Alternative Low-Pressure Surface Chemistry of Titanium Tetraisopropoxide on Oxidized Molybdenum

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Supporting Information

ABSTRACT: Titanium tetraisopropoxide (TTIP) is a precursor utilized in atomic layer depositions (ALDs) for the growth of TiO2. The chemistry of TTIP deposition onto a slightly oxidized molybdenum substrate was explored under ultrahigh vacuum (UHV) conditions with X-ray photoelectron spectroscopy. Comparison of the Ti(2p) and C(1s) peak areas has been used to determine the surface chemistry for increasing substrate temperatures. TTIP at a gas-phase temperature of 373 K reacts with a MoOx substrate at 373 K but not when the substrate is at 295 K, consistent with a reaction that proceeds via a Langmuir–Hinshelwood mechanism. Chemical vapor deposition was observed for depositions at 473 K, below the thermal decomposition temperature of TTIP and within the ALD temperature window, suggesting an alternative reaction pathway competitive to ALD. We propose that under conditions of low pressure and moderate substrate temperatures dehydration of the reacted precursor by nascent TiO2 becomes the dominant reaction pathway and leads to the CVD growth of TiO2 rather than a self-limiting ALD reaction. These results highlight the complexity of the chemistry of ALD precursors and demonstrate that changing the pressure can drastically alter the surface chemistry.

INTRODUCTION

Atomic layer deposition (ALD) is a technique that relies on two sequential gas–surface reactions to grow materials in a layer-by-layer fashion. This method is employed in the semiconductor industry and is most commonly used to deposit metal oxides.1 However, ALD has become an emerging technique for the fabrication of novel and complex catalytic systems and in the process has been extended to the growth of metal films and nanoparticles on catalytic supports.2,3 ALD employs multiple cycles that are combined to build materials with precise thickness control. One ALD cycle is composed of two half cycles that result in the regeneration of the initial surface groups, providing new reactive sites for the following cycle. Given a finite number of surface reaction sites and steric constraints imposed by the ligands, only a finite number of precursor molecules can react, resulting in the self-limiting nature of the technique.4 Reactive sites on oxides include hydroxyl groups, bridging oxygen atoms, and defect sites.

There has been a significant amount of work directed toward elucidating ALD chemistry, utilizing techniques such as X-ray photoelectron spectroscopy (XPS), mass spectrometry, quartz crystal microbalance (QCM), temperature-programmed desorption (TPD), DFT, and ab initio calculations.5,6 The most studied system is the deposition of Al2O3 from trimethylaluminum (TMA) and H2O because it is widely used and considered an “ideal” deposition process. Significant work has been done to establish a mechanism for the reaction, identify the source of self-limiting behavior, and understand the reaction kinetics.7-10 Many of these experiments are summarized in a dedicated review by Puurunen.4 Studies of other ALD metal precursors and corresponding growth processes of metal oxide films, such as Nb2O5, HfO2, ZrO2, Al2O3, and TiO2, have also been performed.11-13 Additional experiments have explored the influence of different oxidizing precursors including H2O, ozone, and O2 plasma.14-16

While TiCl4 is the common precursor for the growth of TiO2, titanium tetraisopropoxide (TTIP) is an important alternative. TTIP is preferable for materials intended for catalytic applications since residual surface ligands can be removed by calcination.16 In contrast with TiCl4, residual surface chlorine induces Brønsted acidity that imparts potentially undesirable catalytic functionality. While the thermal decomposition of TTIP for chemical vapor deposition (CVD) applications is the subject of a number of publications, a smaller number have looked at the ALD chemistry of TTIP.5,17-19 An enlightening study by Rahtu and Ritala combines mass spectrometry, quartz crystal microbalance (QCM), and TPD experiments to explore the reaction mechanism of TTIP deposition onto both a predosed Ti(OCH(CH3)2)x covered surface and SiO2 for TPD and QCM experiments, respec-
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The current understanding is that the TTIP reaction with a metal oxide surface follows eqs 1a and 1b

$$2 - \text{OH}_2 + \text{Ti(O\text{Pr})_2} \rightarrow (\text{O} - \text{OH})_2 \text{Ti(O\text{Pr})_2} + 2(\text{CH}_3)_2 \text{CHOH}_2$$

In this mechanism, half of the precursor ligands are removed upon the initial reaction with surface hydroxyl groups (eq 1a), and the other half are released with a subsequent water dose (eq 1b).

Equations 1a and 1b can be generalized for many ALD processes on metal oxide surfaces for which the majority of the reactive sites are surface hydroxyl groups. However, as ALD applications are broadening more nontraditional substrates are being used, and the chemistry involved is less well understood. In particular, only a few studies have explored reaction mechanisms on noble metal surfaces, such as Cu and Pd, and these studies predominantly involve the TMA/H_2O process.

EXPERIMENTAL METHODS

Instrumentation and Sample Mounting. All experiments were performed in a previously described three-level ultrahigh vacuum (UHV) apparatus with a base pressure that ranged from 5 × 10^{-10} to 2 × 10^{-9} Torr. Briefly, the upper level includes an Extrel quadrupole mass spectrometer, low energy electron diffraction (LEED), ion sputtering gun, heated dosing lines, and a dual-anode Thermo/VC Microtech X-ray photoelectron spectrometer with a hemispherical electron energy analyzer. The middle level houses a high-resolution electron energy loss spectrometer, and the bottom level contains a high-pressure chamber (HPC). Recently, an Arradiance Gemstar-6 ALD system was interfaced to the top level of the UHV apparatus. A 360° rotating XYZ manipulator with a 1 m Z-translator was used to position the sample for sputtering, gas dosing, transferring into the HPC, and performing analytical measurements.

The sample was a 1 cm diameter Mo(100) single-crystal disk that was cut and mechanically polished to within 1° of the 100 plane. It was initially cleaned in a separate UHV chamber by heating to 1500 K in 5 × 10^{-7} Torr of oxygen for 48 h to remove bulk carbon and sulfur. Two 0.25 mm Mo wires were used to suspend the crystal between two thermally isolated copper leads at the bottom of the manipulator shaft. The sample was resistively heated, and the temperature was measured with a K-type thermocouple spot-welded to the back of the crystal. Between TiO_2 deposition experiments the crystal was cleaned with argon ion sputtering using 2 kV ions at normal incidence followed by brief annealing to 1073 K. This procedure was repeated until the crystal was mostly free of titanium. The crystal was subsequently annealed at 773 K under 600 L of O_2 to remove carbide species that had formed during the cleaning process. XPS was used to verify the chemical state and composition of the crystal surface. Peak areas were calculated with the appropriate sensitivity factor for comparison between elements, and key elemental ratios are tabulated for each experiment in the Supporting Information.

TTIP Deposition. Titanium tetraisopropoxide (TTIP, Sigma-Aldrich 97 and 99.9999%) was purified using several freeze–pump–thaw cycles before it was deposited onto the Mo(100) single crystal in the UHV chamber by one of two experimental methods: (1) dosing lines and (2) the Gemstar-6 ALD system. 97% pure TTIP was used in the dosing lines, while 99.999% purity was used in the Gemstar-6 system; however, both systems produced similar deposition chemistry and are detailed below.

Once a dose was complete, the chamber was evacuated for 2–3 h until the pressure reached 10^{-9} Torr for analysis with XPS. A Mo(3d) satellite peak overlaps with the C(1s) region and was removed through subtraction of spectra that were taken of the base substrate prior to precursor dosing.

Gas Delivery via Dosing Lines. The dosing lines were used for experiments with the substrate heated to 573 and 473 K. The dosing line is evacuated with a mechanical pump to ∼10 mTorr and is comprised of a precursor vessel, a leak valve, and a sapphire tube. The precursor vessel is isolated from the dosing line by a needle valve. A leak valve (Granville-Philips) separates the low vacuum side of the line from the UHV system and is used to introduce gaseous precursors into the chamber. The end of the dosing line is a sapphire tube with a 0.25 mm tantalum wire coiled around it for resistive heating to control the temperature of the gas entering the system. Prior to deposition, the head space of the precursor vessels and the dosing lines were evacuated and purged several times with N_2 gas before directed dosing with either TTIP or H_2O to a pressure of 1 × 10^{-6} Torr. All precursor vessels and dosing lines were kept at room temperature, ∼295 K, during the duration of these experiments, while the sapphire tube was heated to 383 K. The vapor pressures of TTIP and water at room temperature are 0.4 and 21 Torr, respectively. After each dose, the lines and the chamber were purged with 1 × 10^{-5} Torr of N_2 for a minimum of 15 min. The QMS was used to verify the presence of the intact precursor during the dose and the disappearance of the precursor during the N_2 purge.

Gas Delivery via the Gemstar-6. A commercial ALD system (Arradiance Gemstar-6) was interfaced to the UHV chamber through an auxiliary port on the system. One end of a 1/4” OD stainless steel tube is inserted into the oven of the
ALD system, and a fraction of the gas stream is directed into the UHV system toward the surface of the Mo substrate. A VCR gasket at the end of the stainless steel tube with a 75 μm diameter laser-drilled hole reduces the pressure from 1 to 10 Torr to ~10^{-7}–10^{-6} Torr. The connecting line could be evacuated with a turbo pump (Pfeiffer-Balzer 070) and heated to 383 K. The temperatures of the TTIP and water containers were 353 and 295 K, respectively. The corresponding vapor pressure for TTIP is ~2.2 Torr.28 The head space of the precursor bottle was evacuated before dosing. Doses were performed by first closing the isolation valve between the ALD system and the mechanical pump evacuating it. The precursor was then dosed into the ALD reaction chamber followed by minimizing the carrier N_{2} flow to prevent large changes to the partial pressures within the reaction chamber over the course of the dose. After 15 s of equilibration time the gas was introduced into the UHV chamber. After each dose was complete the connecting line was purged with N_{2} for a minimum of 20 min, and the concentration of precursor remaining in the chamber was monitored with the QMS. The partial pressure of TTIP and the concentration of precursor remaining in the connecting line was purged with N_{2} for a minimum of 20 min, and the concentration of precursor remaining in the chamber was monitored with the QMS. The partial pressure of TTIP and H_{2}O entering the chamber was less than 3 × 10^{-7} and 3 × 10^{-6} Torr, respectively, based on the changes in the base pressure read by an ion gauge (Granville-Philips). This experimental setup was used for the set of deposition experiments in which the surface of the Mo crystal was heated to 373 K.

### RESULTS

**Base MoO_{x} Surface.** A clean Mo (100) surface is extremely reactive and will dissociatively adsorb gases at room temperature until a passivation layer is formed.29 The annealing temperatures used in the study temporarily removed the carbon, but were not high enough to completely desorb all of the oxygen. The base Mo surface in these experiments was passivated by both carbon and oxygen, as shown in the representative XPS data in Figure 1 for the base substrate used in the 573 K experiments. The integrated peaks from panels a, b and c corresponding to Mo(3d), O(1s) and C(1s) spectra, respectively, give a Mo:O:C ratio of 11:7:1. The binding energies for the Mo(3d_{5/2}) peak from the base substrates in this work ranged between 227.9 and 228.0 eV with a full width half-maximum (fwhm) of ~1.1 eV, Figure 1a. The binding energies for the O(1s) peak range from 530.4 to 530.7 eV with a corresponding range of fwhm of 1.9–3.3 eV, Figure 1b. All O(1s) spectra are well fit with two Gaussians, with peaks at 530.5 and 531.4 eV, consistent with O(1s) spectra from molybdenum oxides found in the literature.30 The C(1s) peak has a binding energy of 285.2 eV and a fwhm of 2.4 eV, consistent with adventitious carbon.

After a brief anneal to 573 K the C(1s) signal disappeared from the base MoO_{x} surface but grew back to the concentration shown in Figure 1c during the experiment. It is difficult with the current XPS orientation, θ = 0°, to determine the exact elemental ratio of the top few layers of the substrate. Previous work from our laboratory has explored the effects of chemisorbed oxygen on the structure, oxidation state, and acidity of Mo(100).31–34 These early experiments used CO dissociation to calibrate the O(1s) signal to establish a metric for the expected intensity ratio of the Mo(3d_{5/2}) to the O(1s) peaks for increasing oxygen coverage ranging from 0.3 to 2 monolayers on a Mo(100) surface.35 For this work, the O/Mo ratios are 0.06, 0.15, and 0.14 for the base substrate in the 573, 473, and 373 K experiments, respectively. These ratios correspond to oxygen surface coverages of 0.7, 1.7, and 1.5 monolayers. For oxygen coverages above 1.5 monolayers, the two higher coverages in our case, it has been reported that the surface has chemical and physical properties similar to MoO_{x}. Oxygen on surfaces with less than 1.5 monolayers is chemisorbed.36,37 Because the surface structure and hence the stoichiometry is not known we refer to the surface as MoO_{x}. The presence of chemisorbed oxygen implies that the Mo(100) surface is passivated by a layer of oxygen atoms onto which the adventitious carbon becomes adsorbed.

**TTIP Deposition onto a 573 K MoO_{x} Surface.** The results of TTIP deposition onto a 573 K base MoO_{x} surface in 300 L (1 Langmuir = 1 × 10^{-6} Torr s) intervals are shown in Figure 2. 573 K is above the reported TTIP thermal decomposition temperature and would be expected to produce chemical vapor deposition, whereby the growth of TiO_{2} is dependent only on the integrated precursor exposure. Panels a and b show the Ti(2p) and C(1s) spectra from the base surface (black) and after three 300 L doses of TTIP (red). The Ti(2p_{3/2}) peak from the base Mo surface is insignificant, but after TTIP exposure there is a large peak with a binding energy of 459.4 eV and a peak splitting of 5.7 eV which is indicative of TiO_{2} formation; however, there is charging in the sample which leads to slightly higher binding energies.38 There is a persistent C(1s) peak from adventitious carbon present on the base surface, but this set of experiments also resulted in a contribution at lower binding energies from carbide carbon. In Figure 2b, the C(1s) spectrum from the base Mo surface and the total C(1s) spectrum taken after 900 L of TTIP are shown in black and red. The C(1s) spectrum from the base surface was subtracted from the total C(1s) spectrum after 900 L of...
TTIP to isolate the C(1s) signal due to the depositions alone. The reported C(1s) spectra have been corrected in this manner. The resultant C(1s) peak shape (Figure 2c) is bimodal with similar peak ratios to that of the spectrum from an isopropoxide ligand (blue) obtained in a previous study from condensed vanadyl triisopropoxide.\(^{38}\)

All elemental ratios and surface densities are summarized in Table S1 (Supporting Information), with an error associated with the integration and background subtraction process of \(\sim 8\%\). The Ti and C surface densities for the base substrate were 0.2 and 1.8 atoms/nm\(^2\), respectively. Figure 2d displays the change in Ti (black squares) and C (open blue circles) surface density above the base substrate value as a function of precursor exposure time. As demonstrated by the graph, the Ti surface density increases linearly with exposure time, while the C surface density is approximately constant. The ratio of peak areas, C(1s):Ti(2p), from the spectra after 900 L of TTIP is \(\sim 1:4.9\). The Ti(2p):O(1s) ratio indicates that at 573 K the films are near stoichiometric. The reported density of ALD grown TiO\(_2\) films at 573 K is 4.1 g/cm\(^3\), resulting in a Ti surface density of 9.9 atoms/nm\(^2\).\(^{39}\) This is a conservative guide to determine when a monolayer of TiO\(_2\) has been deposited. For a substrate temperature of 573 K, after the second 300 L TTIP dose a monolayer of TiO\(_2\) has been grown with 11.3 Ti atoms/nm\(^2\).

### TTIP and Water Deposition onto a 473 K MoO\(_x\) Surface.

TTIP was deposited onto the base MoO\(_x\) surface held at 473 K. The results shown in Figure 3 are from four sequential 300 L doses (1200 total L) of TTIP followed by two sequential water doses of 300 and 600 L. The temperature of the substrate is within the ALD window for TTIP deposition and is commonly used when growing TiO\(_2\) inside an ALD reactor using TTIP as the metal precursor.\(^{13}\) Panels a and b show the respective Ti(2p) and C(1s) spectra for the base MoO\(_x\) (black) and after four sequential 300 L of TTIP (red). While the peak area is significantly lower at this temperature than at 573 K, there is still a significant Ti(2p) signal from deposited TiO\(_2\) which has a slightly lower binding energy of 459.0 eV, likely from reduced sample charging on a thinner deposited metal oxide film. The C(1s) spectrum from the base surface (black line in Figure 3b) is similar to the base signal in Figure 2b but is lacking a contribution from carbidic carbon. The red line represents the increase in C(1s) signal after four 300 L doses. The spectrum is bimodal and resembles the C(1s) spectrum of condensed isopropoxide ligands, similar to Figure 2c. While the water doses reduced the intensity of the C(1s) signal, the shape of the peak remained the same, indicating the loss of exchangeable isopropoxide ligands.

The elemental ratios and surface densities calculated after each dose are shown in Table S2 of the Supporting Information. The base substrate had a Ti and C surface density of 0.4 and 2.0 atoms/nm\(^2\). Figure 3c shows the changes in Ti (black squares) and C (open blue circles) surface densities above the base substrate value after each dose. The C surface density grows in a manner similar to the case of the 573 K MoO\(_x\) surface, in which it remains fairly constant with increasing TTIP exposure. On the other hand, the Ti surface density is almost linear with exposure time. These films are slightly deficient in oxygen, which is consistent with previous studies of TiO\(_2\) ALD with TTIP onto another clean surface, Si(001), at 373 K.\(^{18}\) The Ti atom surface densities suggest that 40% of a full monolayer of titanium oxide was grown by the
Reactions on MoO$_3$, at 295 and 373 K. TTIP was dosed into the UHV chamber and onto a 373 K base Mo surface using the Gemstar-6 system in three 20 L intervals followed by two 70 L intervals. After a total of 200 L of TTIP exposure the surface was dosed with 360 L of water followed by another 20 L dose of TTIP. The results are shown in Figure 4. The substrate temperature is well below reported decomposition temperatures for TTIP. Figure 4a shows the Ti(2p) spectra from a base Mo surface and after 200 L of TTIP in black and red, respectively. The binding energy, 458.9 eV, and peak splitting, 5.9 eV, are similar to the results displayed in Figure 3 and consistent with a Ti–O containing species on the surface.

Figure 3. Results for increasing 300 L doses of TTIP onto a 473 K Mo substrate. (a) Ti(2p) spectra taken before (black) and after (red) a total of 1200 L of TTIP, (b) C(1s) spectra taken before (black) and after (red) a total of 1200 L of TTIP, and (c) Ti and C surface densities as a function of TTIP (black squares and blue circles) and water (red squares and circles) exposure.

Figure 4. Results for increasing three 20 L and two 70 L doses of TTIP onto a 473 K Mo substrate. (a) Ti(2p) spectra taken before (black) and after (red) a total of 200 L of TTIP, (b) C(1s) spectra taken before (black) and after (red) a total of 200 L of TTIP, and (c) Ti (black squares) and C (open blue circles) surface densities as a function of precursor exposure. Surface density changes from H$_2$O doses are shown in red.

end of the final dose. The C surface density is greater than the Ti surface density for the first two doses with a C(1s):Ti(2p) ratio of 1.3:1. This ratio implies that an average of 1.3 C atoms are deposited for every Ti atom. After 1200 L of TTIP exposure the Ti surface density is larger than that of C with a ratio of 1:2.3.

The red squares and red circles in Figure 3c represent the Ti and C surface densities, respectively, after 300 L and then 600 L of H$_2$O. There is a 47% decrease in the C density upon the first 300 L of H$_2$O, but there was no impact on the C density from the subsequent 600 L H$_2$O dose. As expected, the Ti surface density increases only slightly due to partial removal of the carbon overlayer.
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Figure 4b displays the C(1s) peak from the base surface which has a similar shape to previous adventitious carbon spectra. The red line in Figure 4b represents the increase in C(1s) signal on the surface after 200 L of TTIP dosing. While the peak shape and binding energies are very similar to the spectra in Figures 2 and 3, the signal-to-noise ratio is too low for further peak shape analysis.

Elemental ratios and Ti atom surface densities are reported in Table S3 in the Supporting Information. Panel c depicts the changes in the Ti and C surface densities (black squares and open blue circles) above the base substrate values as a function of precursor exposure time. Unlike the previous experiment at 473 K, the C surface density was consistently higher than the corresponding Ti surface density. The C(1s)/Ti(2p) ratio after the first 20 L TTIP dose was approximately 5.8:1 and dropped to 2.8:1 after a total of 200 L of TTIP exposure. Following 200 L of TTIP exposure, the surface was dosed with 360 L of water, and the results are represented by the red markers in Figure 4c. The Ti surface density remained the same, while the C surface density decreased by ~33%. The remaining signal had the same shape as shown in Figure 4b, consistent with the loss of isopropoxide from the surface. After the water another 20 L dose of TTIP was applied which increased both the Ti(2p) and the C(1s) signals. Films grown at 373 K are significantly oxygen deficient. The Ti atom surface densities indicate that 17% of a full monolayer of titanium oxide was grown by the end of the final dose.

Two experiments with the surface at 295 K were also performed. In the first experiment, 40 L of 388 K TTIP was dosed onto a base room temperature MoO₃ surface. No titanium or carbon was deposited. The second experiment involved dosing a room temperature TTIP-terminated surface with 720 L of 388 K water. No detectable changes in the C(1s) spectra were observed.

### Discussion

Several studies have demonstrated that ALD can be carried out under UHV conditions (10⁻⁶ Torr) with pressures that are 6–7 orders of magnitude lower than in traditional ALD reactors (0.1–10 Torr). However, it has been suggested that the pressure difference between UHV conditions and traditional ALD can result in different chemistry, XPS, mass spectrometry, secondary ion mass spectrometry (SIMS), temperature-programmed desorption (TPD), IR spectroscopy, and electron energy loss spectroscopy (EELS) are some of the methods that have been used to study and verify self-limiting growth on flat surfaces at lower pressures.

The most studied process is the growth of Al₂O₃ by deposition of trimethylaluminium and water. IR and EELS experiments conducted by Soto et al. and mass spectrometry experiments performed by Juppo et al. have successfully observed ALD-like behavior from lower-pressure dosing. A few other ALD processes have been explored under UHV conditions, including XPS studies by Roy et al. on the deposition of ZrO₂ and coupled XPS and SIMS experiments by Lemonds et al. to investigate the chemistry of TaF₅ and Si₂H₆ half-cycle reactions. In both cases self-limiting deposition was observed with substrate temperatures up to 523 K. Finally, our own experiments investigating VO₂ deposition onto metal oxide surfaces have observed ALD-like growth of vanadia in an UHV system.

**Room Temperature TTIP Chemistry.** Unlike traditional ALD reactors, our UHV setup allows us to independently control the temperatures of the gaseous precursors and the substrate and therefore study substrate temperature effects in more detail. In the current study we have explored the changes in the chemistry of TTIP with increasing substrate temperatures while keeping the precursor gas temperature at 373 K. On the time scale of our experiments, there is no evidence of reaction with either water or TTIP when the substrate is held at room temperature (295 K). However, deposition was observed when the substrate temperature was increased to 373 K. Our results indicate that thermal activation by the substrate is critical as increasing the gas-phase temperature alone to 373 K is insufficient for achieving growth. This means that the precursor first accommodates to the surface temperature prior to reaction and implies a Langmuir–Hinshelwood rather than an Eley–Rideal mechanism for the surface chemistry.

**Temperature Dependence of TTIP Deposition onto MoO₃.** The growth mode and chemistry of TTIP deposition onto a base MoO₃ surface was studied with XPS as a function of substrate temperature. The shapes of the Ti(2p) and C(1s) spectra, ratio of their peak areas, and Ti and C surface densities after TTIP or water dosing are used to determine the type of growth.

Atomic layer deposition and chemical vapor deposition are related processes for the growth of materials. As mentioned previously, ALD is a process that is composed of two sequential self-limiting gas–surface reactions. Alternatively, CVD is the growth of materials from chemical reactions of gas-phase precursors. CVD can arise from a variety of mechanisms, including gas-phase bimolecular reactions, thermal decomposition of the precursor or surface reactions that regenerate reactive sites. Since CVD and ALD are similar, it can be hard to distinguish between the two. One critical difference is self-limiting growth in ALD.

Chemical vapor deposition through thermal decomposition of TTIP has been well studied. Chemical vapor deposition can include TiO₂, H₂O, propene, H₂, isopropanol, acetone, and diisopropyl ether, depending on the reaction conditions. A common thermal decomposition mechanism includes propene as a product, as represented in eq 2.

\[
\text{Ti(OCH(CH₃)₂)₄(g)} \rightarrow \text{TiO}_2(s) + 4\text{C}_3\text{H}_6(g) + 2\text{H}_3\text{O}_2(g)
\]

(2)

For ALD of TTIP on a metal oxide surface, the reaction in the first half-cycle is eq 1a. It is important to note that the reaction terminates with some number of carbon-containing ligands remaining on the surface, covering potential reactive sites. This is responsible for the self-limiting behavior of ALD. Comparing eq 1a and 2, one critical difference between CVD and ALD is the lack of carbon expected to remain on the surface after CVD. In our studies, we use this difference to determine the growth mode. Not only do we observe surface carbon species but also the shape of the C(1s) spectra is similar to the C(1s) spectrum of condensed vanadyl trisopropoxide observed in previous studies performed in the same apparatus. This indicates that the carbon signal is predominantly composed of isopropoxide ligands remaining on the surface after the reaction. Although the Ti(2p) or Mo(3d) spectra cannot be used to distinguish whether the isopropoxide ligands are bound to Ti or Mo atoms, the decreases in C(1s) intensity after water dosing indicate that exchangeable ligands are present.

The more informative XPS results are the C(1s) to Ti(2p) peak area ratio and corresponding surface densities which should indicate the ratio of ligands to titanium atoms remaining.
after each dose. For ALD-like reactions, we expect that there should be, on average, 1–2 isopropanoxide ligands per Ti atom remaining on the surface if there is less than one monolayer coverage. This would be reflected in the XPS spectra as a C(1s):Ti(2p) ratio that is greater than or equal to 3:1. Instead, for all doses of TTIP onto a 573 K MoO2 surface the Ti(2p) signal is greater than the C(1s) signal (Figure 2d), and the Ti surface density increases linearly with TTIP exposure, therefore indicating that TiO2 is being formed by CVD. This observation is consistent with previous thermal decomposition studies.17,46,47,51

**Chemical Vapor Deposition of TTIP at 473 K.** At 473 K all doses of TTIP also resulted in low C(1s):Ti(2p) atomic ratios which decreased from 1.3:1 to 1:2.3 as the TTIP exposure increased. This indicates that CVD also occurs at 473 K even though this is within the observed ALD temperature window.13,55 Moreover, while thermal decomposition is a common mechanism of CVD, 473 K is below the reported TTIP thermal decomposition temperatures. We have considered the possibility of gas-phase reactions from residual water in the chamber regenerating reactive sites from ligand exchange causing uncontrolled growth, especially during the long evacuation and data collection periods. However, this can be ruled out by our experiment showing the absence of reaction between dosed water and the 295 K TTIP-covered surface.

One possible CVD mechanism which explains our observations is that, under UHV conditions at 473 K, we are observing TiO2-catalyzed dehydration of TTIP molecules. As far as we know, this reaction mechanism has not been proposed before; however, it is well known that TiO2 is a dehydration catalyst that is active for alcohol dehydration above 500 K.56–60 Recent TPD experiments of isopropanol on TiO2(110) reported a low-temperature dehydration pathway around 300 K.38,59 It has also been established that the intermediate for the reaction is the alkoxide which then undergoes β-hydride elimination to form the alkene.56–58,60 While the adsorbed species from TTIP deposition onto TiO2 is not exactly equivalent to the reaction intermediate for isopropanol dehydration on TiO2, the same mechanism and products, H2O and C3H6, have been reported for TTIP decomposition.17,46,47,55,54 It is reasonable that the alkoxide ligand chemistry of a deposited TiOTIP is similar to the chemistry of the intermediate alkoxide formed during alcohol dehydration. Thus, during low-pressure deposition, initially formed TiO2 species catalyze dehydration of subsequent TTIP molecules, to form more TiO2 and regenerate reactive sites rather than terminating the deposition reaction by saturating the surface with isopropanoxide ligands. This alternative dehydration pathway is always possible during TTIP deposition onto/ or near TiO2 but is likely suppressed under the higher-pressure ALD conditions because the increased flux of TTIP molecules hitting the surface leads to a more rapid surface saturation covering the TiO2 sites active for dehydration. We propose that under the experimental conditions of low flux and moderate temperatures the ALD reaction kinetics are slow enough that dehydration becomes the dominant pathway.

Lowering the MoO2 substrate temperature to 373 K causes a significant change in the growth mode. The integrated C(1s) signal is larger than for the Ti(2p) signal for all TTIP and water doses. After the first TTIP dose the calculated C(1s):Ti(2p) ratio is 5:3:1 which means that on average 1–2 ligands are remaining on the surface per reacted TTIP molecule, consistent with ALD chemistry for the first dose. After the second TTIP dose, the total C(1s):Ti(2p) ratio immediately decreases to 2.8:1, indicating that less than one ligand remains on the surface per reacted TTIP molecule and there was an overall loss of ligands from the first dose to the second. The ratio remains relatively constant through 200 L of TTIP exposure. These ratios are more suggestive of CVD-like growth of TiO2 compared to the first dose. These results suggest that ALD chemistry takes place during the first dose because TiO2 is not yet present on the surface, but following doses approach CVD behavior as the TiO2 concentration builds up and the dehydration reaction pathway becomes possible.

We have considered the possible role of the MoO2 surface in this alternative reaction pathway. MoO2 and to a lesser degree MoO3 are also alcohol dehydration catalysts; however, recent studies have shown that the surface alkoxides preferentially desorb as the alcohol rather than dehydrate to the alkene.22,23 The presence of MoO3 was undetectable by XPS, and its presence is not expected on Mo surfaces treated as described. Therefore, substrate-catalyzed dehydration is not expected to contribute to the overall dehydration reaction. To further address the possibility of molybdenum oxide catalyzed dehydration TTIP was deposited onto a 473 K MoO2 substrate with an oxygen coverage of 0.5 monolayer, a significantly lower oxygen concentration than in the previous experiment. Vibrational spectroscopy and surface polarizability studies have shown that oxygen overlayers with this concentration do not have the structure or electronic properties of molybdenum oxide but rather behave as chemisorbed oxygen.34–36 This surface will have even less activity than MoO2 for dehydration of the alkoxide ligand. The elemental ratios, Ti atom surface densities, and a description of the experiment are detailed in Table S4 of the Supporting Information. Due to the low reactivity of TTIP only 45% of a complete TiO2 monolayer is deposited after a total of 2040 L of TTIP exposure. However, we observe low C(1s):Ti(2p) ratios, indicating CVD-like growth which is consistent with the results from the more oxidized substrate. This suggests that the base MoO2 substrate does not play a significant role in the alternative reaction pathway.

**Implications for Atomic Layer Deposition Processes.** This alternative reaction pathway to ALD chemistry for TTIP deposition is not restricted to MoO2 substrates because the active dehydration site is predominantly TiO2. However, it is improbable that the dehydration reaction pathway plays a major role during ALD processes in traditional reactors because the precursor flux on the surface is 106–107 higher. Because of the higher flux, all active dehydration sites are covered by deposited TTIP molecules, and dehydration is quenched. This flux dependence has possible implications for substrate architectures with mass transport limitations, such as long nanoscale pores. Our results suggest that CVD, instead of ALD, occurs at the bottom of these pores because the flux of TTIP molecules may be insufficient to inhibit the dehydration pathway. The CVD reactions would then lead to a filling of the pores rather than a thin conformal coating.

**CONCLUSION**

The chemistry of TTIP deposition on to a MoO2 surface was explored at a series of substrate temperatures in UHV conditions. Compared to successful depositions onto a 373 K MoO2 surface, the lack of reactivity of 373 K TTIP with a 295 K surface indicates that the surface temperature is a critical parameter. TTIP molecules must accommodate to the surface...
prior to reaction and follow a Langmuir–Hinshelwood mechanism.

CVD of TiO₂ from TTIP was observed for substrate temperatures of 573 and 473 K, which are, respectively, within and below the reported thermal decomposition range for TTIP. It is believed that, under the conditions of low pressure (10⁻⁶ Torr) and moderate temperatures (473 K), dehydration of TTIP molecules by nascent TiO₂ not only becomes competitive with the ALD reaction but actually becomes the dominant reaction. At lower temperature, 373 K, ALD-like competitive with the ALD reaction but actually becomes the dominant reaction. At lower temperature, 373 K, ALD-like competitive with the ALD reaction but actually becomes the dominant reaction. At lower temperature, 373 K, ALD-like competitive with the ALD reaction but actually becomes the dominant reaction.

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**REFERENCES**

(26) The dosing lines and the Gemstar-6 system were both used to deposit TTIP onto a MoO₃ substrate at 473 K. It was challenging to quantitatively compare the total flux from each system as the dosing methods are significantly different. In the Gemstar-6 the TTIP had to
be heated to 353 K; there is a carrier gas (N2); and the aperture restricts the pressure of TTIP into the chamber to 3 × 10⁻⁷ Torr. Most importantly, both methods resulted in TiO₂ deposition where the ratio of the Ti(2p) peak area was greater than the C(1s) peak area indicating CVD. In addition, both methods did not result in TiO₂ deposition with the substrate at 295 K, verifying that the chemistry is taking place on the MoO₃ surface and is independent of which dosing technique was used.


