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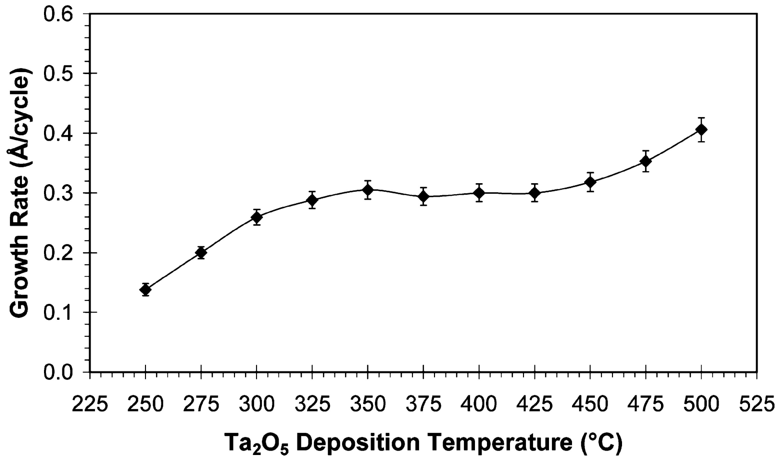

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A Pyrazolate-Based Metalorganic Tantalum Precursor That Exhibits High Thermal Stability and Its Use in the Atomic Layer Deposition of Ta_2O_5

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Tantalum(III) nitride (TaN) and tantalum(V) oxide (Ta_2O_5) thin films have applications in microelectronics devices as barrier materials for copper and as high-k dielectric materials, respectively.[1] Future microelectronics devices require the growth of these and other materials as highly conformal films with sub-nm thickness control in etched features with dimensions as small as 22 nm. Such demands challenge all available film deposition techniques. The emerging atomic layer deposition (ALD) technique is predicted to be widely employed by the microelectronics industry to create nanometer-scale thin films.[1,2] ALD differs from chemical vapor deposition (CVD) in that precursor vapors are delivered to the substrate surface by alternating pulses, which eliminates gas-phase reactions.[2] Any excess precursor molecules beyond those required to saturate the surface sites do not contribute to the growth mechanism, and surface-limited film growth ensues by repeating the deposition cycles. The surface-limited nature of ALD offers excellent thickness control and conformal coverage of substrates containing high aspect ratio features. Due to the distinct growth mechanism of ALD, precursors must have different properties than those used in CVD.[2] Critical properties for ALD precursors include volatility, thermal stability at the film growth temperature to prevent self-decomposition (CVD-like growth) and loss of the layer-by-layer growth mechanism, and high reactivity toward a second precursor species to afford the desired thin film material. Low thermal stability is a pervasive, general problem in ALD, since most ligands in metalorganic precursors have facile decomposition paths that limit the film growth to moderate temperatures.

While metal halides have been widely employed as ALD precursors due to their excellent thermal stability, there is increasing call for halogen-free metalorganic ALD precursors to avoid the formation of corrosive hydrogen halide byproducts during growth and halide impurities in the films.[1,2] Additionally, Ta_2O_5 ALD growth rates from $TaCl_5$ and water decrease at >280 °C due to etching of the deposited film.[3] Common ALD precursors for TaN and Ta_2O_5 have included $Ta(NR)(NEt_2)_3$ (R = Et, tBu),[4] $Ta(NMe_2)_5$,[5] $Ta_2(OEt)_{10}$,[6] and others.[7] While surface-limited growth has been demonstrated with some of these precursors, the deposition temperatures are below 325 °C because of thermal decomposition of the precursors. Higher ALD film growth temperatures can lead to improved crystallinity, lower impurity incorporation, and enhanced materials properties. Herein, we describe surface-limited ALD film growth from a pyrazolate-based precursor, $Ta(NtBu)(tBu_2pz)_3$ (**1**, tBu_2pz = 3,5-di-*tert*-butylpyrazolate), and ozone to afford Ta_2O_5 films with low impurity incorporation. This process exhibits an ALD window between 300 and 450 °C, which demonstrates the exceptional thermal stability of **1**. The results imply that pyrazolate ligands add considerable thermal stability to ALD precursors, without sacrificing reactivity and volatility. These attributes should lead to advances in ALD precursor design.

The deposition of Ta_2O_5 thin films on silicon substrates by ALD was studied using **1** as the tantalum precursor and ozone as the oxygen source. The synthesis and properties of **1** were reported by one of us.[8] Precursor pulse lengths, substrate temperatures, and the number of deposition cycles were varied to assess the growth behavior.[9] The dependence of the film growth rate on the pulse length of **1** was examined at 325 °C (Figure 1a). The number of deposition cycles, the ozone pulse length, and the length of the purge following the ozone pulse were held constant at 1700, 1.5 s, and 2.5 s, respectively. The vessel containing **1** was maintained at 160 °C. The growth rate was constant at about 0.30 Å/cycle with >1.0 s pulse lengths of **1**, which is consistent with surface-limited growth.

The growth rate was also investigated as a function of deposition temperature (Figure 1b). Depositions were carried out using **1** and ozone pulse lengths of 1.5 s each, purge lengths of 2.0 and 2.5 s between the respective pulses, and 1700 deposition cycles. The growth rate was approximately 0.30 Å/cycle for substrate temperatures between 300 and 450 °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".[2] Growth rates of 0.14, 0.20, and 0.41 Å/cycle were observed for substrate temperatures of 250, 275, and 500 °C, respectively. These substrate temperatures are clearly outside of the ALD window.

Time-of-flight-elastic recoil detection analysis (TOF-ERDA) was performed on representative Ta_2O_5 films to determine the elemental compositions (Table 1). The Ta/O ratios were close to that expected for Ta_2O_5. The C, H, and N concentrations were measured for films deposited at intervals of 50 °C over the range of 275−475 °C. The C concentration was $\leq$1% and showed no discernible trend. The H levels were below the detection limit for samples deposited at $\geq$375 °C, but exhibited concentrations of 13 and 1.9% at 275 and 325 °C, respectively. By contrast, N concentrations were $\leq$0.5% at temperatures of $\leq$375 °C, but increased to 0.9 and 1.8% at 425 and 475 °C, respectively. None of the TOF-ERDA analyses revealed any significant compositional variations as a function of depth. X-ray photoelectron spectroscopy (XPS) analyses of films deposited at 325 and 425 °C revealed Ta $4f_{7/2}$ binding energies at 26.2 ± 0.1 eV and were identical to an anodized Ta_2O_5 reference sample.

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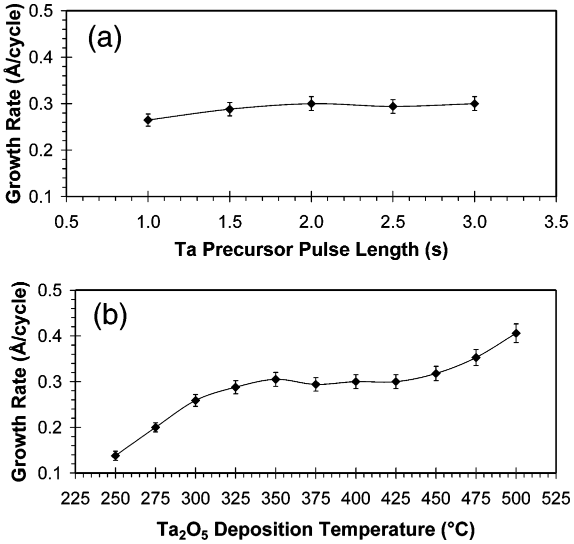

Figure 1. Plots of growth rate versus pulse length of **1** at 325 °C (a) and growth rate versus substrate temperature (b).

Table 1. Elemental Composition of Thin Films Deposited from **1** and Ozone, As Determined by TOF-ERDA

T (°C)	Ta/O ratio	% C	% H	% N
275	0.34 ± 0.03	0.3 ± 0.3	13 ± 4	0.5 ± 0.3
325	0.38 ± 0.03	<0.2	1.9 ± 1.4	<0.2
375	0.41 ± 0.03	0.2 ± 0.2	<1.0	0.5 ± 0.3
425	0.32 ± 0.03	1.0 ± 0.6	<1.6	0.9 ± 0.6
475	0.39 ± 0.04	0.6 ± 0.3	<0.8	1.8 ± 0.5

Carbon and nitrogen ionizations were below the detection limits. All films were amorphous as determined by X-ray diffraction.

The surface morphology of the as-deposited films was studied by atomic force microscopy. Micrographs of characteristic film surface features were collected for 50 nm thick Ta_2O_5 films deposited at 325 °C and 425 °C. Films deposited at both temperatures were smooth and featureless. The rms surface roughness of a typical 2 μm × 2 μm area was 0.8 nm for a film deposited at 325 °C and 0.4 nm for a film deposited at 425 °C.

The present work documents the first example of the use of a pyrazolate-based precursor for the ALD growth of a metal oxide thin film and demonstrates the potential of this ligand type in the design of improved ALD precursors. For comparison, the ALD process employing $Ta(NEt)(NEt_2)_3$ and water afforded Ta_2O_5 films,[4a] while treatment of $Ta(NtBu)(NEt_2)_3$ with ammonia gave ALD growth of TaN films.[4b] These precursors exhibited upper limits for surface-limited growth of 325 and 250 °C, respectively. ALD growth processes employing $Ta(NMe_2)_5$ have an upper limit of 250 °C due to thermal decomposition and loss of surface-limited growth.[4a,5] $Ta_2(OEt)_{10}$ exhibits surface-limited ALD growth between 225 and 325 °C, with thermal decomposition occurring above 325 °C.[6] A series of imido/amido/guanidinato complexes of the formula $Ta(NR^1)(NR^2R^3)(C(NR^2R^3)(NR^4)_2)_2$ has been reported, and selected examples were employed in MOCVD growth.[7a,b] However, these complexes decompose thermally between 195 and 232 °C.[7a] The complex $Ta(NtBu)(NEt_2)_2(Me_2NNSiMe_3)$ was evaluated as an MOCVD precursor for Ta−N−Si films, but undergoes thermal decomposition at about 280 °C.[7c] Since the onset of precursor thermal decomposition and the highest temperature of surface-limited ALD growth are frequently very similar, it is clear that **1** exhibits far higher thermal stability than currently available metalorganic tantalum ALD precursors. Comparison with $Ta(NEt)(NEt_2)_3$, $Ta(NtBu)(NEt_2)_3$, and $Ta(NR^1)(NR^2R^3)(C(NR^2R^3)(NR^4)_2)_2$ implies that the tBu_2pz ligand is the source of the high thermal stability in **1**. Thus, the present study suggests that precursors containing pyrazolate ligands should exhibit enhanced thermal stability relative to many ligands that have been used to create metalorganic ALD film growth precursors. Such new precursors may extend the temperature range at which surface-limited film growth occurs, and may also have broad utility for the growth of tantalum-containing ternary materials. Volatile pyrazolate complexes are known for many different metals,[10] including lanthanides and the group 2 elements. Pyrazolate complexes should be general precursors to oxide phases, since replacement of nitrogen ligands by oxygen ligands is thermodynamically favorable for many metals. In addition, precursors with all-nitrogen coordination spheres may be used in conjunction with ammonia or other nitrogen sources to deposit nitride phases. The results described herein are important, since the design, screening, and implementation of new precursor classes will be a critical aspect of maximizing the utility of the ALD film growth technique.

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

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