I. INTRODUCTION

An atomic layer deposition (ALD) process proceeds by exposing a substrate to alternating pulses of reactive precursor gases separated by purge or evacuation steps. Ideally, the surface reactions during each precursor exposure are self-limiting, meaning that the film deposition rate saturates with prolonged dosage. This behavior is in contrast to chemical vapor deposition (CVD) where continuous film growth occurs with continued exposure. During an ideal ALD process, an excess dose of precursor does not contribute to film growth, and the ultimate film thickness should depend only on the number of cycles if the surface reactions during each half-cycle run to completion. In other words, the growth per cycle (GPC) should be constant even across reactors. In principle, within the temperature window, the GPC should remain constant over a range of temperatures and desorption at high temperatures.

While ALD may be conceptually simple, real ALD processes often deviate from the ideal model. The nonidealities for a given ALD chemistry are most often assessed through growth studies in which the cycle timing and substrate temperature ($T_s$) are varied and the resulting GPCs are determined by film thickness measurements. To be considered “true” ALD, a set of deposition conditions should result in a constant GPC past a certain dosage of precursors. Additionally, the GPC should remain constant over a range of $T_s$, i.e., the ALD window. The $T_s$-dependence of the GPC is responsible for the nonideal growth outside the window. At $T_s$ below the window, an increased or decreased GPC is attributed to precursor condensation or kinetic limitations, respectively. At $T_s$ above the window, an increased or decreased GPC is normally ascribed to thermal decomposition or desorption, respectively. In this way, growth experiments can be used to elucidate the behavior of a given chemistry. In principle, within the temperature window, the GPC should be constant even across reactors.

In the case of ALD of TiO$_2$ using tetrakis(dimethylamido)titanium (TDMAT) and water vapor, growth studies in the literature present contradictory results. The TDMAT/H$_2$O ALD chemistry is of interest for a variety of applications that include next-generation gate dielectrics, memristors, photocatalytic hydrogen production, and photovoltaics, so it has been examined by numerous researchers using various reactors and procedures. In some studies, a window is found, but there are discrepancies in the $T_s$ bounds and the GPC within the window. Other studies have found no ALD window. Outside of an ALD window, reported GPC values generally decrease monotonically with increasing $T_s$. A few exceptions, however, have been reported.

The GPC versus $T_s$ behavior found for TDMAT/H$_2$O could be interpreted as condensation of the precursors at low $T_s$ and desorption at high $T_s$. However, previous growth studies find indications that decomposition also is occurring: In particular, the GPC does not saturate with prolonged TDMAT exposure at high $T_s$. A few studies have reported an increase in GPC at high $T_s$, which would be a clear indication of decomposition. This evidence, however, is contradicted by the fact that the C and N contamination in TiO$_2$ has been observed without any evidence of an adsorbed product. RAIRS measurements indicate that this behavior is not associated with an increase in the impurity concentration or a dramatic change in the growth rate. A desorbing decomposition product is consistent with these observations. RAIRS also indicates that dehydroxylation of the growth surface occurs only among one type of surface hydroxyl groups. Molecular water is observed to remain on the surface and participates in reactions even at a relatively high temperature (110°C) and with long purge times (30 s).
the resulting TiO2 films is found to be low (≈1% or less), which argues against decomposition.\textsuperscript{3,6–9} These contradictions have led some to speculate that Ti-containing products of side-reactions are desorbing\textsuperscript{9} or that decomposition and desorption are occurring simultaneously with the effects of each partially canceling.\textsuperscript{3}

With such large inconsistencies and contradictions in the literature, the surface chemistry and kinetics of the TDMAT/H2O ALD chemistry do not appear to be fully understandable from growth experiments alone. Previous \textit{in situ} studies have examined TiO2 ALD using methods including Fourier transform infrared (FT-IR) spectroscopy,\textsuperscript{12–16} but they have neither examined the TDMAT/H2O chemistry nor have they been under conditions resembling those of typical growth studies in terms of pressures, temperatures, and/or cycle timing. In this work, we examine the kinetics using time-resolved FT-IR spectroscopy \textit{in situ} within a flow reactor. We measure the surface species using a new method based on reflection-absorption IR spectroscopy (RAIRS) and polarization modulation.\textsuperscript{17} The RAIRS data present clear evidence of decreasing absorption by alkylamido surface groups, indicating decomposition of surface species. However, there is no accompanying evidence for an adsorbed product. Together with \textit{ex situ} film measurements that indicate concentrations of film impurities are low, these observations are consistent with decomposition to a desorbing product. In addition, we observe evidence for dynamics in the hydroxyl group population and molecular H2O coverage on the time scale of the ALD cycle.

II. EXPERIMENT

Film growth at three temperatures (110, 190, and 240°C) is investigated using time-resolved, \textit{in situ} RAIRS. To benchmark the process against others in the literature, a second series of TiO2 films is deposited under nominally identical conditions. The results are thus divided into two parts in Sec. III. The first reports the analysis of the benchmark films, and the second presents the time-resolved RAIRS data.

Growth of both the benchmark films and the films used for \textit{in situ} FT-IR spectroscopy is performed using a custom-designed ALD reactor previously described.\textsuperscript{19} A wall temperature of 110°C is used here, and the wafer chuck is heated independently. The wafer temperature is calibrated versus a thermocouple used for controlling the wafer chuck temperature. Four gas lines deliver a total of 300 standard cm\textsuperscript{3}·min (sccm) helium into the reactor. A working pressure of 150 Pa (1.1 Torr) is used. The TDMAT bubbler is at room temperature. Water is introduced through a needle valve into one of the delivery lines. A timing sequence (TDMAT pulse, TDMAT purge, H2O pulse, and H2O purge) of 4, 10, 1, and 30 s is used in this study.

The methods used to obtain time-resolved RAIRS spectra are described elsewhere\textsuperscript{17} but are briefly recounted here. The timing of the ALD cycle is synchronized with a series of regularly timed data acquisitions by the spectrometer. Thus, each spectrum represents one time interval of an ALD cycle that is equivalent to the spectrum for that time interval in the next ALD cycle. This synchronization allows the time-equivalent spectra of the series to be signal-averaged across multiple ALD cycles, which is necessary to decrease the noise. Signal-averaging during each ALD cycle (or purge) would severely limit the time resolution. In this study, we average over 128 cycles with interferograms being acquired every 120 ms.

\textit{In situ} FT-IR measurements of ALD processes are typically limited to the purge steps with the optical windows being shuttered during precursor pulses.\textsuperscript{12,19,20} If, as here, shutters are not employed, then adsorption and deposition occurs on the windows. Furthermore, absorption of IR radiation by gas-phase species complicates the measurement of the surface species. However, the surface selection rules for RAIRS on metals mean that for near-grazing incidence angles, only \textit{p}-polarized radiation is absorbed by surface species and only by dipoles with components normal to the surface.\textsuperscript{21} Therefore, the polarization dependence can provide a means to differentiate surface dipoles from the polarization-insensitive absorption from the gas phase and deposits on the windows. In our method, we alternate between \textit{s}- and \textit{p}-polarizations with each ALD cycle. Doing so yields signal-averaged, time-resolved spectra in each polarization state. We then spectrally subtract the contributions from the gas phase and window deposits (\textit{s}-polarization) from the spectra that include those and the surface absorption (\textit{p}-polarization) to produce spectra that are from the surface only. We use a KRS-5 wire-grid polarizer on a motorized mount to select the polarization state, and an 85° angle of incidence to maximize the absorption from the surface.

While nucleation is an important step in ALD, the focus of this report is the postnucleation TiO2 surface during continued deposition. To avoid potential complications that might arise from nucleation on a metal substrate, we utilize a buried metal layer (BML) substrate for RAIRS.\textsuperscript{22,23} Our BML substrates consist of Cr(10 nm)/Au(200 nm)/SiO2(20 nm) layers sputtered onto an oxidized silicon wafer. The oxide-on-metal configuration allows us to easily nucleate the TiO2 film on the hydroxylated SiO2 surface, but before beginning the time-resolved data collection, we perform 20 ALD cycles to bury the initial SiO2 interface.

The benchmark films are grown for 200 cycles using conditions nominally identical to the \textit{in situ} conditions. Si substrates with a 100-nm thermal oxide were used for these test samples. Vacuum ultraviolet spectroscopic ellipsometry (VUV-SE) measurements are performed, and the data are analyzed to obtain the film thickness and band gap energy gap (E\textsubscript{g}) for each. The GPC is calculated from the layer thickness assuming a linear growth rate. X-ray photoelectron spectroscopy (XPS) is employed to determine the film composition and impurity concentrations. The samples were Ar ion sputtered prior to XPS analysis to remove surface contamination.

III. RESULTS

A. \textit{Ex situ} film measurements

A summary of the film properties determined using VUV-SE and XPS are presented in Table I. The estimated GPC values are similar to others.\textsuperscript{3,8} Furthermore, the GPC
TABLE I. Summary of film properties determined using ex situ methods. The GPC values are calculated from the thickness as determined by VUV-SE, which also measures the band gap energy \( (E_g) \). XPS is used to determine impurity concentrations in the films after sputtering to remove surface contamination.

<table>
<thead>
<tr>
<th>( T_s (°C) )</th>
<th>GPC (Å/cycle)</th>
<th>( E_g (eV) )</th>
<th>C (at. %)</th>
<th>N (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.64</td>
<td>3.40</td>
<td>1.4</td>
<td>0.4</td>
</tr>
<tr>
<td>190</td>
<td>0.49</td>
<td>3.35</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>240</td>
<td>0.55</td>
<td>3.32</td>
<td>0.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The \( E_g \) values determined from VUV-SE decrease with increasing \( T_s \), but they are still slightly above those of bulk anatase \((3.2 \text{ eV})\) and much above rutile \((3.0 \text{ eV})\).\(^{24}\) The film deposited at 240 °C has an \( E_g \) of \( 3.32 \text{ eV} \) very close to that measured for a film deposited at 100 °C using the TiCl\(_4\)/H\(_2\)O chemistry \( (3.33 \text{ eV})^{25} \). Differences in the temperature trends may indicate that the process chemistry has an important role in the electronic properties (e.g., through defect states.)

XPS reveals that the films in each case are stoichiometric TiO\(_2\) within the uncertainties of the measurement. Similar to prior results, additional peaks in the Ti 2p spectrum are observed to arise with increased sputtering time, and we likewise attribute these to reduction by Ar ion bombardment.\(^{3}\) Also in agreement with prior results, the C and N content is found to be very low.\(^{3,6–9}\) Furthermore, contamination is found to decrease with increasing \( T_s \).

B. In situ infrared spectroscopy

Spectra obtained with 120 ms time resolution during the ALD cycle are processed by integrating the absorbance in the ranges for \( \nu(\text{CH}) \) (stretch) modes \((2750 \text{ cm}^{-1} \text{ to } 2965 \text{ cm}^{-1})\) and \( \nu(\text{OH}) \) modes \((3620 \text{ cm}^{-1} \text{ to } 3750 \text{ cm}^{-1})\). The spectra are referenced to the surface before the TDMAT injection of each cycle, so they actually represent a difference from the initial, hydroxylated growth surface. The integrated absorbance is presented in Fig. 1 with indicators to denote the timing of the TDMAT and H\(_2\)O pulses.

From the integrated absorbance of the \( \nu(\text{CH}) \) modes, it is apparent that TDMAT rapidly saturates the surface during the TDMAT pulse while the negative integrated absorbance of the \( \nu(\text{OH}) \) modes indicates that surface hydroxyl groups \( \approx \text{OH}^* \) are consumed. (The asterisk here is used to denote surface species.) During the H\(_2\)O pulse, the \( \nu(\text{CH}) \) absorbance decreases and \( \nu(\text{OH}) \) absorbance increases returning both nearly to the zero baseline. These observations are consistent with ligand exchange at the surface

\[
x\cdot\text{OH}^* + \text{Ti(NMe}\_2\text{)}_4 \rightarrow \text{O}^-\text{Ti(NMe}\_2\text{)}_4 - x^* + x\text{Me}_2\text{NH}.
\]

During the TDMAT half-cycle \([\text{Eq. (1a)}]\), \( \text{–OH}^* \) groups are substituted for alkylamido \( \text{–NMe}_2^* \) groups, and the reverse occurs during the H\(_2\)O half-cycle \([\text{Eq. (1b)}]\). Together, the reactions generate dimethylamine (DMA), Me\(_2\)NH, which desorbs, and TiO\(_2\), which deposits.

A closer examination of the data, however, reveals dynamics that are not attributable to ligand exchange. At 240 °C, the \( \nu(\text{CH}) \) absorbance exhibits an obvious decrease during the purge that follows the TDMAT pulse (Fig. 1). A decrease is also apparent in the 190 °C data but to a lesser degree. Additionally, during the H\(_2\)O pulses at 190 °C and 240 °C, the integrated absorbance from \( \nu(\text{OH}) \) “overshoots” the zero baseline and decays over the course of seconds. In other words, the surface during and immediately following the H\(_2\)O pulse contains more \( \text{–OH}^* \) groups than it does immediately before the TDMAT pulse. Neither of these dynamics can be explained by Eq. (1).

To clarify what may be occurring, individual spectra are inspected. First, we examine the disappearance of \( \nu(\text{CH}) \) absorbance. In Fig. 2, we present spectra obtained at the end of the TDMAT pulse [Fig. 2(a)] and at the end of the purge that follows it [Fig. 2(b)] during the 240 °C experiment. To improve the signal-to-noise ratio, five spectra are averaged in each case; these occur in the ranges of \((4.15–4.64) \text{ s}\) and \((14.14–14.63) \text{ s}\) in Fig. 1. The two spectra are very similar, and subtraction of the two yields a difference spectrum [Fig. 2(c)] very similar to the minuend and subtrahend. It
can be concluded, therefore, that absorbance from the –NMe₂* groups diminishes and no new species containing C–H bonds, which would give rise to different spectral features, are created during the purge. Neither do we observe evidence for a decomposition product on the surface in other portions of the spectra in Fig. 2. Absorption at around 1600 cm⁻¹–1650 cm⁻¹, which has been attributed to ν(C=N) stretch modes of adsorbed imines, is absent. Absorption between 2060 cm⁻¹ and 2150 cm⁻¹, which could be due to C=C, C=N=N, or N=N groups, is also absent.

Now, we examine the dynamics in the ν(OH) absorbance. In Fig. 3, we plot a portion of the averaged spectra immediately before the H₂O pulse (14.14–14.63 s in Fig. 1) and averaged spectra immediately after it (15.71–16.19 s in Fig. 1). Each ν(OH) band is fit using a Gaussian peak shape on a linear baseline. The –OH* groups created during the H₂O pulse (and lost during the subsequent purge) are centered at lower wavenumbers (3670 cm⁻¹ at 110 °C to 3685 cm⁻¹ at 240 °C) than those that remain until being ultimately consumed during the TDMAT pulse (≈3700 cm⁻¹). There is no indication of interchange between these populations, which would produce a “derivative-like” feature in the spectra.

We do not observe evidence for ν(OH) from molecular H₂O, which should produce bands at lower wavenumbers (around 3400 cm⁻¹) than the –OH* groups. The H₂O scissors mode, δ_s(H₂O), however, is apparent at around 1600 cm⁻¹ at T_s = 110 °C and 190 °C (insets in Fig. 3). At 110 °C, there is a positive feature after the H₂O pulse and a negative feature after the TDMAT pulse. The timing of the features indicates that molecular H₂O adsors during the H₂O pulse and partially desors during the purge, and the remainder is consumed by TDMAT. At 190 °C, a weak, positive feature at 1600 cm⁻¹ is observed after the H₂O pulse, but a corresponding negative feature is not in the post-TDMAT spectrum. This timing indicates that molecular H₂O is present briefly after the H₂O pulse but none is consumed by TDMAT. Presumably, it has desorbed at that point. At 240 °C, there is no evidence for molecular H₂O in either spectrum.

IV. DISCUSSION

The following discusses the main observations of this paper that do not conform to ligand exchange. First, observations regarding surface H₂O are explained along with their implications for growth and in situ studies. Then, the loss of –NMe₂* groups is addressed, and a model is proposed that explains the contradictory evidence for and against thermal decomposition. Finally, the dynamics in the –OH* groups are discussed.

A. Molecular water

As mentioned above and shown in Fig. 3, the observation of molecular H₂O on the surface is made through the δ_s(H₂O) mode instead of the ν(H₂O) modes, which are absent. Increased intensity of the δ_s(H₂O) mode versus the ν(H₂O) mode on TiO₂ has been noted before; the ν(H₂O) modes may be present but too weak to observe here.
However, it is also possible that the adsorbed H$_2$O is parallel to the surface. If it is in this orientation, then our RAIRS measurement would not detect it because only the $p$-polarized electric field of the IR radiation is significant at the surface.

The observation of molecular H$_2$O under the present deposition conditions is surprising. The relatively long purge time (30 s) is insufficient to completely desorb all the adsorbed H$_2$O at 110 °C, and this H$_2$O reacts with TDMAT in non-ALD reactions. Since 110 °C is also the wall temperature in the present study, it can be assumed that H$_2$O is molecularly adsorbed on the TiO$_2$-coated walls as well. If the stoichiometry [i.e., $x$ in Eq. (1)] were determined by comparing the amount of DMA produced in each half-cycle, adsorbed H$_2$O would be one source of inaccuracy. Furthermore, the persistence of molecular H$_2$O likely explains the higher GPC values typically observed at low $T_s$ or when using cold-walled reactors.

B. Alkylamido ligands

We observe that absorbance from the $\nu$(CH) modes decreases at 190 °C and 240 °C during the purge that follows the TDMAT pulse (Fig. 1). While this observation could indicate that adsorbed TDMAT is desorbing, desorption of Ti-containing species would decrease the GPC, the opposite of what we observe at 240 °C (Table I). Thermal decomposition of adsorbed TDMAT or –NMe$_2$ groups is also consistent with the decrease of $\nu$(CH) modes, but surface species produced by decomposition, which are observed in other IR studies of adsorbed TDMAT, are not apparent in our spectra (Fig. 2). (Although, a recent IR study of TDMAT adsorbed on SiO$_2$ similarly found that, at 250 °C, only subtle changes in the $\nu$(CH) modes occurred.) We further note that decomposition products are normally thought to increase film impurities, which are not observed (Table I).

While neither desorption nor thermal decomposition (as normally encountered) can explain all these observations, one explanation is consistent with most of them: If –NMe$_2$ groups slowly decompose into a product that rapidly desorbs, then the $\nu$(CH) absorbance would be observed to decrease with no new species apparent from surface IR spectroscopy. The loss of the decomposition product would also explain the lack of C and N contamination observed at 240 °C.

Prior work allows us to speculate on the nature of the decomposition product. From research involving TiN CVD using TDMAT, the prevailing view is that –NMe$_2$ groups react by $\beta$-hydrogen elimination during surface pyrolysis. The resulting N-methylmethyleneimine (MMI), Me$_2$N=CH$_2$, is thought to be complexed with surface Ti atoms perhaps in a metalloccycle arrangement. The MMI ligand is believed to be the origin of the C and N in TiC$_x$N$_y$ films deposited by TDMAT pyrolysis. Recent density functional calculations examining the decomposition of alkylamido organometallics on Si found that MMI desorption could occur with no significant kinetic barrier although the formation of a Si–C bond was more favorable thermodynamically. It seems plausible that MMI on certain surfaces may preferentially desorb, but on other surfaces, it may readily form bonds with surface atoms. Indeed, some experiments find evidence of gas-phase MMI during TDMAT pyrolysis but others do not. If our interpretation is correct, it indicates that caution should be exercised in comparing precursor behavior on surfaces that differ significantly from ALD growth surfaces.

The modest increase ($\approx$10%) in GPC that we observe when $T_s$ is increased from 190 °C to 240 °C is difficult to explain based on the decomposition/desorption mechanism we propose. The increase may be due to TDMAT adsorption at secondary adsorption sites (i.e., not –OH*) that are sterically unavailable when the surface is fully covered with –NMe$_2$ groups. Oligomerization of TDMAT is another possible explanation for the increased GPC. At present, this aspect of our work remains unexplained.

Significantly, the $\nu$(OH) absorbance does not continue to decrease with the $\nu$(CH) absorbance at 240 °C in Fig. 1. This observation along with increasing GPC is inconsistent with a proposed “desorbing intermediate” mechanism based on the growth study of Ref. 9

$$\text{–OTi(NMe}_2)_3^\ast + \text{–OH}^\ast \rightarrow \text{–O}^\ast + \text{HOTi(NMe}_2)_3^3. \quad (2)$$

The formation of a desorbing species with a hydroxyl ligand is not supported by the data since both –OH* and –NMe$_2$* groups would be lost simultaneously in equal measure from the surface. That occurs neither during the TDMAT pulse nor during the purge that follows it.

In light of our results, some of the confusion from TDMAT/H$_2$O ALD growth studies can be understood. The typical interpretation of the data obtained from growth studies generally associates decomposition with increased impurity incorporation. The current study suggests this assumption is not always correct. The concept of a desorbing decomposition product could possibly be exploited with carefully designed precursors that take into account the reactivity of the growth surface toward the decomposition product. Regardless, viewing the growth surface as a coreactant with surface ligands and their decomposition products may be useful for understanding ALD processes.

C. Hydroxyl groups

As shown in Fig. 1, the integrated $\nu$(OH) absorbance becomes negative as –OH* groups are consumed during the TDMAT pulse, becomes positive during the H$_2$O pulse, and returns to the zero baseline during the H$_2$O purge. The $\nu$(OH) bands appear to be centered on two modes: (3670–3685) cm$^{-1}$ appear as positive features during the H$_2$O pulse, and (3700–3760) cm$^{-1}$ are negative following the reaction with TDMAT (Fig. 3). In the case of anatase surfaces, two bands are typically observed near 3675 cm$^{-1}$ and 3715 cm$^{-1}$. Rutile surfaces similarly exhibit two bands centered near 3660 cm$^{-1}$ and 3690 cm$^{-1}$. The assignments of these bands remain controversial. However, the lower- and higher-wavenumber bands are frequently understood to correspond to bridging ($\mu_2$–OH) and terminal ($\mu_1$–OH)
configurations, respectively. We tentatively assign the two bands we observe to these two bonding configurations acknowledging that our growth surfaces probably are highly disordered. (Previous studies studying ALD of TiO₂ using TiCl₄/H₂O at 327 °C found differing peak locations. It seems likely that a more crystalline material perhaps of a different phase was being deposited.)

Both types of –OH* groups are formed during the H₂O pulse, but the μ₁–OH groups are apparently more stable. Those lost during the post-H₂O purge are primarily the lower-wavenumber μ₂–OH groups. From surface studies, μ₂–OH groups are known to recombine according to

\[ 2 > \text{OH}^* \iff > \text{O}^* + \text{V}_\text{O} + \text{H}_2\text{O}, \tag{3} \]

where >OH* and >O*, respectively, denotes a bridging hydroxyl and a bridging oxygen (i.e., the O atom in each case is coordinated to two Ti atoms). V₆ is a bridging oxygen vacancy. The reverse process (disproportionation) also occurs. If a similar process is occurring during ALD, then oxygen vacancies are being created during the purge. What possible role these defects might play in ALD surface reactions or film properties is not known.

V. CONCLUSIONS

In situ measurements during ALD can provide much greater insight into reaction mechanisms than growth experiments alone can provide. Although in situ IR spectroscopy has been used extensively to examine processes at the time scale of ALD half-cycles and longer, this work shows that dynamics can occur within the half-cycle and that IR spectroscopy is capable of observing them. Few other techniques can make surface measurements during half-cycles, and none provide direct chemical information.

In examining the TDMAT/H₂O growth chemistry, we note several processes that are much slower than the ligand exchange surface reactions but faster than the half-cycle timing. These include the desorption of molecularly adsorbed H₂O. At 110 °C, H₂O remains bound to the surface after a 30 s purge and then reacts with TDMAT. At the higher substrate temperatures investigated, no H₂O was observed to remain long enough to react with TDMAT, but at 190 °C, it possibly could with shorter purge times. The reaction of molecular H₂O with TDMAT may explain a great deal of disagreement in literature values of the GPC at lower temperatures since the amount of adsorbed H₂O should depend on experimental details like partial pressures, purge times, and reactor design.

Another relatively slow process is the loss of –NMe₂* groups at 240 °C and 190 °C. We do not observe new IR-active modes on the surface. These observations, together with ex situ measurements showing a modest increase in the GPC and very little C and N incorporation, indicate that the –NMe₂* groups do not produce a surface-bound contaminant. Our interpretation is that a desorbing product is formed from the thermal decomposition of these surface ligands. How the loss of –NMe₂* groups might affect film growth is unknown, but the rate of the loss is such that cycle timing could result in significant differences in surface coverage between growth experiments.

Finally, we observe dynamics in the –OH* groups during the purge following the H₂O pulse. Two populations are clearly observed based on the difference in the location of the respective ν(OH) bands. The lower wavenumber band is lost during the purge while the higher wavenumber band persists until the TDMAT pulse. The slow loss of –OH* groups may explain the monotonic decrease in GPC with increasing Tₚ (assuming purge times are long enough to desorb molecular H₂O). However, in the present study, some other mechanism counteracts this effect and gives rise to a slight increase in the GPC.

This work agrees with previous growth studies: The TDMAT/H₂O ALD chemistry is not purely ligand exchange. We have identified three processes that may explain some of the disagreement between growth experiments. Despite exhibiting non-ideal ALD behavior, TDMAT/H₂O demonstrates interesting features that may be of practical use. In particular, the growth of high-purity films while thermal decomposition occurs means that this chemistry is not necessarily limited to low temperatures. This finding may be of use for titanate film growth using Ba or Sr precursors requiring high temperatures.

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