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Atomic Layer Deposition of Tungsten(III) Oxide Thin Films from $W_2(NMe_2)_6$ and Water: Precursor-Based Control of Oxidation State in the Thin Film Material

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In thin film growth from molecular precursors, the nature and chemical reactivity of the precursors affect the material that is deposited as well as its properties.[1] In deposition processes leading to oxide and nitride phases, a common approach is to employ a metal precursor in combination with an oxygen source such as water or dioxygen or a nitrogen source such as ammonia. In these procedures, the metal-containing precursors fall into one of the following classes: (1) the precursor is in its highest accessible oxidation state and leads to a phase in which the metal is in the same oxidation state,[1,2] (2) a mid- or low-valent precursor is oxidized during the deposition process to afford a phase in a higher oxidation state,[1,2] or (3) the precursor is in its highest accessible oxidation state, but an additional reducing agent is added to yield a phase in a lower oxidation state.[3] In the chemical vapor deposition (CVD) growth of tungsten oxide films to date, WO_3 is selectively deposited regardless of the oxidation state of the tungsten precursor employed.[2] Many other oxide and nitride depositions show similar preferred oxidation states in the film material.[4] Growth processes in which a mid- or low-valent precursor affords oxide or nitride materials without change in the oxidation state of the metal are very rare and are limited to the CVD growth of SnO films from $Sn(OCH(CF_3)_2)_2(HNMe_2)$ and water,[5a] PbO films from various Pb(II) precursors,[5b] and tantalum(IV) nitride films from $Ta(NEt_2)_2(N(C_6H_{11})_2)_2$ and ammonia.[5c]

There is considerable interest in the development of the atomic layer deposition (ALD) film growth method, because this technique is predicted to be widely employed by the microelectronics industry to create nanometer-scale thin films.[6] ALD is a variant of CVD in which precursor vapors are delivered to the substrate surface by alternating pulses, thereby eliminating gas-phase reactions. ALD growth is surface-limited as long as each pulse provides enough precursor molecules to react with the available surface sites. ALD film growth frequently occurs at lower temperatures than comparable CVD processes as a result of the highly reactive metal-based precursors allowed by elimination of the gas-phase reactions.

Herein we describe the ALD growth of W_2O_3 films from the tungsten(III) precursor $W_2(NMe_2)_6$ and water. In these depositions, the oxidation state of $W_2(NMe_2)_6$ determines the oxidation state in the thin film. The growth of low-valent tungsten oxide thin films remains poorly documented because low-valent precursors are oxidized to higher oxidation states during the growth processes.[2] Control of the thin film oxidation state by precursor design, as described herein, is likely to be general for ALD and offers opportunities for the growth of materials that are difficult to prepare or are inaccessible by other film growth methods.

The deposition of W_2O_3 thin films by ALD was studied using $W_2(NMe_2)_6$[7] and water as the precursors. The film growth rate was investigated as a function of $W_2(NMe_2)_6$ pulse length at a deposition temperature of 180 °C (Figure 1a). The number of deposition cycles, the water pulse length, and the length of the purge following the water pulse were held constant at 800, 1.5, and 1.5 s, respectively. The growth rate was constant at about 1.4 Å/cycle for $W_2(NMe_2)_6$ pulse lengths of $\geq$2.0 s, which demonstrates that such pulse lengths afford surface-limited ALD growth. The growth rate was also investigated as a function of deposition temperature (Figure 1b), using $W_2(NMe_2)_6$ and water pulse lengths of 2.0 and 1.5 s each, purge lengths of 1.5 s between pulses, and 800 deposition cycles. The growth rate was about 1.4 Å/cycle for substrate temperatures between 140 and 200 °C. Observation of such a temperature range of constant growth rate is a common feature of many ALD processes and has been referred to as the "ALD window".[6] Growth rates of 1.60 and 2.10 Å/cycle were observed for substrate temperatures of 220 and 240 °C, respectively. These temperatures are clearly outside of the ALD window. Film thickness was examined as a function of the number of deposition cycles. At a temperature of 180 °C and with $W_2(NMe_2)_6$ and water pulse lengths of 2.0 s each, the film thicknesses varied nearly linearly ($r^2 = 0.943$) with the number of deposition cycles. A film deposition consisting of 800 cycles at 180 °C with a tungsten precursor pulse length of 2.0 s was performed without a water pulse. No detectable film growth was observed under these conditions. Thus, film growth through self-decomposition of $W_2(NMe_2)_6$ does not occur.

Time-of-flight elastic recoil detection analysis[8] (TOF-ERDA) was performed on representative films to determine the elemental compositions (Table 1). The films possessed tungsten-to-oxygen ratios of 0.68−0.72 for films deposited at 160 to 200 °C, which are within experimental error of the W_2O_3 stoichiometry (0.67). Carbon, hydrogen, and nitrogen were also present and may result from a small amount of dimethylamido ligand decomposition. X-ray photoelectron spectroscopy was performed on representative samples to establish the oxidation state of the tungsten atoms present in the films. After argon ion sputtering, tungsten $4f^{5/2}$ and $4f^{7/2}$ ionizations were observed at 34.2 ± 0.1 and 32.1 ± 0.1 eV, respectively. For comparison, WO_3, WO_2, and tungsten metal exhibit tungsten $4f^{7/2}$ ionizations at 35.5 ± 0.2, 32.5 ± 0.2, and 31.2 ± 0.2 eV,

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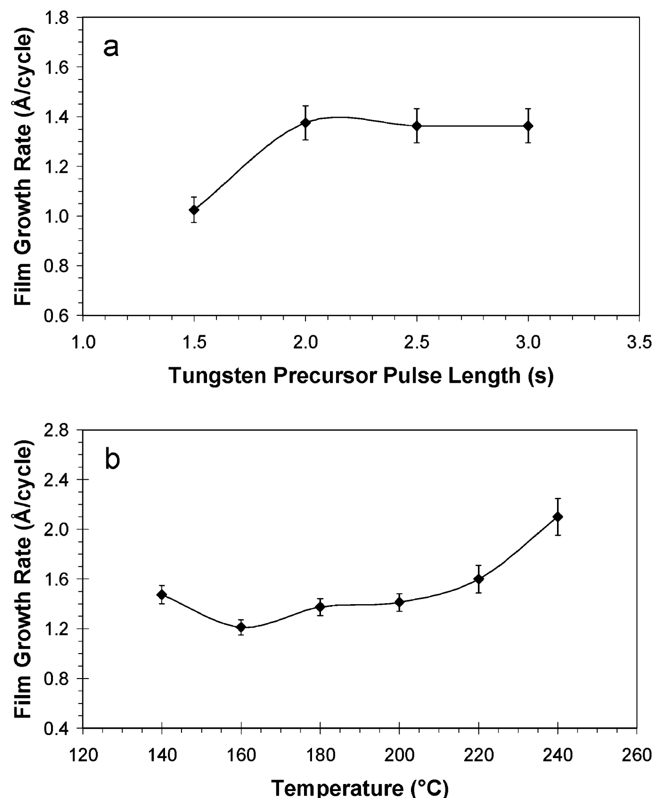

Figure 1. Plots of (a) growth rate versus $W_2(NMe_2)_6$ pulse length and (b) growth rate versus substrate temperature.

Table 1. Elemental Composition of Thin Films Deposited from $W_2(NMe_2)_6$ and Water, as Determined by TOF-ERDA

T (°C)	O/W	%W	%O	%C	%H	%N
160	1.46	31.2	45.7	6.3	12.1	4.7
180	1.41	31.1	43.8	8.6	11.9	4.6
200	1.39	30.8	42.8	7.1	14.2	5.0
uncertainty	0.09	±1.5	±3.0	±2.0	±5.0	±1.0

respectively.[9] The $4f^{7/2}$ binding energy observed in the present work is 0.4 eV lower than that of WO_2, which supports the tungsten(III) oxidation state.

Atomic force microscopy was used to assess surface roughness and morphology. The films were flat, featureless, and smooth, with rms roughness values of 0.7 and 0.9 nm for films deposited at 180 and 200 °C, respectively. X-ray diffraction spectra of films grown at 160, 180, and 200 °C indicated that they were amorphous. The resistivity of a film grown at 180 °C was 8500 microhm cm. This is much lower than the value reported for bulk WO_3 (0.17 ohm cm)[10a] and is consistent with values reported for oxygen deficient WO_x films (1×10^4 microhm cm for $x = 2$).[10b]

The present work documents retention of the tungsten(III) oxidation state in the ALD growth of W_2O_3 films from $W_2(NMe_2)_6$ and water. Such behavior is particularly important because all other CVD tungsten oxide depositions afford WO_3 films or entail an oxidation state increase in going from the precursor to the thin film material.[2] Reasons for the observed growth of W_2O_3 in the present work include the low deposition temperatures, the high reactivity of $W_2(NMe_2)_6$ toward water, as well as the low oxidizing power of water at the growth temperatures. Our results imply that many other ALD processes employing mid- or low-valent metal precursors should afford oxide or nitride phases that have the same oxidation state as the precursor. Such precursor control over thin film oxidation state offers potential access to many new materials that have been previously inaccessible or are difficult to prepare with film growth techniques employing molecular precursors. Low valent tungsten oxides are very poorly documented compared to WO_3 and slightly oxygen deficient WO_{3-x}.[11] Cubic W_2O_3 has been described, but only the lattice parameter was reported.[12] A thin layer of W_2O_3 was proposed to form at 600−1300 °C upon dosing of a tungsten single crystal with O^+.[13] W_3O is a well-known phase.[14] ALD studies are limited to growth of WO_3 from WOF_4, WO_2F_2, and WCl_6.[15] The growth of TaN films using molecular precursors has been very difficult, owing to the high stability of Ta_3N_5 and the difficulty in reducing tantalum(V) precursors to the required tantalum(III) oxidation state.[3,16] Our present results and the work of Hoffman et al. with $Ta(NEt_2)_2(N(C_6H_{11})_2)_2$[5c] suggest that a thermal ALD process employing a volatile, thermally stable tantalum(III) precursor and ammonia should afford TaN films that are not contaminated with Ta_3N_5. The growth of SnO and PbO films from metal precursors in the +2 oxidation state[5a,b] is likely related to the inert lone pair effect, which provides extra stability to the MO phases.

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Supporting Information Available: Film characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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