine if the oxidation state of the precursors would be retained in the CVD-generated materials to form stoichiometric UO2 films, as suggested by the thermal decomposition experiments. Since the sublimation temperatures and decomposition temperatures at a pressure of  $10^{-3}$  mbar were in very close vicinity (  $\approx 130$  °C for 7,  $\approx 120$  °C for 8), CVD experiments were performed at a pressure of  $10^{-6}$  mbar to favor sublimation of the precursors. To ensure a proper precursor flow, the precursor temperatures were set to 160 °C. Since TG analysis displayed a complete decomposition of both precursors at a temperature of 500°C, substrate temperatures of 500 °C were chosen for both CVD processes. Precursor 7 sublimed without prior decomposition in the precursor flask, and black films were generated during

the CVD process. In contrast, the deposition process using complex **8** was not successful; we postulate that this may be due to the weakly bound  $\kappa_1$ -*O*-coordinated ligands and thus a thermal instability of the precursor.

Following the deposition process, the films were characterized without an additional annealing step to determine if UO<sub>2</sub> was prepared directly. As shown by XPS (Figure 3) and XRD (Figure 4) analyses, the film surface and the bulk are composed of phase-pure UO<sub>2</sub>. This finding is noteworthy given the pronounced tendency of uranium dioxide to exhibit surface oxidation, resulting in hyperstoichiometric compositions (O:U > 2:1). The XPS survey spectrum exhibited signals attributable solely to uranium, oxygen, and carbon (Figure 3, left). The high-resolution U 4f XPS spectrum showed two main signals at 380.4 eV and 391.4 eV, corresponding to the U 4f<sub>7/2</sub> and U 4f<sub>5/2</sub> orbitals, respectively (Figure 3, bottom). The peak positions of the main signals and the satellites (binding-energy distance to the main signals of DE<sub>sat</sub> = 6.9 eV) are consistent with the reported data.<sup>[5]</sup> The Bragg



**Figure 3.** XPS survey spectrum (top) and high-resolution U 4f XPS spectrum (bottom) of crystalline  $UO_2$  films prepared via CVD using **7**.



Scheme 3. Proposed decomposition mechanism of 7 and 8. Alkene, amide, and nitrile byproducts were observed by NMR; intermediate decomposition products D-1 and D-2 are postulated.

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*Figure 4.* Powder XRD pattern of the film deposited using **7** at a precursor temperature of 160 °C and a substrate temperature of 500 °C.

reflections in the XRD pattern were assigned to cubic fluorite-type UO<sub>2</sub> (Figure 4). The peaks at  $2\theta = 13.0^{\circ}$ , 15.0°, 21.2°, 24.9°, and 26.0° were indexed to the (111), (200), (220), (311), and (222) planes, respectively. Since the diffraction peaks are broadened anisotropically, the crystallite sizes were calculated using the Scherrer equation and amounted to 146 nm, 195 nm, and 99 nm for the (111)/(222), (200), and (311) planes, respectively. Although the anisotropic broadening suggests the formation of anisotropic crystallite shapes, the predominant intensity of the reflection indexed to the (111) plane hints towards a preferred growth direction that was confirmed by the surface topography (Figure 5). Taken together, these results strongly suggest that phase-pure UO<sub>2</sub> films were prepared directly via decomposition of the molecular precursor.



*Figure 5.* Top-view SEM images with different magnifications of crystalline UO<sub>2</sub> films, prepared via CVD from precursor **7**.

The vapor-deposited UO<sub>2</sub> films exhibited a homogeneous distribution of fir tree-like structures at the surface and good adhesion to the silicon substrate, as depicted in the top-view (Figure 5) and side-view (Figure 6) SEM images, respectively. The side-view SEM images additionally revealed the formation of a dense layer with a thickness of  $\approx 400$  nm at the substrate interface, which seamlessly continues into a branchlike structure with a thickness of  $\approx 2.5 \,\mu\text{m}$ . This change in the microstructure from 2D to 1D growth is likely due to the good lattice match between silicon (a = 5.431 Å) and UO<sub>2</sub> (a = 5.471 Å), which facilitates epitaxial growth of UO<sub>2</sub> onto Si



**Figure 6.** Side-view SEM images with different magnifications of crystalline  $UO_2$  films, prepared via CVD from precursor **7**. The thickness of these films is 2.9  $\mu$ m.

up to a thickness of about 400 nm. Beyond this thickness, the cubic  $UO_2$  crystals act as seeds for 1D nanostructures that grow with equal probability in multiple directions, leading to the formation of branch-like structures.

In summary, we have developed an effective single-source route to fabricate crystalline, phase-pure UO<sub>2</sub> films through chemical vapor deposition of U<sup>IV</sup> amidate molecular precursors, which decompose cleanly via alkene elimination. Small changes in the ligand substituents were seen to affect both the molecular geometry and the decomposition behavior of the precursors, with the eightfold coordinated complex 7 performing much more favorably in thin-film deposition than the sixfold coordinated complex 8. XRD and XPS measurements confirmed the vapor-deposited uranium oxide films to be stoichiometric UO<sub>2</sub>, and SEM images showed good epitaxial growth of the UO<sub>2</sub> layer on the Si substrate. Above a film thickness of about 400 nm, the UO<sub>2</sub> crystals formed fir treelike structures with an isotropic growth of 1D branches and a large accessible surface area. Given the anisotropic microstructure and high surface area of these films in conjunction with high charge-carrier mobilities in UO<sub>2</sub>, we plan to investigate the performance of these films as photoanodes in photoelectrochemical water splitting reactions.

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#### Conflict of interest

The authors declare no conflict of interest.

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Chemical Vapor Deposition of Phase-Pure Uranium Dioxide Thin Films from Uranium(IV) Amidate Precursors

Uranium deposit: Volatile uranium(IV) amidate complexes are used as singlesource molecular precursors to uranium oxide films. Chemical vapor deposition

(CVD) of these single-source precursors yields crystalline, phase-pure UO<sub>2</sub> films with a fir tree-like microstructure and a high surface area.

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M. D. Straub, J. Leduc, M. Frank, A. Raauf, T. D. Lohrey, S. G. Minasian, S. Mathur,\* J. Arnold\* \_\_\_\_\_

Chemical Vapor Deposition of Phase-Pure Uranium Dioxide Thin Films from Uranium(IV) Amidate Precursors

CVD molekularer U(IV Precursor

Oh Tannenbaum, Uran-Tannenbaum: Flüchtige Uran(IV)-Amidatkomplexe werden als molekulare Präkursoren zur Abscheidung von Uranoxidfilmen genutzt. Die chemische Gas-

phasenabscheidung (CVD) dieser Präkursoren ergibt kristalline, phasenreine UO<sub>2</sub>-Filme mit einer tannenbaumartigen Mikrostruktur und großen Oberfläche.

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