Probing the Chemistry of Alumina Atomic Layer Deposition Using Operando Surface-Enhanced Raman Spectroscopy

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INTRODUCTION

Atomic layer deposition (ALD) relies on sequential self-limiting binary reactions between gaseous precursor molecules and a substrate to deposit thin films in a layer-by-layer fashion. 1–4 ALD provides angstrom-level precision over film thickness. Unlike films deposited by line-of-sight techniques, ALD films are highly uniform and can be deposited on most substrates regardless of whether they are flat, porous, or have complex three-dimensional topologies. A wide range of materials can be deposited by ALD including metal oxides, metal nitrides, metal nanoparticles such as Pd,5–15 alloys for applications in catalysis. A deep understanding of ALD reactions at the molecular level is crucial to optimize ALD processes and grow materials efficiently. Operando spectroscopic techniques, in which reactions are studied in situ under temperatures and pressures employed in ALD reactions,16,20 can provide valuable insight toward understanding mechanistic details of ALD processes. Most in situ characterization techniques that have been used to investigate the mechanisms of ALD reactions either do not provide detailed chemical structural information or are performed under conditions that differ from realistic ALD conditions.18 Examples include quartz crystal microbalance (QCM),21 quadrupole mass spectrometry (QMS),22 Fourier transform infrared (FTIR) spectroscopy,23 and spectroscopic ellipsometry.24 QCM studies are used to monitor mass gains on the surface during ALD deposition and determine the growth rate per cycle and film thickness as a function of the number of cycles. A major limitation of QCM measurements is that they do not provide any chemically specific information.18 QMS is

ABSTRACT: This work demonstrates for the first time the capability of measuring surface vibrational spectra for adsorbates during atomic layer deposition (ALD) reactions using operando surface-enhanced Raman spectroscopy (SERS). We use SERS to study alumina ALD growth at 55 °C on bare silver film-over nanosphere (AgFON) substrates as well as AgFONs functionalized with thiol self-assembled monolayers (SAMs). On bare AgFONs, we observe the growth of Al–C stretches, symmetric C–H and asymmetric C–H stretches during the trimethylaluminum (TMA) dose half-cycle, and their subsequent decay after dosing with H2O. Al–C and C–H vibrational modes decay in intensity with time even without H2O exposure providing evidence that residual H2O in the ALD chamber reacts with −CH3 groups on AgFONs. The observed Al–C stretches are attributed to TMA dimeric species on the AgFON surface in agreement with density functional theory (DFT) studies. We observe Al–C stretches and no thiol vibrational frequency shifts after dosing TMA on AgFONs functionalized with toluenethiol and benzenethiol SAMs. Conversely, we observe thiol vibrational frequency shifts and no Al–C stretches for AgFONs functionalized with 4-mercaptobenzoic acid and 4-mercaptophenol SAMs. Lack of observed Al–C stretches for COOH- and OH-terminated SAMs is explained by the spacing of Al–(CH3)2 groups from the SERS substrate. TMA penetrates through SAMs and reacts directly with Ag for benzenethiol and tolenethiol SAMs and selectively reacts with the −COOH and −OH groups for 4-mercaptobenzenoic acid and 4-mercaptohenol SAMs, respectively. The high sensitivity and chemical specificity of SERS provides valuable information about the location of ALD deposits with respect to the enhancing substrate. This information can be used to evaluate the efficacy of SAMs in blocking or allowing ALD deposition on metal surfaces. The ability to probe ALD reactions using SERS under realistic reaction conditions will lead to a better understanding of the mechanisms of ALD reactions.

1 Supporting Information

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used to detect products that desorb into the gas phase during ALD reactions, which helps to identify possible mechanisms of ALD reactions. However, QMS does not provide direct molecular-level information about adsorbed surface species. In addition, some of the gas-phase species generated during ALD processes may not be stable, and many undergo further conversion in the gas phase, upon collision with the walls of the reactor, or in the ionizer of the mass spectrometer before detection. Spectroscopic ellipsometry provides information about the thickness, growth rate, optical properties, crystalline phase, and material composition of ALD films but does not directly probe the presence of chemical bonds at surfaces. X-ray photoelectron spectroscopy (XPS) is another technique often used to study ALD reactions but is usually performed in ultrahigh vacuum (UHV), an environment that is different from typical conditions at which ALD reactions are performed. As a result, the data collected may not be representative of the proper surface species during the ALD process. Operando XPS setups typically require the use of a specially constructed electrostatic lens system and a differential pumping stage between the sample cell and the electron energy analyzer to minimize the scattering of photoelectrons by gas-phase molecules. Additionally, a synchrotron radiation source that can deliver a much higher photon flux than a conventional X-ray source is often used to increase the total photoelectron signal, although Tao and co-workers recently designed and built an operando XPS setup that uses a benchtop Al Kα X-ray source. Compared to a synchrotron-based setup, a laboratory-based operando XPS instrument has limited spectral resolution and surface sensitivity because of its X-ray source intensity and fixed photon energy, which affects the accuracy of the quantitative analysis. FTIR provides molecular-level information about adsorbed surface species and does not need a UHV environment. FTIR readily detects vibrational modes in the ~1000–3000 cm⁻¹ region but has difficulty measuring low frequency vibrations (~100–1000 cm⁻¹). Raman spectroscopy is a complementary technique to FTIR that can probe both low frequency and high frequency molecular vibrations. However, Raman scattering has inherently low sensitivity because of small Raman scattering cross sections (~10⁻²⁰ cm² steradian⁻¹ molecule⁻¹). Surface-enhanced Raman spectroscopy (SERS) overcomes the sensitivity limitations of normal Raman scattering. The enhancement of Raman signals is attributed to the excitation of localized surface plasmon resonances (LSPRs) that result in enhanced electromagnetic fields around noble metal nanostructures such as Ag, Au, and Cu. The high sensitivity and distance dependence of SERS should make it possible to evaluate the location of ALD deposits with respect to the enhancing substrate. To the best of our knowledge, in situ studies that use SERS to monitor ALD reactions do not exist in the literature. Most of the studies published so far use SERS to monitor catalytic reactions occurring on thermally robust SERS substrates. In contrast, our study focuses on demonstrating that operando SERS can be used to monitor adsorbed surface species during the ALD process itself, which results in an improved understanding of the surface chemistry involved.

Using in situ QCM and ex situ LSPR spectroscopy, it was demonstrated that ALD Al₂O₃ grows on bare Ag surfaces with a growth rate of ~1.1 Å/cycle and induces a redshift in the LSPR peak position due to a change in refractive index. The deposition of Al₂O₃ by ALD on hydroxylated surfaces is the model ALD process and has been the subject of extensive investigations. A few studies have investigated the growth of ALD Al₂O₃ on metallic substrates. ALD Al₂O₃ thin films have been shown to protect metal nanoparticles from sintering at elevated temperatures. This offers both a promising route to stabilize metal nanoparticles, which have applications in catalysis, and in situ monitoring of catalytic reactions using operando surface-enhanced optical spectroscopies.

In this work, we demonstrate, for the first time, that SERS can be used to probe ALD reactions in situ with high sensitivity. We use SERS to monitor the surface chemistry of Al₂O₃ ALD at 55 °C on Ar plasma-cleaned silver-film-over nanosphere (AgFON) substrates. We also use SERS to monitor ALD Al₂O₃ growth on AgFONs functionalized with thiol self-assembled monolayers (SAMs). Thiol SAMs are ideal molecular systems to use because they form well-defined and well-ordered structures on metal surfaces that have been extensively studied in the literature. SAMs provide a well-characterized starting surface that can be used as an internal standard against which spectral changes after ALD growth can be measured. Further, thiol SAMs on AgFONs are known to displace carbon contamination and offer an alternative way to clean SERS substrates. They also preserve the enhancing nature of SERS substrates and eliminate the need for plasma cleaning, which reduces the SERS signal. Using operando SERS, we investigate the nucleation and growth of ALD Al₂O₃ around SAMs possessing different terminal groups. The use of SAMs possessing different terminal functional groups provides a way to tailor the surface and direct ALD Al₂O₃ growth to achieve area-selective ALD.

## EXPERIMENTAL SECTION

**Fabrication of AgFON SERS Substrates.** AgFONs were fabricated on polished 25 mm silicon wafers according to a standard procedure described in previous publications. Silicon wafers were cleaned by immersion in piranha solution (3:1 by volume H₂SO₄/30% H₂O₂) for 1 h. Caution: Piranha is extremely corrosive, and appropriate personal protective equipment should be used during handling. Clean silicon wafers were thoroughly rinsed with deionized (DI) water. The wafers were then sonicated for 1 h in 5:1:1 by volume H₂O/ NH₄OH/30% H₂O₂ followed by rinsing with DI water. Silica nanospheres (390 nm, Bangs Laboratories) were diluted to 5% silica by volume. The solvent was replaced twice with Millipore (Milli-Q, 18.2 MΩ cm⁻¹) H₂O by a conventional centrifugation/supernatant removal procedure, followed by sonication for 1 h. The solvent-replaced nanosphere solution (10–12 μL) was drop-coated and distributed homogeneously across the prepared silicon wafer surface. The solvent was then allowed to evaporate under ambient conditions and spheres assembled in a hexagonal close-packed array as verified by SEM measurements. Ag films (200 nm) 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, Fort Collins, CO). AgFONs, which were not plasma-cleaned, were incubated in 1 mM ethanolic solutions of benzenethiol, toluenethiol, 4-mercaptobenzoic acid, or 4-mercaptophenol (Sigma-Aldrich) for a minimum of 4 h. The extinction spectra of AgFONs were measured using a fiber-optic coupled halogen light source (World Precision Instruments) and UV/vis spectrometer (SD...
2000, Ocean Optics) in specular reflectance mode. A Ag mirror was used as a spectral reference and was fabricated by depositing 200 nm of Ag film on cleaned glass using thermal vapor deposition.

**Surface-Enhanced Raman Spectroscopy.** A 532 nm continuous wave (CW) laser (Innovative Photonic Solutions) was used for all spectroscopic measurements. Laser light was directed using protected silver mirrors to a 3 mm right-angle prism and then focused using a visible achromatic doublet lens (1 in. diameter, 4 in. focal length) through a quartz window to a plasmonic substrate placed inside the ALD reactor. The spot size radius measured at the sample was ∼124 μm and ∼57 μm for the 532 and 633 nm lasers, respectively, using a scanning knife-edge technique. Raman scattered light was collected in a 180° backscattering geometry and focused onto a 0.3 m imaging spectrograph (Acton SpectraPro 2300i) using a visible achromatic doublet lens (1 in. diameter, 4 in. focal length). Scattered light was dispersed (1200 grooves/mm grating, 500 nm blaze) onto a liquid N2-cooled CCD detector (Princeton Instruments, Model 7509-0001). SER spectra were collected with 1–7 mW of laser power ($P_{\text{L}}$), 1–10 s of acquisition time ($t_\text{acq}$), and 1–10 accumulations each, depending on the system investigated. No background contribution or SERS signal attenuation was observed from the quartz window (Figure S1).

**Computational Modeling.** Electronic structure calculations presented in this work have been performed with the Amsterdam density functional (ADF) computational chemistry package.56 Full geometry optimization, frequency, and polarizability calculations for isolated monomer and dimer TMA complexes were completed using the Becke–Perdew (BP86) generalized gradient approximation (GGA) exchange correlation functional and a triple-$\zeta$ polarized (TZP) Slater orbital basis set.

Static Raman polarizabilities ($\omega = 0$) were calculated in the RESPONSE package by two-point numerical differentiation using the RAMANRANGE keyword. Raman scattering intensities were determined by the scattering factor $I_1$ + $\gamma_1$ where $I_1$ and $\gamma_1$ are the isotropic and anisotropic polarizability tensors with respect to the jth vibrational mode. The Raman intensity for each vibrational mode were broadened to a Lorentzian line shape with full-width at half-maximum (fwhm) of 10 cm$^{-1}$ for comparison to experimental data.

**Atomic Layer Deposition.** ALD was performed in a home-built viscous flow reactor that has been described previously and is shown in Figure 1.21 SERS substrates were mounted on a movable sample holder, placed inside the ALD chamber under vacuum (∼0.05 Torr), and heated to ∼55 °C to preserve their fine nanostructure. SER spectra were taken before and after ALD Al2O3 growth on an Ar plasma-cleaned AgFON at 55 °C. In Figure 3A, only peaks below 900 cm$^{-1}$ are shown because Ar plasma cleaning was chosen because it had no adverse effects on the pillar-like structure of the AgFONs while still removing background signal due to carbonaceous species. Additionally, Figure S2D shows that the LSPR of the AgFONs was optimized for 532 nm laser excitation, with a reflectance minimum indicative of the LSPR at 534 nm.

**Reaction of TMA with Bare AgFON.** Figure 3 shows SER spectra acquired before and after two cycles of ALD Al2O3 growth on an Ar plasma-cleaned AgFON at 55 °C. In Figure 3A, only peaks below 900 cm$^{-1}$ are shown because Ar plasma removes most of the surface contaminants observed in that region. Two peaks at 583 and 671 cm$^{-1}$ are observed after the second TMA half-cycle. The 583 and 671 cm$^{-1}$ peaks decay after dosing H2O for 10 s. TMA dosing for 5–10 s was long enough to saturate the surface as shown in Figure S3. Figure 3B shows SER difference spectra for the first two ALD cycles. The 583 and 671 cm$^{-1}$ peaks decay after dosing H2O for 60 s and reappear after 10 s of TMA dosing in the second cycle. The 583 and 671 cm$^{-1}$ peaks are assigned to the symmetric and asymmetric Al-CH3 stretching modes,58 respectively (see Table 1 and Table S1).

**RESULTS**

**SEM and LSPR Characterization of AgFONs.** Reactive ion etching (RIE) using Ar plasma was used to remove carbon contamination on AgFONs, decreasing the background of SER spectra prior to *operando* monitoring of ALD reactions, and ultimately improve the sensitivity of the AgFONs (Figure S2). To ensure that the AgFON structure was not altered during RIE, scanning electron microscopy (SEM) was used to observe the Ag film morphology. Figure 2 shows SEM images of AgFONs after RIE exposure times of 25 s (Figure 2A,B) and 300 s (Figure 2C,D). The top-down views (Figures 2A,C) clearly show that the Ag film undergoes dramatic structural changes upon long (300 s) Ar plasma exposure, with the appearance of a vitreous-like, smoothened film (Figure 2C). A similar trend was observed on the side observation of the substrates (Figures 2B,D). It is also important to notice that the metal pillars that act as electromagnetic hot spots55,57 in bare AgFONs are maintained after 25 s of Ar plasma exposure. This is consistent with the high intensity of the SER spectra (Figure S2C). On the basis of these observations, 25 s of Ar plasma cleaning was chosen because it had no adverse effects on the pillar-like structure of the AgFONs while still removing background signal due to carbonaceous species. Additionally, Figure S2D shows that the LSPR of the AgFONs was maintained after 25 s of Ar plasma exposure.

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TMA half-cycle. All positive peaks observed after TMA exposure (red curves, Figures 3B and 4B) switch and become negative after dosing H₂O, indicative of loss of surface-bound Al−(CH₃)₃ species (blue curves, Figures 3B and 4B). TMA dosing in the second cycle restores the positive peaks, however, with reduced signal intensity because of the distance dependence of the electromagnetic enhancement in SERS (red curves, Figures 3B, 4B). The 2822 and 2892 cm⁻¹ peaks are assigned to two different symmetric C−H stretches of Al−(CH₃)₃ surface species.⁷² The 2921 cm⁻¹ peak is assigned to the asymmetric C−H stretch.⁵⁹−⁶² The observation of surface-bound species from ALD precursors shows that operando SERS is capable of monitoring ALD half-reactions and can provide valuable insight into the mechanistic details of the surface chemistry of ALD processes.

**Reaction of TMA with Toluene-thiol and Benzenethiol.** The nucleation and growth of ALD Al₂O₃ on AgFONs functionalized with thiol SAMs was also investigated at 55 °C. Figure 5 shows the first ALD Al₂O₃ cycle performed on a toluene-thiol (TT)-functionalized AgFON. TMA was dosed on the surface for 10 min to ensure complete saturation. Ten minutes of TMA exposure was long enough to allow TMA to completely react with Ag (Figure S9). In Figure 5A, a peak at 585 cm⁻¹ (symmetric Al−CH₃ stretch) is observed after the first TMA half-cycle. A slight reduction in TT peak intensities after TMA exposure is also seen. The 585 cm⁻¹ peak disappears after dosing H₂O (see Figure S10 for difference spectra). On a benzenethiol (BT)-functionalized AgFON, peaks at 883 cm⁻¹ (symmetric Al−CH₃ stretch) and 1211 cm⁻¹ (symmetric Al−CH₃ stretch + CH₃ bend)⁶⁵ appear and decay after TMA and H₂O exposures, respectively (see Figures S11 and S12). Figure 5B−D and Table S2 show the absence of vibrational frequency shifts of TT and BT SAMs after dosing TMA on the surface. Figure 5B−D and Table S3 shows that the 622 (CC bend), 1081 (CCC in-plane bend + C−S stretch), and 1381 cm⁻¹ (CC stretch)⁶⁷,⁷³ peaks of TT decrease in intensity after TMA exposure. The fwhm of the peaks is roughly the same before and after TMA exposure (see Table S3).

**Reaction of TMA with Mercaptobenzoic Acid and Mercaptophenol.** The reaction of TMA with 4-mercaptopenzoic acid (MBA) and 4-mercaptophenol (MP) on AgFONs was also investigated because the −COOH and −OH groups could react directly with TMA.⁷⁴,⁷⁵ Figure 6 shows the first ALD cycle of Al₂O₃ performed on MBA-functionalized AgFON at 55 °C. After 10 min of TMA exposure, thiol peak shifts from 845 to 849 cm⁻¹ (COO− out-of-plane bend)⁶³ and 1080−1082 cm⁻¹ (CCC ring deformation and C−S stretch),⁶⁵ and the appearance of a broad shoulder peak at ∼1397 cm⁻¹ (COO− stretch)⁷¹ is seen. On MP-functionalized AgFON, thiol peak shifts from 1074 to 1075 cm⁻¹ (CCC ring deformation and C−S stretch)⁶⁵ 1290−1276 cm⁻¹ (C−OH stretch + ring breathing),⁶⁶ 1577−1584 cm⁻¹ (CC stretch and OH bend)⁶⁵,⁶⁶ are observed (Figure S13). In addition to thiol peak shifts, the peak intensities generally decreased after TMA exposure (except for the 845 cm⁻¹ peak of MBA) for both MBA and MP SAMs (Table S3). Table S3 also shows dramatic changes in the fwhm of MBA peaks after TMA exposure; the fwhm of the 845 cm⁻¹ peak increases from 33 to 52 cm⁻¹. For MP, the fwhm of the 1290 cm⁻¹ peak increases from 86 to 113 cm⁻¹. The fwhm of the 1577 cm⁻¹ peak decreases from 45 to 37 cm⁻¹ after TMA exposure.

**C−H Stretching Region of Functionalized AgFONs.** Figure 7 displays SER and difference spectra of TT- and MBA-functionalized AgFONs in the C−H stretching region. On a TT-functionalized AgFON, the 2822 and 2892 cm⁻¹ peaks, assigned to two different symmetric C−H stretches of Al−CH₃ surface species, are observed after TMA exposure (Figure 7A,B). They decay after H₂O exposure and reappear after TMA exposure in the second cycle (Figure 7B). On an MBA-functionalized AgFON, the symmetric C−H stretch of TMA appears at 2898 cm⁻¹ after TMA exposure (Figures 7C,D). Similarly to a bare AgFON, the TMA symmetric C−H stretch peak decays after H₂O exposure and reappears after TMA exposure in the second cycle (Figure 7D).

Figure 2. SEM images of AgFONs after 25 s (A, B) and 300 s (C, D) of Ar plasma cleaning. Top-down view is shown in A and C and side view is displayed in B and D.
**DISCUSSION**

Reaction of TMA with Bare AgFON. The 583 (symmetric Al−CH₃ stretch) and 671 cm⁻¹ (asymmetric Al−CH₃ stretch) modes shown in Figure 3 and Table 1 match well with the vibrational frequencies of dimeric TMA calculated by DFT (see Figure S5 and Table 1). In the first ALD cycle, we propose that TMA reacts directly with Ag and decomposes into Al atoms and Al−(OH)ₓ surface species. The Al−CH₃ stretches observed at 583 and 671 cm⁻¹ (Figure 3B) become negative after H₂O exposure because H₂O replaces Al−(CH₃)ₓ surface species with Al−(OH)ₓ species. They reappear after TMA dosing because TMA reacts with Al−(OH)ₓ species and replaces them with Al−(CH₃)ₓ species. Previous DFT studies suggest that TMA reacts directly with metals such as Pd, Pt, and Ir by dissociative chemisorption to form Al−CH₃ and Al surface species, which transform to Al−(OH)ₓ surface species.

**Table 1. Vibrational Modes and Corresponding Assignments**

<table>
<thead>
<tr>
<th>peak positions (cm⁻¹)</th>
<th>TMA</th>
<th>thiol SAMs</th>
<th>assignment</th>
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<tr>
<td>583</td>
<td>572</td>
<td>TT</td>
<td>ν(Al−CH₃)sym</td>
</tr>
<tr>
<td>671</td>
<td>671</td>
<td>BT</td>
<td>ν(Al−CH₃)asym</td>
</tr>
<tr>
<td>691</td>
<td>845</td>
<td>MBA</td>
<td>γ(CC)</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td>MP</td>
<td>β(CCC) + ν(C−S)</td>
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<tr>
<td>1022</td>
<td></td>
<td></td>
<td>γ(COO⁻)</td>
</tr>
<tr>
<td>1081</td>
<td>1080 1074</td>
<td></td>
<td>β(C−H)ring</td>
</tr>
<tr>
<td>1211</td>
<td>1190 1190</td>
<td></td>
<td>ν(Al−C)asym, bending CH₃</td>
</tr>
<tr>
<td>1290</td>
<td>1381 1397 1432 1577 1599</td>
<td></td>
<td>ν(C−OH) + ring breathing</td>
</tr>
<tr>
<td>2822</td>
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<td></td>
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<td>ν(C−H)sym</td>
</tr>
<tr>
<td>2917</td>
<td>2919</td>
<td></td>
<td>ν(C−H)sym, (CH₃ group)</td>
</tr>
<tr>
<td>2921</td>
<td>2996, 3022 2960, 3008, 3032</td>
<td></td>
<td>ν(C−H)asym</td>
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*Experimental and DFT-calculated vibrational frequencies and peak assignments. TMA = trimethylaluminum, mon = monomer, dim = dimer, TT = toluenethiol, MBA = 4-mercaptobenzoic acid, BT = benzenethiol, MP = 4-mercaptophenol. γ, β, and ν indicate the out-of-plane bending, in-plane bending, and stretching modes, respectively.*

Figure 3. (A) SER spectra of a 25 s Ar plasma-cleaned AgFON before ALD (a) and after 10 s of TMA (1st cycle) (b), 60 s of H₂O (1st cycle) (c), 10 s of TMA (2nd cycle) (d), and 60 s of H₂O (2nd cycle) (e). (B) Difference SER spectra for the first 2 ALD cycles. SER spectra were acquired with λₑ = 532 nm, Pₑ = 2 mW, tₑ = 5 s and 10 accumulations each. Data are shifted on y-axis for clarity.
after H₂O exposure. Nucleation of TMA could also occur on hydroxyl (−OH) groups adsorbed on a very thin layer of oxide on the AgFON surface. The percentage of oxygen atoms in the volume sampled by XPS was calculated to be ∼8% for both 0 and 25 s Ar plasma-cleaned AgFONs (Figure S14). If nucleation of TMA occurs on −OH groups, then Al−O stretches could be observed by SERS but they were not observed in our studies even with an optimized AgFON for the low frequency Al−O stretching region (Figure S2D). Raman peaks from Al₂O₃ compounds are typically observed in the

Figure 4. SER spectra (A) of a 25 s Ar plasma-cleaned AgFON depicting the C−H stretching region before ALD (a) and after 30 s of TMA (1st cycle) (b), 60 s of H₂O (1st cycle) (c), 30 s of TMA (2nd cycle) (d), and 60 s of H₂O (2nd cycle) (e). Difference spectra (B) showing C−H stretching region after 2 ALD Al₂O₃ cycles. SER spectra were acquired with λ_{exc} = 532 nm, P_{exc} = 5 mW, t_{aq} = 10 s and 10 accumulations each.

Figure 5. (A) SER spectra of a AgFON functionalized with toluenethiol (TT) before and after 1 ALD Al₂O₃ cycle. (B–D) SER and difference spectra showing no thiol peak shifts before and after ALD Al₂O₃. The red curves in B–D represent Lorentzian peak fits. SER spectra were acquired with λ_{exc} = 532 nm, P_{exc} = 1 mW, t_{aq} = 2 s, and 10 accumulations each.
The scarcity of SERS studies that report the observation of Al–O vibrations is attributed to the low Raman cross sections of amorphous Al$_2$O$_3$ as reported by Stair and co-workers.$^{76}$

The TMA C–H stretches positioned at 2822, 2892, and 2921 cm$^{-1}$ in Figure 4B become negative after H$_2$O exposure because H$_2$O replaces (CH$_3$)$_x$ surface species with (OH)$_x$ species. In the second cycle, TMA replaces (OH)$_x$ species with (CH$_3$)$_x$ species. Figure S6 shows gradual decay over time of the TMA symmetric C–H stretch at 2892 cm$^{-1}$ during constant 5 mW of laser irradiation after TMA exposure. The peak intensity decreases to 50 and 15% of the initial intensity after 240 and 780 s, respectively. A control experiment shown in Figure S7 provides evidence that the decay of the C–H stretches over time was not caused by laser irradiation but was due to the reaction of residual H$_2$O inside the ALD chamber with adsorbed Al–(CH$_3$)$_x$ surface species. A power dependence study of the 2892 cm$^{-1}$ peak is displayed in Figure S8 and shows increasing SERS intensity when the laser power was increased from 0.2 to 7 mW. The study was performed very quickly for each laser power using 3 s acquisition time and 10 accumulations to minimize the reaction of TMA with residual H$_2$O.

Reaction of TMA with Toluenethiol and Benzenethiol.

The toluenethiol SAM does not prevent TMA from reacting with the AgFON since the symmetric Al–CH$_3$ stretch of TMA (585 cm$^{-1}$) is observed (Figure 5A). We propose that TMA penetrates through the monolayer and reacts with Ag as shown in Scheme 1. It is also possible that TMA displaces some surface toluenethiol molecules and reacts with the AgFON as indicated by the slight reduction in toluenethiol SERS signal after TMA exposure (Figures 5A–D and Table S2). Another possible explanation for the decrease in the toluenethiol signal is that TMA changes the spatial orientation of toluenethiol molecules. The toluenethiol molecules are initially oriented almost perpendicular to the AgFON surface.$^{77}$ When TMA reacts with the AgFON surface, it changes the orientation of the toluenethiol molecules to a more tilted position. The change in molecular orientation lowers the Raman scattering cross-section and affects the SERS signal as seen previously for other molecular systems.$^{78}$

As with the reaction of TMA with an unfunctionalized AgFON, the Al–CH$_3$ peak at 585 cm$^{-1}$ (Figure 5A) and TMA C–H symmetric stretches at 2822 and 2892 cm$^{-1}$ (Figures 7A, 7B) decay after H$_2$O exposure because H$_2$O reacts with Al–(CH$_3$)$_x$ groups to produce Al–(OH)$_x$ species. Figure SB–D and Table S2 show that toluenethiol vibrational modes do not shift after TMA exposure. Lack of vibrational frequency shifts indicate that toluenethiol molecules are not significantly perturbed by TMA and this supports the claim that TMA reacts directly with the Ag surface. In addition, the fwhm of toluenethiol peaks does not change significantly after TMA exposure (Table S2), which might further indicate that TMA does not react directly with toluenethiol but with the Ag
surface. We observed that the fwhm of vibrational modes of SAMs with nonreactive groups to TMA did not change significantly after TMA exposure unlike SAMs with reactive groups as we discuss in the following section. In similar fashion, the symmetric Al−CH3 stretch at 583 cm$^{-1}$ and the Al−CH3 deformation mode at 1211 cm$^{-1}$ were observed after TMA exposure on benzenethiol-functionalized AgFON and no thiol vibrational frequency shifts were observed (Figures S11, S12 and Table S2). We believe that TMA also reacts with Ag rather than the benzenethiol molecules similar to the TT-functionalized AgFON.

**Reaction of TMA with Mercaptobenzoic Acid and Mercaptophenol.** On MBA-functionalized AgFON, vibrational frequency shifts are seen after TMA exposure as depicted in Figure 6B–D. The 4 cm$^{-1}$ shift of the COO$^-$ bending vibration at 845 cm$^{-1}$ is due to complexation with TMA as illustrated in Scheme 1. A shoulder also appears at 1397 cm$^{-1}$, which is attributed to the replacement of −COOH−H groups with −COO−Al− species after TMA exposure. This assignment is consistent with literature studies that reported stronger COO$^-$ stretches of adsorbed MBA at ~1400 cm$^{-1}$ in its deprotonated form than the protonated one. Chabal and co-workers observed a 1476 cm$^{-1}$ band after TMA exposure on COOH-terminated SAMs on Si and assigned it to the C≡O stretch mode found in acid salt structures. They also observed complete disappearance of the C≡O stretch mode at 1718 cm$^{-1}$ after TMA exposure. Unfortunately, C≡O stretches of MBA are usually very weak in SERS. The 2 cm$^{-1}$ peak shift of the 1080 cm$^{-1}$ peak (CCC ring deformation mode and C−S stretch) and the shifted position of the TMA C−H stretch at 2898 cm$^{-1}$ (Figure 7C,D) are explained by the direct reaction of TMA with the −COOH groups of MBA, which perturbs MBA molecules and changes their vibrational frequencies. Similarly to a bare AgFON and TT-functionalized AgFON, the TMA C−H stretch at 2898 cm$^{-1}$ (Figure 7D) decays after H2O exposure because H2O reacts with Al−(CH3)$_x$ surface groups and replaces them with Al−(OH)$_x$ groups. TMA regenerates Al−(CH3)$_x$ species in the second TMA half-cycle.

For the MP-functionalized AgFON, vibrational frequency shifts of MP peaks were seen after TMA exposure (Figures S13A–D and Table S3). The CCC ring deformation and C−S
Scheme 1. Proposed Scheme for the Reaction of TMA with AgFONs Functionalized with Toluenethiol and 4-Mercaptobenzoic Acid SAMs

“The structure of dimeric TMA contains bridging pentacoordinated carbon atoms as determined by gas-phase electron diffraction.”

stretch mode shifted from 1074 to 1075 cm⁻¹. The C=O stretch shifted from 1290 to 1276 cm⁻¹ after the reaction of TMA with the C=OH group. The CC stretch and OH bending mode shifted from 1577 to 1584 cm⁻¹ as a result of TMA reacting with the C=O group (Figures S13B–D).

Vibrational frequency shifts of SAMs suggest that TMA selectively reacts with the C=O and C=OH groups of SAMs on AgFONs. The fwhm of MBA- and MP peaks associated with the C=OH and C=O groups increases significantly (Table S3) after TMA exposure, which suggests that TMA reacts directly with the C=OH and C=O groups of the SAMs. Changes in the peak intensities after TMA exposure did not reveal significant differences in the reactivity of TMA with the types of SAMs investigated. The observation of the symmetric CH₃ stretch on TT- and BT-functionalized and not on MBA- and MP-functionalized AgFONs is consistent with the distance dependence of SERS in which vibrational modes of molecules closer to the plasmonic substrate show stronger signals than those spaced further away. Furthermore, the TMA C=H stretches for MBA-functionalized AgFONs (Figure 7C,D) are ~7X weaker than TMA C=H stretches for TT-functionalized AgFONs (Figures 7A,B). This could be explained by the larger distance of the TMA–CH₃ groups from the AgFON surface for MBA-functionalized AgFONs than TT-functionalized AgFONs as illustrated in Scheme 1. It is also possible that there is a difference in the amount of TMA deposited on MBA- and TT-functionalized AgFONs. For example, if the amount of TMA deposited on MBA-functionalized SAMs is higher than on TT-functionalized AgFONs, then the TMA–CH₃ groups will be much farther away from the surface and would appear much weaker for MBA-functionalized AgFONs. At present, we assume that the amount of TMA deposited on MBA- and TT-functionalized AgFONs is the same (~1.1 Å/cycle).

The S:Ag atomic ratio, determined by XPS, provides information about the relative packing density of SAMs on AgFONs. Figure S15 shows S 2p and Ag 3d peaks for all SAMs; the calculated S:Ag ratio increases from 0.0575 to 0.0824 in the following order: TT < BT < MP < MBA. This indicates a lower packing density of TT and BT SAMs on AgFONs than MP and MBA SAMs. This is consistent with the work of Lee and co-workers who observed a lower packing density of BT SAMs compared to MP and MBA SAMs on Au. These studies support our claim that TMA is able to penetrate through less densely packed, unreactive SAMs and react directly with the AgFON surface.

Comparison with Other Studies. Several studies have used SAMs as enablers of area-selective ALD, a process in which ALD material is deposited only where desired. On SiO₂ surfaces, Chen et al. showed that to completely block H₂O, ALD, long (>12 carbon units), linear, densely packed, hydrophobic alkyltrichlorosilane SAMs are necessary. Using in situ IR spectroscopy, Chabal and co-workers observed disappearance of C=O stretches and no perturbation of alkyl chain modes and concluded that COOH-terminated SAMs on Si were effective in blocking TMA from reacting with Si. To the best of our knowledge, studies that investigate ALD blocking mechanisms using SAMs have been extensively studied on Au but not as thoroughly on Ag. Preiner et al. showed that SAMs with hydrophobic tail groups such as 1-dodecanethiol on Au act as ALD resists and block Al₂O₃ growth while SAMs with hydrophilic groups such as MBA allow faster growth of Al₂O₃. Our study on CH₃-terminated SAMs is consistent with Hooper et al., who studied the interaction of vapor-deposited Al atoms with CH₃-terminated SAMs on Au and observed Al–S species by XPS to indicate penetration of Al atoms through the SAM to the Au/SAM interface. Furthermore, lack of major perturbations in the SAM IR spectra indicated that no chemical interaction occurred between Al and the SAM. On COOH-terminated SAMs on Au, Fisher et al. concluded that the C=O group reacts with Al to prevent Al atoms from penetrating into the monolayer. XPS data indicated that Al atoms bind with both oxygen atoms of the SAM to form metal–organic species. IR spectra showed a 14 cm⁻¹ shift and 25% drop in intensity of the SAM’s C=O stretch after Al deposition to indicate direct reaction of Al atoms with the COOH group. Similarly, they observed significant perturbation of the C=O stretch (a decrease in intensity and 35 cm⁻¹ shift) of OH-terminated SAMs on Au.
using IR spectroscopy and concluded that deposited Al selectively reacts with −OH groups to form −OAl groups.75

These observations are consistent with our studies in which we observe vibrational frequency shifts of OH- and COOH-terminated SAMs after TMA exposure. Finding the ideal SAM on AgFON to completely block ALD growth is beyond the scope of this investigation. Rather, the focus of this study is to demonstrate that operando SERS provides unique information about where ALD deposition occurs on SAM-functionalized surfaces, information that is difficult to obtain from techniques such as FTIR, QCM, QMS, and spectroscopic ellipsometry. SERS provides valuable information about surface-bound molecular species and on where the ALD deposition occurs on the surface under realistic ALD working conditions. Our study reveals that TMA forms dimeric species on the AgFON surface and this information is difficult to obtain from other techniques. The rich structural information provided by SERS can be used to provide insight about the surface chemistry of ALD reactions.

CONCLUSIONS

This work demonstrates the capability of operando SERS to measure surface vibrational spectra of adsorbates during ALD reactions. On bare AgFONs, Al−C, symmetric C−H, and asymmetric C−H stretches were observed after TMA exposure at 55 °C, and they decayed after dosing H2O. Residual H2O in the ALD chamber reacted with −CH3 groups on AgFONs as evidenced by the decay of the Al−C and C−H stretches even before H2O exposure. DFT studies revealed that the observed Al−C stretches were consistent with TMA dimeric species on the AgFON surface. On thiol SAM-functionalized AgFONs, Al−C stretches and no thiil vibrational frequency shifts were seen after TMA exposure in the case of toluenethiol and mercaptophenol SAMs. Thiol vibrational frequency shifts and no Al−C stretches were observed after TMA exposure on AgFONs functionalized with 4-mercaptobenzoic acid and 4-mercaptophenol SAMs. For COOH- and OH-terminated SAMs, the absence of observable Al−C stretches was due to their larger distance away from the enhancing SERS substrate. Operando SERS revealed that TMA selectively reacted with the AgFON surface for benzenethiol and tolenethiol SAMs and with the −COOH and −OH groups for 4-mercaptobenzoic acid and 4-mercaptophenol SAMs, respectively. This shows that SAMs can be used to tailor the surface and direct ALD Al2O3 growth to achieve area-selective ALD. The surface sensitivity and rich structural information provided by operando SERS will allow for the probing of the deposition mechanisms of other ALD reactions such as metal ALD processes under realistic reaction conditions. Knowledge of the surface chemistry of ALD reactions will help in the selection of better precursors and in the optimization of ALD processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b11487.

Extinction spectra of AgFONs, SER spectra acquired with and without the quartz window, SER spectra of AgFONs before and after Ar plasma cleaning, DFT-calculated Raman spectra of TMA, SER spectra showing reaction of surface species with residual H2O, laser power dependence study, SER spectra of benzenethiol and 4-mercaptophenol before and after ALD, and XP spectra (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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