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

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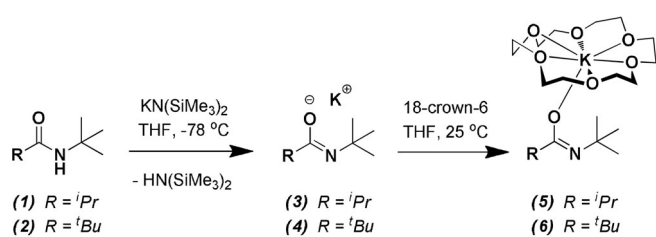
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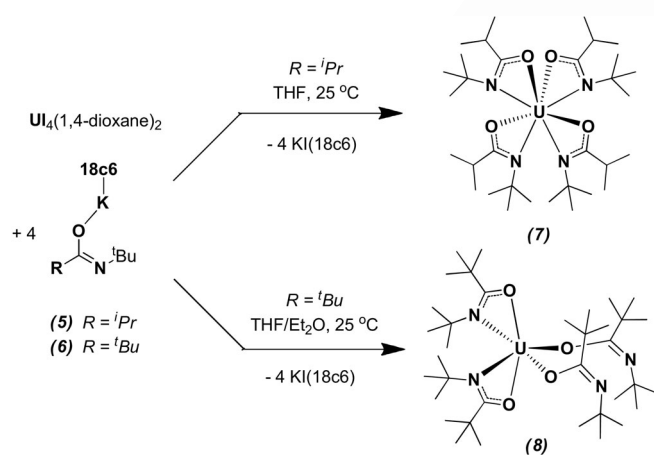
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Scheme 1. Synthesis of the crowned potassium amidates K(ITA) (18c6) (5) and K(TTA) (18c6) (6).

The homoleptic amidate complexes $U(ITA)_4$ (**7**) and $U(TTA)_4$ (**8**) were synthesized by treating $U(1,4\text{-dioxane})_2$ with four equivalents of **5** or **6**, respectively (Scheme 2). We also synthesized **7** and **8** via a protonolysis route with $[(Me_3Si)_2N]_2U[\kappa^2\text{-}(C,N)\text{-}CH_2Si(Me)_2N(SiMe_3)]$ 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_2O 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 ($\kappa_2\text{-}N,O$) to the uranium center. By comparison, **8** is sixfold coordinated and C_1 -symmetric, with two ($\kappa_2\text{-}N,O$) amidate ligands and two ($\kappa_1\text{-}O$) amidate ligands bound to the uranium center. This difference in geometry can possibly be attributed to the higher electron-donating 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 $C\text{-}tBu$ substituent contributes to the lower coordination number of **8**.

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

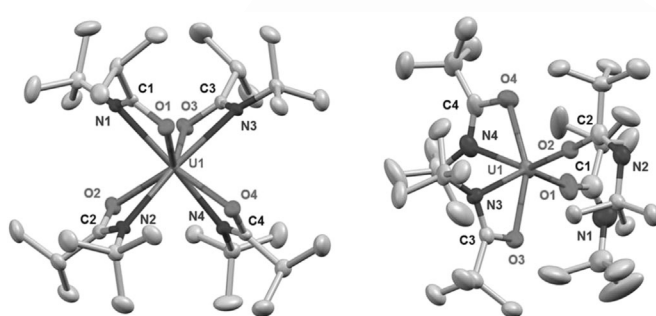


Figure 1. 50% probability thermal ellipsoid view of $U(ITA)_4$ (**7**) (left) and $U(TTA)_4$ (**8**) (right). Hydrogen atoms are omitted for clarity.

Table 1: Selected bond lengths in **7** and **8**.

Atoms	Bond lengths (Å)	
	7	8
$U1\text{-}O1$	2.333(2)	2.123(5)
$U1\text{-}O2$	2.350(2)	2.135(4)
$U1\text{-}O3$	2.366(2)	2.284(4)
$U1\text{-}O4$	2.346(2)	2.296(4)
$U1\text{-}N1$	2.499(3)	–
$U1\text{-}N2$	2.507(2)	–
$U1\text{-}N3$	2.502(2)	2.495(5)
$U1\text{-}N4$	2.493(3)	2.457(5)
$C1\text{-}O1$	1.307(4)	1.375(9)
$C2\text{-}O2$	1.311(3)	1.361(7)
$C3\text{-}O3$	1.296(4)	1.323(7)
$C4\text{-}O4$	1.303(4)	1.323(7)
$C1\text{-}N1$	1.305(4)	1.141(11)
$C2\text{-}N2$	1.292(4)	1.240(9)
$C3\text{-}N3$	1.296(4)	1.297(8)
$C4\text{-}N4$	1.310(4)	1.309(9)

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

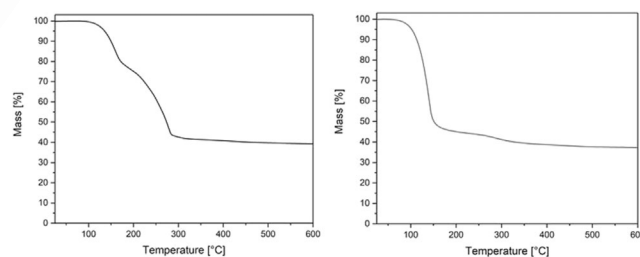


Figure 2. Thermograms of **7** (left) and **8** (right) collected under nitrogen at a heating rate of 5°C min^{-1} .

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 ^1H 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.^[26] We also observed slow formation of the same products by heating solutions of **7** and **8** to 150 °C in $[\text{D}_8]\text{toluene}$ 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 (**D-2**). Because this is a low-coordinate system, it is likely that the intermediate **D-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_2 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 UO_2 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 ($\approx 130^\circ\text{C}$ for **7**, $\approx 120^\circ\text{C}$ 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 κ_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_2 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_2 . This finding is noteworthy given the pronounced tendency of uranium dioxide to exhibit surface oxidation, resulting in hyperstoichiometric compositions ($\text{O}:\text{U} > 2:1$). 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 $\text{U } 4f_{7/2}$ and $\text{U } 4f_{5/2}$ orbitals, respectively (Figure 3, bottom). The peak positions of the main signals and the satellites (binding-energy distance to the main signals of $\text{DE}_{\text{sat}} = 6.9$ eV) are consistent with the reported data.^[5] The Bragg

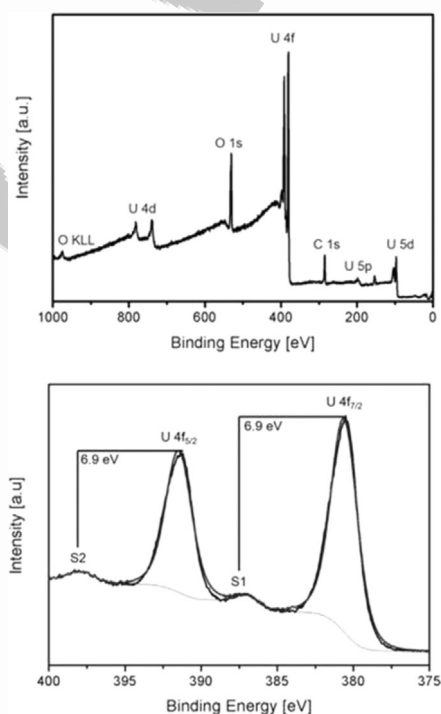
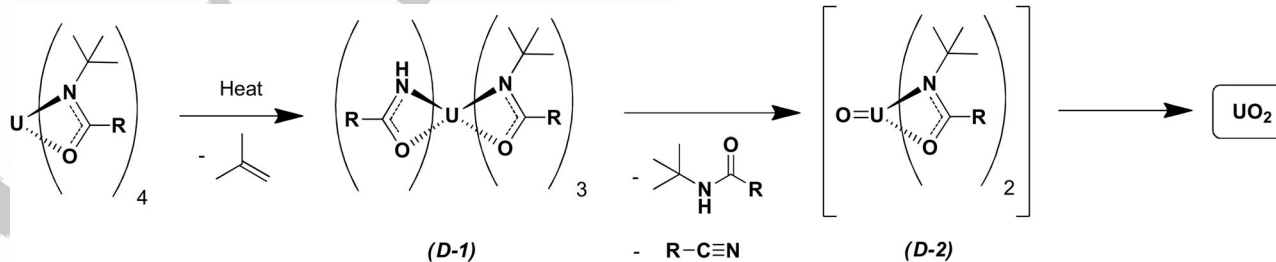


Figure 3. XPS survey spectrum (top) and high-resolution U 4f XPS spectrum (bottom) of crystalline UO_2 films prepared via CVD using **7**.



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.

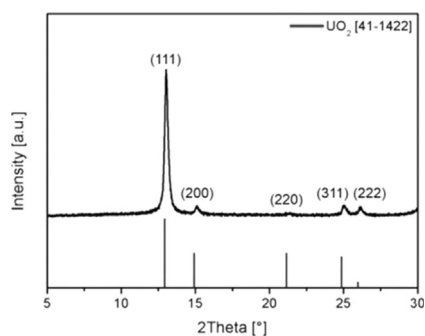


Figure 4. Powder XRD pattern of the film deposited using **7** at a precursor temperature of 160 °C and a substrate temperature of 500 °C.

reflections in the XRD pattern were assigned to cubic fluorite-type UO_2 (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_2 films were prepared directly via decomposition of the molecular precursor.

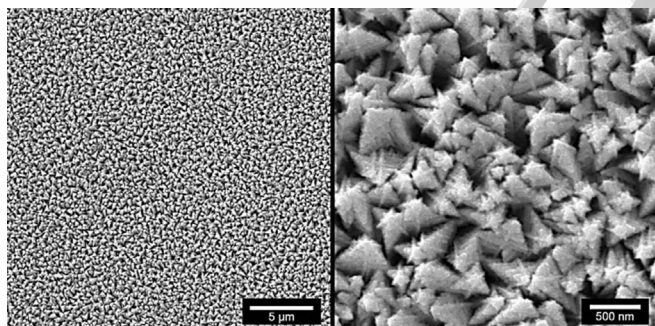


Figure 5. Top-view SEM images with different magnifications of crystalline UO_2 films, prepared via CVD from precursor **7**.

The vapor-deposited UO_2 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 ≈ 400 nm at the substrate interface, which seamlessly continues into a branch-like structure with a thickness of ≈ 2.5 μm . 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_2 ($a = 5.471$ Å), which facilitates epitaxial growth of UO_2 onto Si

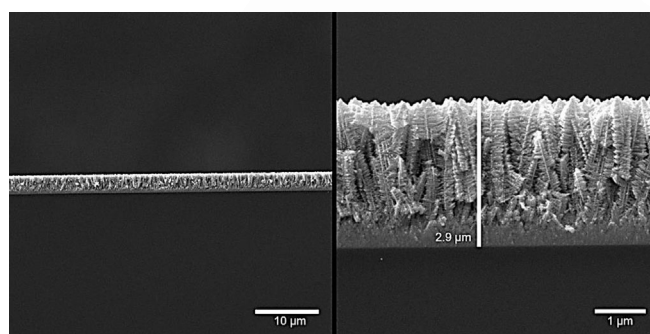


Figure 6. Side-view SEM images with different magnifications of crystalline UO_2 films, prepared via CVD from precursor **7**. The thickness of these films is 2.9 μm .

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_2 films through chemical vapor deposition of U^{IV} 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_2 , and SEM images showed good epitaxial growth of the UO_2 layer on the Si substrate. Above a film thickness of about 400 nm, the UO_2 crystals formed fir tree-like 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_2 , we plan to investigate the performance of these films as photoanodes in photoelectrochemical water splitting reactions.

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8 Conflict of interest

9 The authors declare no conflict of interest.

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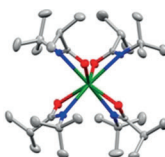
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Uranium Chemistry

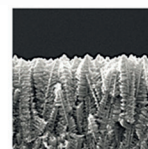
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A. Rauf, T. D. Lohrey, S. G. Minasian,
S. Mathur,* J. Arnold* — ■■■■—■■■■

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

U(IV) molecular
precursor



CVD



Uranium dioxide
nano-forest

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

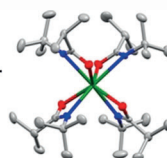
(CVD) of these single-source precursors
yields crystalline, phase-pure UO_2 films
with a fir tree-like microstructure and
a high surface area.

Uranchemie

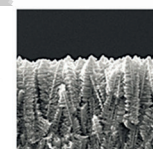
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A. Rauf, T. D. Lohrey, S. G. Minasian,
S. Mathur,* J. Arnold* — ■■■■—■■■■

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

molekularer U(IV)-
Precursor



CVD



Urandioxid-
Nanowald

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

phasenabscheidung (CVD) dieser Prä-
kursoren ergibt kristalline, phasenreine
 UO_2 -Filme mit einer tannenbaumartigen
Mikrostruktur und großen Oberfläche.

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