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Growth of Tantalum(V) Oxide Films by Atomic Layer Deposition Using the Highly Thermally Stable Precursor Ta(NtBu)(iPrNC(Me)NiPr)$_2$(NMe$_2$)

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The atomic layer deposition (ALD) growth of Ta_2O_5 films was demonstrated using Ta(NtBu)(iPrNC(Me)NiPr)$_2$(NMe$_2$) and water with substrate temperatures between 225 and 400 °C. At 325 °C, self-limited growth was demonstrated with Ta(NtBu)(iPrNC(Me)NiPr)$_2$(NMe$_2$) and water pulse lengths of ≥ 0.5 s. An ALD window was observed between 275 and 350 °C, with a growth rate of 0.28 Å/cycle. The growth rates were 0.33 and 0.37 Å/cycle at 250 and 225 °C, respectively. At 375 and 400 °C the growth rate increased slightly to 0.31 Å/cycle, and precursor thermal decomposition may contribute to growth at these temperatures. In a series of films deposited at 325 °C, the film thickness increased linearly with the number of deposition cycles. X-ray photoelectron spectroscopy of films deposited at 300 and 350 °C revealed stoichiometric Ta_2O_5 with carbon and nitrogen levels below the detection limits. The films were amorphous as deposited, but annealing at 700 °C in dry air resulted in crystallization of hexagonal δ-Ta_2O_5. Atomic force microscopy found root-mean-square surface roughnesses of 0.6−0.7 nm for 45 nm thick films deposited at 300 and 350 °C. The index of refraction of films grown at 325 °C was determined to be 2.12−2.16 at 633 nm using ellipsometry.

Introduction

Tantalum(V) oxide (Ta_2O_5) has many desirable properties and attendant materials applications. It possesses considerable thermal and mechanical stability, as well as chemical inertness, and is compatible with silicon and SiO_2 in semiconductor devices.[1,2] The refractive index of Ta_2O_5 is high ($n > 2$), and it has very high transparency over a broad wavelength range of the visible spectrum, as well as significant ultraviolet photosensitivity.[1,3] As a result of these characteristics, Ta_2O_5 films have been used in antireflective coatings,[4] as waveguides for light,[1,5] and in electrochromic devices.[6] Ta_2O_5 films have also been employed as ion-sensitive field effect transistors in pH sensors,[7] and have applications in humidity sensors.[8] Thin films of Ta_2O_5 have been studied as barrier materials in magnetic tunnel junctions.[9] Because of the high dielectric constant, Ta_2O_5 thin films have received considerable attention for use in microelectronics devices as gate dielectrics in metal-oxide-semiconductor field effect transistors and as capacitor dielectrics in dynamic random access memories.[1,10] Additionally, tantalum oxide is a main component of materials such as strontium bismuth tantalate, which has generated significant interest as a ferroelectric material for nonvolatile ferroelectric memory applications,[11] and Pb(Sc$_{0.5}$Ta$_{0.5}$)O$_3$, which exhibits pyroelectric and ferroelectric properties.[12]

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Atomic layer deposition (ALD) is a thin film growth technique that is able to deposit very thin, conformal films in high aspect ratio features.[13] In ALD, two or more precursors are introduced sequentially into the deposition chamber, and are separated by an inert gas purge that removes excess precursor as well as reaction byproducts. This pulse sequence results in film growth by self-limiting surface reactions, and allows the film thickness to be precisely controlled by adjusting the number of deposition cycles. ALD requires precursors that are thermally stable at the substrate temperature to avoid loss of the self-limited growth mechanism.[13]

Ta_2O_5 has been deposited by ALD using several different precursors. $TaCl_5$ has been widely used together with water, but corrosive HCl is released as a byproduct, and the growing film is etched above 280 °C by excess $TaCl_5$, resulting in lower growth rates.[14] TaI_5 has been used with an aqueous hydrogen peroxide solution, but generates HI and also etches the growing Ta_2O_5 film at elevated temperatures.[15] Use of TaI_5 together with O_2 afforded Ta_2O_5 films only between 500 and 700 °C.[16] TaF_5 releases HF upon treatment with water as the oxygen source.[17] The undesirable attributes of HX formation and generation of species that etch the growing film have led to the development of halogen-free precursors. Widely used metalorganic precursors for the ALD growth of Ta_2O_5 and TaN_x ($x = 1-1.67$) films include $Ta(OEt)_5$,[18] $Ta(NMe_2)_5$,[19] and $Ta(NtBu)(NEt_2)_3$.[20] Self-limited ALD growth is observed with $Ta(OEt)_5$ at temperatures of up to 275 °C,[18] whereas $Ta(NMe_2)_5$ and $Ta(NtBu)(NEt_2)_3$ have corresponding upper limits of 250 °C.[19,20] $Ta(NtBu)(tBu_2pz)_3$ (tBu_2pz =3,5-di-*tert*-butylpyrazolate) has extraordinary thermal stability, and exhibits self-limited Ta_2O_5 ALD growth between 300 and 450 °C.[21] However, its bulky ligands and attendant low reactivity toward water required ozone as the oxygen source, which can lead to substrate oxidation and potentially deleterious effects on reactor parts.

We have recently reported the synthesis, structure, and properties of tantalum complexes of the formula $Ta(NtBu)(RNC(Me)NR)_2(NR'R'')$, where R = iPr or tBu and R′, R″ = Me or Et.[22] These complexes are volatile, and sublime without decomposition between 120 and 170 °C at low pressures. Among this series, $Ta(NtBu)(iPrNC(Me)NiPr)_2(NMe_2)$ (**1**) possesses the best properties as an ALD precursor, since it sublimes at 120 °C/0.05 Torr and decomposes at 340 °C in the solid state. It is also water sensitive, which should assist in efficient oxide growth. Herein, we describe the ALD growth of Ta_2O_5 films using **1** and water. This process exhibits an ALD window between 275 and 350 °C. The high thermal stability of **1** permits self-limited ALD growth at much higher temperatures than with existing ALD precursors such as $Ta(OEt)_5$, $Ta(NMe_2)_5$, and $Ta(NtBu)(NEt_2)_3$.

Results

Ta_2O_5 Film Growth Studies. Film growth studies were carried out using **1** as the tantalum source and water as the oxygen source. To assess self-limited ALD growth, the pulse length of **1** was varied while the sublimation temperature was kept constant at 160 °C (Figure 1). Other parameters were kept constant, with a deposition temperature of 325 °C, a 0.5 s water pulse length, a 4.0 s purge length after each precursor pulse, and 2000 cycles per deposition. The films were of uniform thickness, with a typical variation of $\leq 5\%$ across each 5×5 cm substrate. As shown in Figure 1, the growth rate (0.28 Å/cycle) did not change within experimental error at pulse lengths of 0.5 s and above, indicating that self-limited growth occurs under these conditions. A central feature of ALD is that growth proceeds by self-limited surface reactions.[13] Once the surface reactive sites have been consumed, additional precursor molecules cannot react and are removed during the subsequent purge cycle, and therefore do not contribute to film growth.

The water pulse length was also varied to confirm self-limited growth. Other parameters were kept constant, with a deposition temperature of 325 °C, a 0.5 s pulse length of **1**, a 4.0 s purge length after each precursor pulse, and 2000 cycles per deposition. The growth rate remained constant with water pulse lengths of ≥ 0.5 s (Figure 2).

The deposition temperature was varied between 225 and 400 °C to investigate the growth behavior (Figure 3). Other parameters were kept constant, with a 160 °C sublimation temperature for **1**, 0.5 s pulse lengths each for **1** and water, 4.0 s purge lengths, and 2000 cycles per deposition.

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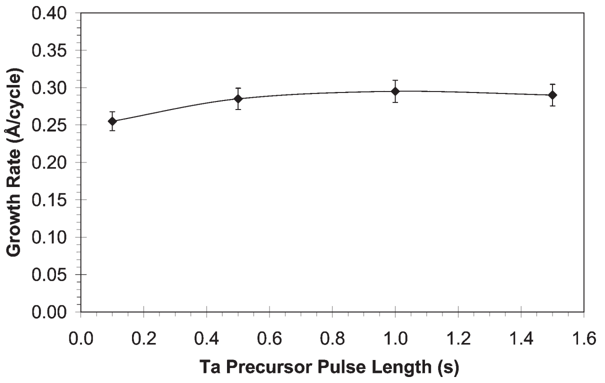

Figure 1. Growth rate as a function of the pulse length of **1**. Depositions were carried out at 325 °C.

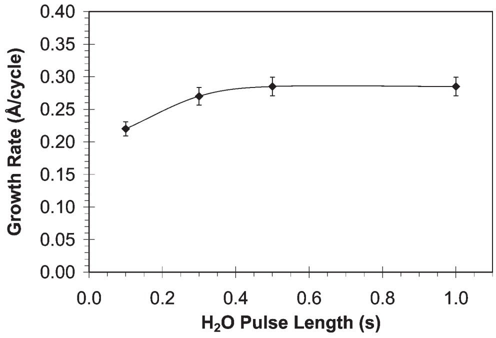

Figure 2. Growth rate as a function of water pulse length. Depositions were carried out at 325 °C.

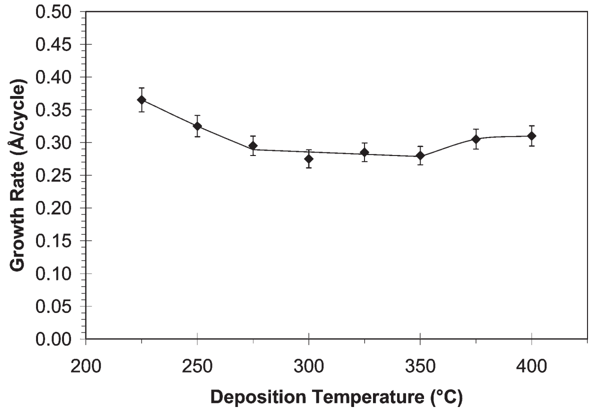

Figure 3. Growth rate as a function of deposition temperature.

The growth rate was approximately 0.28 Å/cycle between 275 and 350 °C. Such a temperature region of constant growth rate has been termed the ALD window.[13] At lower temperatures, the growth rate increased to 0.33 Å/cycle at 250 °C and 0.37 Å/cycle at 225 °C. At higher temperatures the growth rate also increased slightly to 0.31 Å/cycle at 375 and 400 °C.

To assess the potential of chemical vapor deposition (CVD)-like growth, a series of films were grown at 400 °C where the pulse length of **1** was varied from 0.5 to 2.0 s in 0.5 s intervals. The pulse lengths for water, the purge lengths, and the number of cycles were otherwise identical to those of the previous experiments shown in Figure 3. As depicted in Figure 4, the growth rate increased from 0.31 Å/cycle with a 0.5 s pulse length of **1** to 0.34 Å/cycle with a 2.0 s pulse of **1**. While there is an apparent increase in growth rate with increasing pulse length of **1** at 400 °C, the magnitude is small and suggests that the CVD-like growth contribution is minor at this temperature.

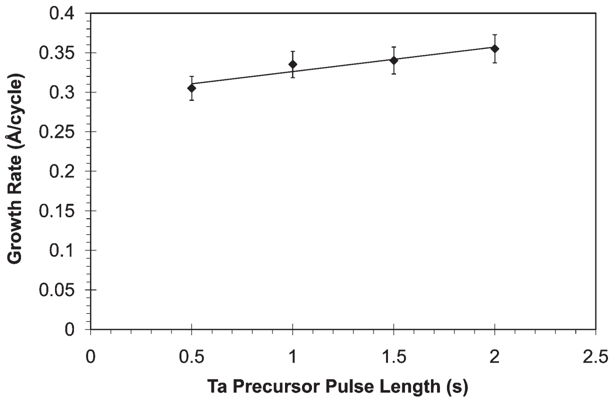

Figure 4. Growth rate as a function of the pulse length of **1** at a deposition temperature of 400 °C.

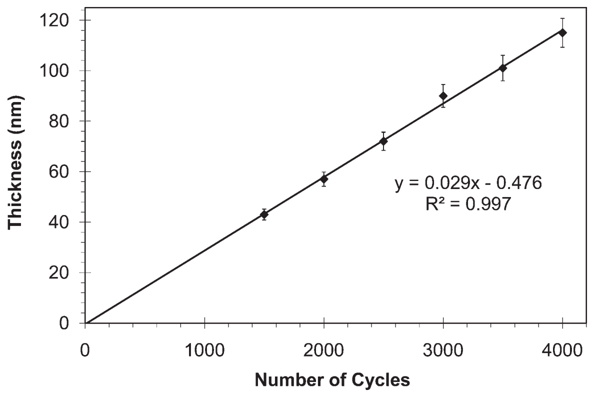

Figure 5. Film thickness as a function of the number of deposition cycles at a deposition temperature of 325 °C.

Depositions were also carried out by varying the number of cycles at 325 °C, using pulse lengths for **1** and water of 0.5 s and purge lengths of 4.0 s. The number of cycles was varied from 1500 to 4000. Figure 5 shows that the film thickness increases linearly with increasing number of cycles, and that the *y*-intercept passes through zero within experimental error.

Ta_2O_5 Film Characterization. X-ray photoelectron spectroscopy (XPS) was performed on films grown at 300 and 350 °C to determine their elemental compositions. Unsputtered films afforded Ta $4f_{7/2}$, Ta $4f_{5/2}$, and O 1s binding energies that were identical within experimental error to values that we recently reported for an anodized Ta_2O_5 reference sample.[21] Accordingly, the films consisted of stoichiometric Ta_2O_5. The N 1s ionization was below the detection limit (< 1%), both in the unsputtered films and in films that had been sputtered for 60 s with argon ions. Unsputtered films showed a C 1s ionization at 286.5 eV, but this ionization was below the detection limit (< 1%) in films that were sputtered with argon ions for 60 s. Figure 6 shows the survey spectrum for a film grown at 350 °C after sputtering with argon ions to remove surface contaminants, as well as high-resolution spectra of the Ta 4f, O 1s, and C 1s regions.

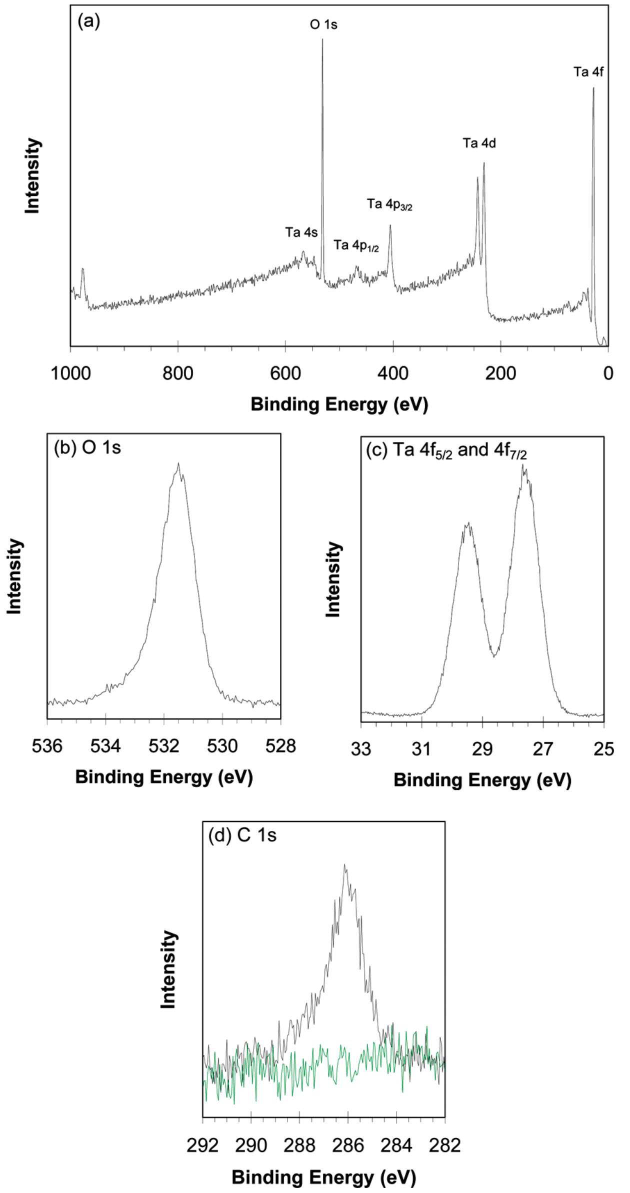

Figure 6. XPS spectra of a Ta_2O_5 film deposited at 350 °C, showing (a) the survey spectrum after argon ion sputtering to remove adventitious carbon, (b) the O 1s ionization, (c) the Ta $4f_{5/2}$ and Ta $4f_{7/2}$ ionizations, and (d) the C 1s ionization before (black trace) and after (green trace) argon ion sputtering.

X-ray diffraction (XRD) was carried out on films grown at 250, 300, 350, and 400 °C to assess film crystallinity. All films were amorphous as deposited. Annealing in dry air for 1 h at 600 °C did not result in any change, but annealing at 700 °C for 1 h caused the films to crystallize (Figure 7). The XRD patterns of the crystallized films are consistent with formation of the hexagonal δ-Ta_2O_5 phase upon annealing.[23]

The surface roughnesses of 45 nm thick Ta_2O_5 films grown at 300 and 350 °C were probed by atomic force microscopy (Figure 8). Representative 2 × 2 μm areas of both films had root mean square (rms) roughnesses of 0.6−0.7 nm. For comparison, the silicon(100) substrates had rms roughnesses of 0.1−0.2 nm. These results indicate that the films are smooth and featureless. The index of refraction of several films grown at 325 °C was determined by ellipsometry. The index of refraction ranged from 2.12 to 2.16 at 633 nm, which is close to the bulk value of 2.2.[24]

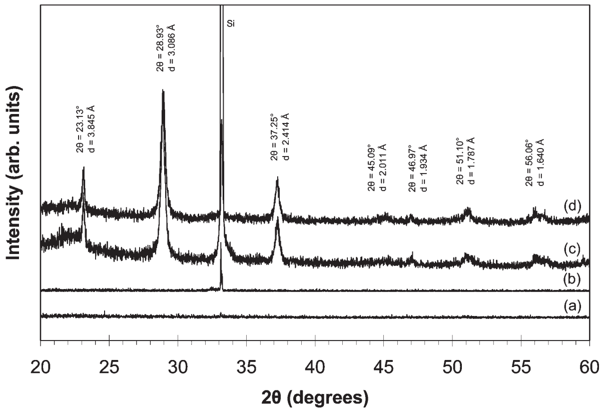

Figure 7. XRD patterns for a 60 nm thick Ta_2O_5 film grown at 400 °C (a) as-deposited, and after annealing for 1 h in dry air at (b) 600 °C, (c) 700 °C, and (d) 800 °C.

Discussion

We have previously reported that **1** sublimes at 120 °C/0.05 Torr with <1% residue after sublimation, undergoes thermal decomposition in the solid state at about 340 °C as evidenced by a color change from colorless to black, and does not melt below its decomposition temperature.[22] The widely used ALD precursors $Ta(OEt)_5$ and $Ta(NtBu)(NEt_2)_3$ are liquids at ambient temperature, and decompose in the liquid state at 175 and 183 °C, respectively.[25,26] $Ta(NMe_2)_5$ decomposes upon melting at 180 °C.[27] Accordingly, the condensed phase decomposition temperature of **1** is 155−165 °C higher than those of standard metalorganic ALD precursors for tantalum-containing materials. The high thermal stability of **1** permits self-limited Ta_2O_5 ALD growth with water as the coreactant at temperatures up to 350 °C. For comparison, $Ta(OEt)_5$ shows evidence for thermal decomposition during ALD growth with water as the coreactant at > 275 °C,[18] and $Ta(NMe_2)_5$ and $Ta(NtBu)(NEt_2)_3$ have upper limits of 250 °C for self-limited ALD growth with water or ammonia as the coreactant.[19,20] As documented herein, the solid state decomposition temperature of **1** corresponds closely to the upper temperature limit of self-limited Ta_2O_5 growth. We have previously observed that the upper temperature ranges of self-limited ALD growth are similar to the solid state decomposition temperatures

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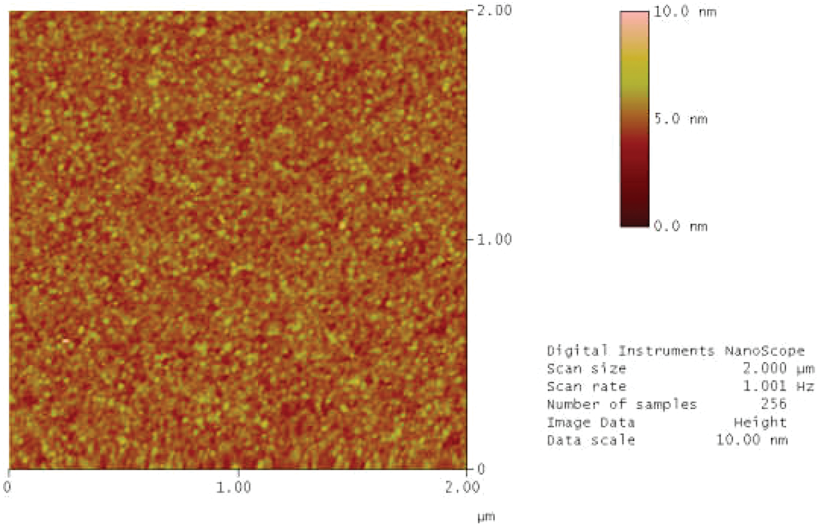

Digital Instruments NanoScope
Scan size 2.000 µm
Scan rate 1.001 Hz
Number of samples 256
Image Data Height
Data scale 10.00 nm

Figure 8. AFM image of a representative 2 × 2 μm area of a 45 nm thick Ta_2O_5 film deposited at 300 °C. The rms roughness is 0.7 nm.

of several metalorganic ALD precursors,[28] although this relationship is not rigorous for all metalorganic precursors as exemplified by the 75−100 °C temperature differences between liquid state decomposition temperatures and the upper limit of self-limited ALD film growth for $Ta(OEt)_5$, $Ta(NMe_2)_5$, and $Ta(NtBu)(NEt_2)_3$.[18−20,25−27]

It is useful to compare the decomposition temperature and ALD growth behavior of **1** with those of previously reported amidinate-based precursors. The thermal decomposition temperatures or upper limit of self-limited ALD growth of various amidinate precursors range from 180 to 350 °C.[29−35] $Ni(iPrNC(Me)NiPr)_2$ decomposes in the solid state at 180 °C,[29] and a theoretical study suggested that the decomposition occurs by abstraction of an isopropyl methine hydrogen atom by the nickel center.[30] The precursor $Zr(MeNC(Me)NMe)_4$ afforded self-limited ALD growth of ZrO_2 films using water as the coreactant at substrate temperatures up to 350 °C.[31] Several lanthanide amidinate precursors have been evaluated for the growth of lanthanide-containing oxide phases, including $Er(tBuNC(Me)NtBu)_3$,[32] $La(iPrNC(Me)NiPr)_3$,[33] $Y(iPrNC(Me)NiPr)_3$,[34] and $Sc(iPrNC(Me)NiPr)_3$.[35] Oxygen sources included water or ozone. An ALD window was not observed for $Er(tBuNC(Me)NtBu)_3$, which may be associated with precursor thermal decomposition.[32] It has been proposed that ALD growth of lanthanide oxides from amidinate precursors and water affords lanthanide hydroxides, which slowly evolve water at the film growth temperatures.[33] If sufficiently long purge cycles are not employed, the evolved water reacts with the next pulse of $M(RNC(Me)NR)_3$, thereby destroying the self-limited ALD process. Gordon and co-workers addressed this issue by creating lanthanum aluminum oxide nanolaminates, where Al_2O_3 layers are interspersed between La_2O_3 layers.[33] The Al_2O_3 layers block water diffusion into the La_2O_3 layers, thereby allowing shorter purge times. In the ALD growth of Sc_2O_3 and Y_2O_3 films from $M(iPrNC(Me)NiPr)_3$ and water, the growth rates increased with increasing substrate temperature starting at 280 and 290 °C, respectively, which may be due to precursor thermal decomposition.[34,35]

The solid state decomposition temperature (340 °C) and upper limit of Ta_2O_5 self-limited ALD growth (350 °C) indicate that **1** is among the most thermally stable amidinate precursors reported to date. The upper limit of self-limited ALD growth with **1** is comparable to that of $Zr(MeNC(Me)NMe)_4$.[31] At temperatures of 375 and 400 °C, the growth rate with **1** is only slightly higher than within the ALD window, which extends the temperature range at which Ta_2O_5 films can be deposited. For comparison, $Ta(NtBu)(tBu_2pz)_3$ exhibits self-limited Ta_2O_5 ALD growth with ozone as a coreactant between 300 and 450 °C.[21] However, $Ta(NtBu)(tBu_2pz)_3$ does not react with water fast enough to support ALD growth. The facile reaction of **1** with water makes it a superior ALD precursor for Ta_2O_5, compared to $Ta(NtBu)(tBu_2pz)_3$, in applications where ozone is not a suitable oxygen source. In addition, **1** supports ALD growth at much higher temperatures than currently available metalorganic precursors such as $Ta(OEt)_5$, $Ta(NMe_2)_5$, and $Ta(NtBu)(NEt_2)_3$.[18−20] The all-nitrogen coordination sphere of **1** may also allow ALD growth of nitride materials such as TaN and Ta_3N_5 in conjunction with ammonia or a

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hydrazine-based precursor. The higher deposition temperatures allowed by **1** represent a significant step toward the growth of crystalline tantalum oxide-containing thin films by ALD, since ferroelectric tantalates must be grown in crystalline form to exhibit their desired properties.[11,12] The high thermal stability of **1** may also reduce undesired film impurities, such as carbon, nitrogen, and hydrogen, compared to $Ta(OEt)_5$, $Ta(NMe_2)_5$, and $Ta(NtBu)(NEt_2)_3$. As such, **1** represents a significant advance in ALD precursor development for tantalum.

Fischer and co-workers have reported a series of imido/amide/guanidinate complexes of the formula $Ta(NR^1)(R^2NC(NR^3R^4)NR^2)_2(NR^3R^4)$ (R^1-R^4 = alkyl),[26,36] and have described the use of these compounds in the CVD growth of TaN films.[26] Complex **1** has a molecular structure that is similar to those of $Ta(NR^1)(R^2NC(NR^3R^4)NR^2)_2(NR^3R^4)$; however, the latter compounds melt with decomposition in the range of 195 to 232 °C.[26,36] Hence, the decomposition temperature of **1** exceeds those of $Ta(NR^1)(R^2NC(NR^3R^4)NR^2)_2(NR^3R^4)$ by 108−140 °C, even though the compounds are structurally similar. Fischer and co-workers observed free amine and carbodiimide as products of the thermal decompositions of $Ta(NR^1)(R^2NC(NR^3R^4)NR^2)_2(NR^3R^4)$,[36] suggesting that the complexes undergo decomposition through deinsertion of carbodiimide. Analogous deinsertion of carbodiimide from **1** is clearly less favorable, since the decomposition temperature of **1** is much higher than those of $Ta(NR^1)(R^2NC(NR^3R^4)NR^2)_2(NR^3R^4)$. Barry has demonstrated that aluminum complexes containing guanidinate ligands undergo carbodiimide deinsertion at much lower temperatures than related alkyl amidinate ligands.[37]

Interestingly, the Ta_2O_5 growth rates from **1** and water at 225 °C (0.37 Å/cycle) and 250 °C (0.33 Å/cycle) are higher than those observed between 275 and 350 °C (0.28 Å/cycle). Hydrated tantalum oxide has been reported to dehydrate significantly between 230 and 330 °C.[38] Thus, it is possible that self-limited ALD growth occurs at 225 and 250 °C, and that the higher growth rates reflect the higher concentrations of surface hydroxyl groups on the growing film surfaces, compared to $\geq$275 °C. It has been proposed that precursor decomposition and surface dehydration occur concurrently above 275 °C in the ALD growth of Ta_2O_5 from $Ta(OEt)_5$ and water, which leads to a decreased growth rate between 325 and 375 °C.[18a,b] Finally, we observed that the growth rate with **1** only saturated with a 0.5 s pulse of water, which corresponds to very large dose in our Picosun reactor. It has been proposed that large doses of water increase the surface hydroxyl group concentrations in metal oxide ALD, which afford more surface reactive sites for the next metal dose and attendant higher growth rates.[39]

Experimental Section

Ta_2O_5 Film Deposition. A SUNALE R-75 ALD reactor manufactured by Picosun (Espoo, Finland) was used for the thin film deposition experiments. The reactor was operated with a pressure of ~1 mbar in the deposition chamber. The growth of Ta_2O_5 thin films was studied using **1** as the tantalum source and water as the oxygen source. Complex **1** was prepared as recently reported.[22] Because of the air sensitivity of **1**, it was stored and loaded into a cartridge in a glovebox. The cartridge containing **1** was then transferred to the ALD reactor without exposure to air. The sublimation temperature of **1** was varied between 150 and 172 °C. Depositions were carried out using substrate temperatures between 225 and 400 °C. Nitrogen was used as the carrier and purge gas, and was obtained from air using a GeniSys NG5 nitrogen generator (purity >99.9995%). Films were deposited on 5 × 5 cm Si (100) substrates with the native oxide present. These substrates were obtained from Silicon Quest International (Santa Clara, California).

Film Characterization Methods. Film thicknesses were determined by fitting of optical reflectance spectra using the method of Ylilammi and Ranta-aho.[40] The index of refraction measurements were obtained by ellipsometry. Reflectance spectra were measured between 1100 and 190 nm using a Jasco V-570 UV/vis/NIR spectrophotometer. A Gaertner L116 A null ellipsometer with a wavelength of 633 nm was used for the ellipsometry measurements. Each film growth rate was determined by dividing the measured film thickness by the number of deposition cycles. X-ray photoelectron spectroscopy was performed on a Perkin-Elmer 5−5500 VHI XPS system using monochromatized Al Kα radiation. Surface contaminants were sputtered away using 1 kV Ar ions. XRD patterns were collected with a Rigaku RU2000 rotating anode powder diffractometer using Cu Kα radiation. Atomic force micrographs were obtained using a Veeco 3100 atomic force microscope and were performed in the tapping mode using a scan rate of 1 Hz.

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