Analysis of TiO₂ Atomic Layer Deposition Surface Chemistry and Evidence of Propene Oligomerization Using Surface-Enhanced Raman Spectroscopy

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Supporting Information

ABSTRACT: Atomic layer deposition (ALD) of TiO₂ was performed in tandem with in situ surface-enhanced Raman spectroscopy (SERS) to monitor changes in the transient surface species across multiple ALD cycles. A self-assembled monolayer of 3-mercaptopropionic acid was used as a capture agent to ensure that nucleation of the titanium precursor (titanium tetraisopropoxide [TTIP]) occurs. Comparisons between the Raman spectra of the neat precursor and the SER spectra of the first ALD cycle of TiO₂ reveal typical ligand exchange chemistry taking place, with self-limiting behavior and intact isopropoxide ligands. However, subsequent cycles show drastically different chemistry, with no isopropoxide ligands remaining at any point during the second and third cycles. Continuous exposure of either TTIP or isopropyl alcohol after the first cycle shows unlimited chemical vapor deposition (CVD)-type growth. Comparisons with alternative precursors (aluminum isopropoxide, titanium tert-butoxide, and titanium propoxide) and DFT calculations reveal that, for the TTIP precursor, isolated TiO₂ sites play a role in the dehydration of off-gassing isopropyl alcohol. The resulting propene then undergoes oligomerization into six-carbon olefins before polymerizing into indistinguishable carbon products that accumulate on the surface. The emergence of the dehydration chemistry is expected to be exclusively the result of these isolated TiO₂ sites and, as such, is expected to occur on other surfaces where TiO₂ ALD is feasible. This work showcases how seemingly innocuous ALD can evolve into a CVD process when the products can participate in various side reactions with newly made surface sites.

INTRODUCTION

Atomic layer deposition (ALD) of TiO₂ has been done on a variety of substrates for applications ranging from thin film overcoats to stabilize various catalysts and plasmonic substrates to photovoltaic and catalyst fabrication. Due to the interplay between thin film structure and function, much work has been done to optimize ALD processes for various TiO₂ thin film applications. Despite efforts to optimize thin film depositions, there is still ambiguity regarding the reaction mechanisms and intermediates associated with these ALD processes and how they play a role in properties such as film growth, purity, and uniformity. For example, concluded titanium tetraisopropoxide (TTIP) surface reaction intermediates influence TiO₂ growth rate by comparing their TTIP/O₂ ALD results with TTIP/H₂O ALD results. As such, any technique that can yield novel information about the TiO₂ ALD process and its intermediates would prove invaluable in developing sophisticated materials.

Surface-enhanced Raman spectroscopy (SERS) is one such technique that is capable of probing molecules and intermediates near a surface by exciting the localized surface plasmon resonance (LSPR) of a noble metal (Ag, Au, or Cu) nanostructure. The electromagnetic (EM) mechanism requires the probe molecule to be near the plasmonic surface (<5 nm) but not necessarily directly bonded to the surface. The proximity requirement is convenient because it allows for the use of an adsorbed molecule to act as an anchoring site for molecules that do not adsorb directly to the metal. In this case, the TiO₂ precursor is unable to directly nucleate onto a silver surface, due to a lack of viable surface hydroxyl groups. This contrasts with the alumina precursor trimethylaluminum (TMA), which was previously shown to nucleate directly onto a silver surface at relatively low temperatures (<100 °C). By using a capture agent that both binds to the metal and bonds with the TiO₂ precursor, however, one can maintain a reasonable distance between the surface and the TiO₂ intermediate species, thus allowing for an appreciable SERS signal of the intermediate to be acquired. Furthermore, by nucleating on the carboxylic acid group, one can emulate surfaces more characteristic of traditional metal oxide supports used for TiO₂ ALD (i.e., native hydroxyl groups). The method of using capture-agent-enabled surface-enhanced Raman spec-
The ALD pathway leads to uniform growth with off-gassing isopropyl alcohol, whereas the CVD pathway involves dehydration of the isopropyl alcohol byproduct, which then becomes incorporated into the film after oligomerization.

**EXPERIMENTAL SECTION**

**Fabrication of AgFON SERS Substrates.** AgFONs (silver film-over-nanospheres) were fabricated on 18 mm glass slides according to a standard procedure described in a previous publication. Briefly, glass slides were cleaned by immersion in piranha solution (3:1 by volume H₂SO₄/30% H₂O₂) for 1 h. Clean glass slides were thoroughly rinsed with deionized (DI) water. The slides were then sonicated for 1 h in 5:1:1 by volume H₂O/NaOH/30% H₂O₂ followed by rinsing with DI water. Next, 390 nm silica (Bangs Laboratories) nanospheres were diluted to 5% silica by volume. The solvent was then replaced twice with Millipore H₂O (Milli-Q, 18.2 MΩ cm⁻¹) by a conventional centrifugation/supernatant removal procedure, followed by sonication for 1 h. The solvent-replaced nanosphere solution (8 μL) was drop-coated and distributed homogeneously across the glass surface. The solvent was then allowed to evaporate in ambient conditions where the drop-coated spheres assembled in a hexagonal close-packed array as verified by SEM measurements. The 200 nm Ag films were deposited at a rate of 2 Å/s under vacuum (6 × 10⁻⁶ Torr) over the nanospheres using a home-built thermal vapor deposition system. The substrates were spun during deposition while the metal thickness and deposition rate were measured by a 6 MHz gold-plated QCM (Sigma Instruments).

**Surface-Enhanced Raman Spectroscopy.** A 532 nm continuous-wave (CW) laser (Innovative Photonic Solutions) was used for all SERS experiments. Laser light was directed, using protected silver mirrors, to a 3 mm right-angle prism and then focused using a visible achromatic doublet lens (2.54 cm diameter, 10.16 cm focal length). Scattered light was dispersed (1200 grooves/mm, 500 nm visible) onto a 0.3 m imaging spectrograph (Acton SpectraPro 2300i) using a visible achromatic doublet lens (2.54 cm diameter, 10.16 cm focal length). Scattered light was dispersed (1200 grooves/mm, 500 nm blaze grating) onto a liquid-N₂-cooled CCD detector (Princeton Instruments, model 7509-0001, 1340 × 400 pixels). SER spectra were collected with 0.5–1.0 mW of laser power (P₂), 1–10 s of acquisition time (t₁), and 10–100 accumulations each. No background contribution or SERS signal attenuation was observed from the quartz window, as previously established. Also, X-ray photoelectron spectroscopy (XPS) was used after 1 and 5 cycle(s) of ALD to confirm that a TiO₂ film was growing on the surface, while also suggesting undercoordinated Ti³⁺ sites were present for dehydration of isopropyl alcohol to oleins. Surprisingly, the SERS results and DFT modeling indicate that oleins are the dominant product after the first cycle during what should have been an ALD process. Scheme 1, which we explain later, shows a comparison of conventional ALD with the apparent mechanism for olefin production. We also show that this non-ALD behavior is due to both the nature of the TiO₂ site and the alkoxide ligand. Aluminum isopropanoxide and titanium tert-butoxide do not participate in the deviational chemistry, whereas titanium propoxide shows non-ALD behavior. Quartz crystal microbalance (QCM) measurements show multiple-layer growth rates after the first cycle, in agreement with non-ALD behavior. This highlights the potential for seemingly straightforward ALD reaction schemes to enter unlimited growth regimes and generate undesired intermediates/products through previously unestablished side reactions. These undesirable side products can later be incorporated into the film and significantly alter the properties and integrity of the film.
shown in Figure S1. SERS substrates were mounted on a movable sample holder, placed inside the ALD chamber under vacuum (∼0.05 Torr), and heated to ∼70 °C for all ALDs. SERS spectra were acquired before and after dosing 50 sccm of either titanium(IV) tetraisopropoxide (TTIP) (Sigma-Aldrich, 97%), titanium(IV) tert-butoxide (TTB) (Sigma-Aldrich, dep. grade), aluminum isopropoxide (AlIPO) (Sigma-Aldrich, ≥98%), titanium(IV) propoxide (TP) (Sigma-Aldrich, 98%), or 60 sccm deionized water, using ultrahigh purity (UHP) N2 as the carrier gas. The timing sequence for TiO2 and Al2O3 ALD was 60 s−60 s−60 s−60 s, with SERS measurements collected between half-cycles. The TTIP, TTB, TP, and AlIPO bubblers were heated to 65 °C, and the precursor inlet line was heated to 75 °C. The water bubbler was left at room temperature, and the inlet line was heated to 90 °C.

SERS Substrate Incubation. AgFONs were incubated in a 2 mM ethanolic solution of MPA (Sigma-Aldrich, >99%) for 24 h.

In Situ QMS Measurements. In situ QMS (RGA300 Stanford Research Systems) was used to measure the TiO2 ALD reaction products. TiO2 ALD was performed during QMS measurements in the same manner as the SERS experiments (with a timing sequence of 60 s−60 s−60 s−60 s). MS signals for propene (m/z = 41) and isopropyl alcohol (m/z = 45) were monitored during the deposition. An acquisition time of 1 s was used for all QMS measurements.

In Situ QCM Measurements. In situ QCM (Infinicon Q-POD + 6 MHz Colorado Crystal Corp.) was used to measure the TiO2 ALD growth rate over several cycles. To emulate the AgFON surface used in SERS experiments, 200 nm of Ag was thermally deposited onto the crystal and incubated in a 2 mM ethanolic solution of MPA (Sigma-Aldrich, >99%) for 24 h. The crystal was exposed to TTIP and water for 180 s each, with purge steps of 60 s.

X-ray Photoelectron Spectroscopy. XPS was performed at the Keck-II Center at Northwestern University on a Thermo Scientific ESCALAB 250Xi. A monochromatic Al Kα (1486.74 eV) X-ray source was used with a 400 µm spot size.

Computational Methods. All Raman spectra were calculated using the Amsterdam density functional (ADF) software package. Full geometry optimization, frequency, and polarizability calculations presented in this study were carried out using a triple-ζ polarized type Slater basis set and the Becke–Perdew23,24 generalized gradient approximation exchange-correlational functional. For the surface-bound species, a Ag20 cluster was used as a surface. The zero-order regular approximation25,26 was used to include the relativistic effect for all calculations.

Static polarizability derivatives were calculated by two-point numerical differentiation of the polarizability using the RESPONSE module implemented in ADF. The differential Raman scattering cross sections for the pth vibrational mode was calculated according to the following equation:

$$\sigma_p = \frac{\alpha_i}{\epsilon_0} (\omega - \omega_p)^4 \frac{h}{8\pi c \omega_p} \left( \frac{S_p}{45(1 - \exp(-h\omega_p/k_B T))} \right)$$

where $\omega$ is the incident field frequency (532 nm) and $\omega_p$ and $S_p$ are the frequency and the Raman activity of pth mode, respectively. $S_p$ is composed of the isotropic polarizability derivative, $\alpha_i$, and the anisotropy, $\gamma$: $S_p = 45\alpha_i + 7\gamma^2$

$$\alpha_i = \frac{1}{3} \sum_i (\alpha_{ij})_p$$

$$\gamma = \frac{1}{3} \sum_{ij} \sum_i (\alpha_{ij})_p (\alpha_{ij})_p - (\alpha_{ij})_p (\alpha_{ij})_p$$

The temperature was assumed to be 298 K, and each Raman peak was broadened with a Lorentzian function with a full width at half-maximum of 20 cm⁻¹.

Table 1. Vibrational Modes and Corresponding Assignments from In Situ SER Spectra during ALD (Shaded Rows Represent Vibrations Associated with Olefins)^

<table>
<thead>
<tr>
<th>TTIP Precursor</th>
<th>1c TTIP SERS</th>
<th>1c H2O SERS</th>
<th>2c TTIP SERS</th>
<th>2c H2O SERS</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTIP</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$\nu$(Ti-O)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>684</td>
<td>695</td>
<td>$\tau$(CH3)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>831</td>
<td>831</td>
<td>$\rho$(CH2)</td>
</tr>
<tr>
<td>850</td>
<td>834</td>
<td>861</td>
<td>-</td>
<td>-</td>
<td>$\nu$(CCC), $\nu$(Ti-O)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>899</td>
<td>-</td>
<td>$\nu$(C-CO)=C</td>
</tr>
<tr>
<td>923</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$\rho$(CH3)</td>
</tr>
<tr>
<td>1023</td>
<td>1019</td>
<td>1018</td>
<td>-</td>
<td>-</td>
<td>$\nu$(C-O), $\nu$(Ti-O)</td>
</tr>
<tr>
<td>1123</td>
<td>1155*</td>
<td>1167*</td>
<td>1148</td>
<td>1150</td>
<td>$\nu$(CCC)</td>
</tr>
<tr>
<td>1181</td>
<td>1155</td>
<td>1167</td>
<td>-</td>
<td>-</td>
<td>$\rho$(CH3), $\nu$(Ti-O)</td>
</tr>
<tr>
<td>1331</td>
<td>1347</td>
<td>1347</td>
<td>-</td>
<td>-</td>
<td>$\delta$(C-H)</td>
</tr>
<tr>
<td>1445</td>
<td>1462</td>
<td>1474</td>
<td>-</td>
<td>-</td>
<td>$\delta$(C-H)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1492</td>
<td>1471</td>
<td>$\delta$(C-H(vinyl))</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1543</td>
<td>1517</td>
<td>$\nu$(C=C)</td>
</tr>
<tr>
<td>2867</td>
<td>2863</td>
<td>2860</td>
<td>2860</td>
<td>2862</td>
<td>$\nu$(CH3), $\nu$(C-H)</td>
</tr>
<tr>
<td>2916</td>
<td>2922*</td>
<td>2920*</td>
<td>2920*</td>
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<td>2966</td>
<td>2966</td>
<td>2965</td>
<td>$\nu$(CH3)</td>
</tr>
</tbody>
</table>

*i.p. = in-plane.*
SER spectra were taken of the AgFON after incubation in MPA to verify that nucleation sites were available for TiO$_2$ ALD (see Figure S2). Most of the vibrational modes agree with previously reported values (Table 1).$^{27}$ The strongest modes at 652 ($\nu$(C−S)$_2$), 734 ($\nu$(C−S)$_{eq}$), and 904 ($\nu$(C−COO)) cm$^{-1}$ in the Raman spectrum of the TTIP precursor can be found in the low wavenumber region, most of the peaks present in the normal Raman spectrum of the TTIP precursor. Likewise, the only mode that uniquely shows up in the first H$_2$O dose is at 1232 cm$^{-1}$.

In the first TTIP and first H$_2$O difference spectra, the asymmetrical peaks found at 1155 and 1167 cm$^{-1}$, respectively, are likely the agglomeration of two or three peaks, two of which can be seen in the normal Raman spectrum of TTIP (1123 and 1181 cm$^{-1}$). The modes found in SER spectra match up well with the modes found in the Raman of the neat liquid, suggesting some amount of isopropoxide ligands stay coordinated to the titanium center, whereas the other ligands undergo typical ligand exchange chemistry at the carboxylic acid site of the thiol self-assembled monolayer. The parity in intensity of the peaks between the two spectra suggest essentially all surface species generated are removed with water, as expected in ALD-type behavior. The CH region (see Figure S3) shows the same self-limiting behavior.

During the second cycle, however, a different type of surface chemistry emerges (see Figure 1b). Not only do the SER spectra show new peaks indicative of new species, but the spectra also lack any modes associated with the neat TTIP precursor. The most noticeable of these missing peaks is the strong C−O stretching mode located at 1023 cm$^{-1}$. This would suggest that the second ALD cycle results in unique ligand exchange chemistry, where all four of the isopropoxide ligands are displaced from the titanium center during the first half cycle. Alternatively, a different deposition mechanism, akin to chemical vapor deposition (CVD), takes place during the second cycle and introduces new surface species. The peak seen at 1267 cm$^{-1}$ in the first cycle shows up more prominently in the second cycle, suggesting the new surface chemistry was mildly present during the first cycle. Multiple spectra were also collected throughout the course of a single dose to evaluate the new surface chemistry taking place and the identity of the new surface species. By monitoring the change in peaks from spectrum to spectrum while a single dose is occurring, one can determine whether the chemistry is self-limiting. If the chemistry is not self-limiting, one can evaluate the continual generation of specific chemical species. During the first 30 s of exposure to the TTIP precursor (see Figure 2a), multiple modes indicative of TTIP surface species can be seen. These modes match up well with the modes seen in the first ALD cycle in Figure 1. Another 30 s of TTIP exposure shows a small disappearance of the 1155 cm$^{-1}$ mode and the appearance of modes associated with the new surface species as previously seen in the second ALD cycle (i.e., the mode at 1267 cm$^{-1}$). A cumulative exposure of 90 s of TTIP, however, shows the reduction of these unknown modes, leaving only TTIP modes. The subsequent water exposure shows removal of the TTIP modes (see Figure 2b), with 90 s being sufficient to remove the isopropoxide ligands. These spectra are clear indicators of the self-limiting chemistry that is expected in ALD.

The exposures during the second cycle (see Figure 2c,d), however, show a more complex and continuous surface reaction taking place. Throughout the 30 s pulses of TTIP during the second cycle, modes around 1587, 1269, 1148, 899, and 684 cm$^{-1}$ continue to grow in. Modes around 1492 and 1543 cm$^{-1}$ fluctuate as either positive or negative peaks during the TTIP exposures. During the first 30 s of water exposure for the second ALD cycle, almost all the peaks observed are positive, and it is only after 60 s of water exposure that removal of these surface species begins to take place. Overall, it appears

Figure 1. SER difference spectra collected in situ during the TiO$_2$ ALD process on MPA-functionalized AgFON. Panel (a) shows the first TTIP dose (in red) and first H$_2$O dose (in blue), with the normal Raman spectrum (NRS) of the TTIP precursor (in black) for comparison. Panel (b) shows the second TTIP dose (in red) and second H$_2$O dose (in blue), with the TTIP precursor spectrum shown for comparison. All major peaks are annotated, and data are shifted vertically for clarity. Data are displayed in arbitrary data units.
that extended exposure of water is not sufficient to remove these new surface species being generated from the second cycle TTIP exposure. Furthermore, this trend of incomplete species removal continues onto the third ALD cycle (see Figure S4), where the peak area during TTIP exposure is larger than the peak area during water exposure. These spectra suggest new, strongly adsorbing species are forming from constant exposure of TTIP during a CVD-like process. The peak fluctuations also suggest a multitude of species created from the isopropoxide ligands are present during this process. QCM measurements of the deposition process (see Figure S5) corroborate the behavior observed via SERS and show that the expected submonolayer growth rates occur only during the first ALD cycle, with multiple-layer growth rates occurring in subsequent cycles. These growth rates range from 1 to 4 Å per cycle and are indicative of non-ALD reaction behavior.

The isopropoxide ligands from TTIP are suspected to form either isopropyl alcohol, acetone, diisopropyl ether, and/or propene, the most likely of which being isopropyl alcohol. It is possible that the resulting isopropyl alcohol then undergoes β-hydride elimination to form propene, based on the work by Johnson and Stair, who saw ALD-type behavior for TTIP on a MoO₃ substrate (at 100 °C and base pressure 1 × 10⁻⁶ Torr) for the first ALD cycle but, upon a second ALD cycle, saw more CVD-type behavior where propene is likely to form. They concluded the dehydration pathway becomes dominant under lower pressures because the lower flux of TTIP molecules leaves the submonolayer of initial TiO₂ sites unsaturated and available for dehydration chemistry. These findings agree with the results Bondarchuk et al.²⁹ found on TiO₂(110) from 300 to 450 K on undercoordinated Ti⁴⁺ ions. Whereas the system interrogated herein was done under pressures higher than those of Johnson, the dehydration pathway can still play a role under the reaction conditions listed due to the potential for undercoordinated TiO₂ sites. XPS results suggest such sites are on the surface as Ti³⁺ sites after five ALD cycles (see Figures S6–S8). QMS results from TiO₂ ALD on just the steel walls of the reactor show negligible amounts of propene as an off-gassing species (see Figure S9). This would suggest the isolated TiO₂ sites are capable of dehydration, due to being undercoordinated, whereas normal TiO₂ sites cannot perform this chemistry given the high flux of TTIP. If undercoordinated TiO₂ sites are playing a role in the formation of propene, then we should see evidence of propene. Furthermore, if we move away from undercoordinated TiO₂ sites to fully coordinated TiO₂ sites, then we should see a

Figure 2. SER difference spectra taken from 30 s doses of TTIP (in red) and H₂O (in blue) during the first (a,b) and second (c,d) cycles. Positive peaks represent new species being generated from the previous spectrum. Negative peaks represent removal of surface species from the previous spectrum. Data are displayed in arbitrary data units.
dramatic decrease in propene production near the surface. Use of several ALD cycles appears to be enough to grow fully coordinated TiO$_2$ sites, as the SER signal from the products being generated on the surface decreases significantly (see Figure S8).

Several control experiments were performed to confirm that propene was in fact forming due to dehydration via the TiO$_2$ sites. First, isopropyl alcohol was dosed onto AgFON-MPA after one TiO$_2$ cycle and monitored via SERS (see Figure 3) to determine whether the isopropoxide ligands were participating in the change in chemistry, regardless of whether additional TiO$_2$ sites were being generated at the same time. Second, three alternative precursors (aluminum isopropoxide [AlIPO], titanium tert-butoxide [TTB], and titanium propoxide [TP]) were used and monitored via SERS during the deposition to determine the role TiO$_2$ and ligands play in the new chemistry. AlIPO was used to determine whether the TiO$_2$ sites were responsible for the dehydration chemistry or if Al$_2$O$_3$ could perform a similar role. TTB was chosen because tert-butoxide ligands are not expected to undergo dehydration as easily, and therefore, the CVD-type behavior was not expected to occur despite TiO$_2$ being present. Conversely, TP was selected as a comparable precursor to TTIP where dehydration chemistry was expected to occur. SER spectra collected for AlIPO and TTB experiments showed ALD behavior during multiple cycles (see Figures S10 and S12), whereas SER spectra from TP ALD exhibited CVD growth akin to TTIP ALD (see Figures S13 and S14).

SER spectra of the extended isopropyl alcohol exposures onto TiO$_2$/AgFON-MPA (see Figure 3) show several modes that appear to match up with the peaks seen during the second cycle of TiO$_2$ ALD, most noticeably various modes in the 1500–1600 cm$^{-1}$ region as well as peaks at 1369, 1256, and 1156 cm$^{-1}$. The peaks seen during the varying amounts of isopropyl alcohol exposure are far broader than during TiO$_2$ ALD; however, the peaks are still distinguishable up until 300 s of dosing. The lack of noticeable features by 300 s of dosing is expected to be the result of product buildup, where access to the TiO$_2$ sites responsible for dehydration becomes blocked.

The sum of all the spectra highlights the nature of the species that builds up on the surface as amorphous carbon products. Without new TiO$_2$ sites being generated on the surface or prolonged access to the initial TiO$_2$ sites, the products evolving from propene eventually cease, leaving only the amorphous carbon.

The AlIPO dosing in both the first cycle and subsequent cycles (see Figures S10 and S11) showcases exemplary ALD-type behavior seen through SERS, as well as confirms that the TiO$_2$ plays a role in the dehydration chemistry following the first cycle. All peaks that appear with each AlIPO dose are removed with the subsequent water dose. Furthermore, the peaks seen in later cycles match what was observed in the first cycle, suggesting there is no new chemistry occurring. Most of the peaks seen experimentally also match up with DFT-calculated spectra for suspected surface species; the only differences are a shift in the COO$^-$ stretch from MPA and the absence of the lower Al–O vibrational modes. The lack of Al–O vibrations is due to the low Raman scattering cross section of those moieties. Spectra taken from dosing TTB (see Figure S12) also show ALD behavior with little to no changes in the chemistry upon multiple cycles. Vibrational modes associated with the neat precursor match up with peaks in the SER difference spectra during the ALD process, except for an unknown additional peak at 1092 cm$^{-1}$. The use of TTB
showcases how tert-butyl alcohol is incapable of undergoing this dehydration chemistry, and thus no buildup of carbonaceous material occurs. The SER spectra from TP ALD, on the other hand, showed ALD chemistry for only the first cycle. Peaks analogous to the olefin species from TTIP were also found in the second and third TP ALD cycles (see Figures S13 and S14). The dehydration chemistry is believed to occur via an E2 mechanism as established previously on TiO2, and, as such, is the reason why the primary and secondary alcohols underwent dehydration while the tertiary alcohol did not.

Finally, DFT calculations of several molecules were performed to determine the exact structure of the surface species being made in the second and third ALD cycles (see Figure 4). Comparisons between the DFT calculations and experimental results show six-carbon olefins as the most likely candidate. Models of 2,4-hexadiene and 1,3,5-hexatriene coordinated to a TiO2−Ag20 cluster yielded all the appropriate vibrational modes within reasonable proximity to the experimental data. Calculations were performed with and without the silver cluster to ensure the emulated surface had a negligible impact on the vibrational modes (see Tables S1 and S2). Modes within the 1600 to 1480 cm−1 range are indicative of a conjugated system (likely olefin). The fact that multiple peaks show up in this region experimentally suggests that a few unique olefins are present. The 1350 to 1200 cm−1 region contains one strong and wide band that matches the vinyl C=H bending mode in both olefin models. The other lesser modes match up well as an asymmetric C=C=C stretch (1150 cm−1), C=O stretch (1018 cm−1), C=(CO)=C stretch (899 cm−1), CH2 rocking (831 cm−1), and CH2 twisting (684 cm−1). The 1,3,5-hexatriene model shows strong Ti−O vibrational modes that are not expected to show up in the experiment due to the amorphous nature of the resulting TiO2.

A similar phenomenon was seen in the case of Al2O3 ALD byproduct after the occurrence between the titania sites and the isopropyl alcohol behavior seen during SERS is the result of an interaction that were not seen via SERS. All in all, the deviation in ALD experimental results show six-carbon olefins being made in the second and third ALD cycles (see coordinated to a TiO4+ candidate. Models of 2,4-hexadiene and 1,3,5-hexatriene underwent dehydration while the tertiary alcohol did not.

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### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10689.

SUPPORTING INFORMATION

SER spectra of MPA-functionalized AgFON, SER difference spectra in the CH region and after several cycles during TiO2 ALD using TTIP and TTIP, as well as Al2O3 ALD using AllPO, QMS measurements during depositions, and tabulated data for DFT calculations of surface species present during TiO2 ALD (PDF)

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Northwestern University Institute for Catalysis in Energy Processes (ICEP). ICEP is funded through the U.S. Department of Energy, Office of Basic Energy Sciences (Award Number DE-FG02-03ER15457). G.K., G.C.S., and R.P.V.D. acknowledge support from the Air Force Office of Scientific

**Journal of the American Chemical Society**

Article

DOI: 10.1021/jacs.8b10689

J. Am. Chem. Soc. 2019, 141, 414−422

420
of Growth Mechanism.


